SYNTHESIS OF PARTICULATES FOR FUNCTIONAL APPLICATIONS:
EXAMPLES OF NANOCOMPOSITES AND HEMATITE

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by

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ABSTRACT

The size and shape dependence of optical properties for particulate materials were investigated in this thesis research. Specific materials of interests include α-Fe₂O₃ pigments, Ag/SiO₂ core-shell structured nanocomposites and tabular SiO₂ nanoparticles. The main focus was on the processing parameters related to the particulate morphologies, dispersion and optical properties of each model system and optimization of those conditions so that a general prediction for the optical behavior of the particulate materials was achievable.

Iron oxide (hematite) particles with various shapes (platelet, polyhedron, pseudocube and peanut-like) were synthesized by hydrothermal treatment of a Fe(OH)ₓOᵧ precursor under various conditions. The size and shape of hematite particles could be adjusted by carefully controlling the processing parameters such as holding time, temperature and adsorption ions present in the system. The nearly monosized α-Fe₂O₃ platelets possessed face diameters of approximately 3 μm and a thickness of 0.5 μm under scanning electron microscope (SEM). The apparent color of the particles changed as particle size and shape varied. Munsell color notation was employed to compare the color of hematite particles with various size and shape. Diffuse reflectance spectra showed that a “red-shift” of 40 nm was observed in platelet, pseudocube and peanut-like particles compared to conventional particles. The band at 850 nm for the ⁶A₁ → ⁴T₁ transition was split in the pseudocubic and peanut-like particles. Raman spectra of the hematite particles also revealed that the vibrational modes of α-Fe₂O₃ particles diminished as particle size decreased, and dependence of vibrational band intensity to
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Nanoscale Ag/SiO\(_2\) composite particles with a uniform core-shell structure were synthesized by reverse micelle techniques. The silver cluster was about 5 nm and the silica shell thickness was 10 nm when \( R=2 \) (\( R=\text{[water]}/[\text{surfactant}] \)), \( H=100 \) (\( H=\text{[water]}/[\text{TEOS}] \)) and \( X=1 \) (\( X=\text{[NH}_4\text{OH]}/[\text{TEOS}] \)) was employed for the cyclohexane/Igepal/water tertiary system. A model calculation indicated that the optical properties of the nanocomposites, especially the refractive index for core-shell structured nanoparticles were governed by the ratio of the core to the shell. The spherical nanocomposite particles were washed and concentrated with high performance liquid chromatography (HPLC) in order to remove the surfactant added during synthesis. Spherical SiO\(_2\) submicron particles were packed in the HPLC column as a stationary phase for the washing and dispersing of Ag/SiO\(_2\) nanocomposite particles. Surface modification of Ag/SiO\(_2\) nanocomposite particles with the silane coupling agent 3-
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Amorphous tabular SiO₂ nanoparticles were synthesized from the self-assembled octylamine/water bilayer via a template-directed growth mechanism. Morphology of the tabular SiO₂ nanoparticles was analyzed by high-resolution TEM both for room temperature dried and calcined powders. The tabular SiO₂ nanoparticles demonstrated well-defined thickness (4~6 nm) with a relative spread face diameter (100~300 nm), which lead to a wide distribution of aspect ratio based on AFM. High surface area up to 1158 m²/g was readily obtained with a very uniform micropore size of about 0.63 nm after thermal treatment at 700°C for 2 hours. Metallic Pd clusters were embedded into the microporous SiO₂ matrix via a solution reduction of Pd(NO₃)₂ by hydrazine hydrate. The infiltration of 33 wt% Pd leads to a 13 % porosity loss of tabular SiO₂ nanoparticles. The presence of Pd in the pores was demonstrated by energy dispersive X-ray spectroscopy (EDS) and X-ray diffraction (XRD). The metallic guest species presumably resided in the
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Chapter 1

Objectives of Research

The objectives of this research are the understanding of optical properties of particulate materials as a function of particle size and shape, thereby theoretically predicting the macroscopic optical responses of nano to micron scale particulates. The primary materials of interest are ferric oxide (hematite), metal/silica nanocomposites and silica because of their tunable morphologies and excellent optical activities. The accomplishment of the objectives requires controllable and reproducible synthesis and dispersion of particulate materials. The size and shape dependence of optical properties for particles has been noticed but not so well elaborated, and the challenges are to obtain atomic scale correlations of optically active stable nanodispersion and anisotropic particles. Further details on the advancement of this subject will be comprehensively and thoroughly addressed in the following literature review (Chapter 2). Hence, the chapters of this thesis are organized so that the experimental section of this thesis starts out with preparation of anisotropic hematite particles and Ag/SiO$_2$ nanodispersion. The goal of this research is achieved by creatively conducting critical experiments and systematically analyzing data. A summary of each of the experimental chapters is therefore outlined below:
Chapter 3 Synthesis and Optical Properties of Hematite Particles

- Determine the synthetic parameters that affect the morphology of hematite particles prepared by hydrothermal reaction.
- Evaluate optical properties of hematite particulates with respect to crystal size and shape via spectroscopic analysis.
- Provide guidelines for the prediction of optical properties of pigments based on their crystal structure, size and geometrical shape.

Chapter 4 Synthesis and Optical Properties of Ag/SiO$_2$ Nanocomposites

- Comparison of agglomeration state of Ag/SiO$_2$ nanocomposites suspensions using various washing protocols.
- Determine the microscopic mechanisms that induce the agglomeration in nanoparticle dispersions.
- Elaborate the quantum confinement effect of nanocomposite particles through spectroscopic analysis.
- Develop a theoretical approach to estimate the refractive index of nanocomposite particles.

Chapter 5 Dispersion of Silica-Based Nanocomposites with High Performance Liquid Chromatography (HPLC)

- Develop a dispersion scheme to wash and concentrate silica-based nanoscale particles with appropriate modification of particle surfaces.
• Determine the state of dispersion for nanocomposite suspensions so as to understand the mechanisms and generate reproducible products.

• Evaluation of parameters that are pertinent to well-dispersed nanoparticle suspension using HPLC.

Chapter 6 Synthesis and Infiltration of Tabular SiO$_2$ Nanoparticles

• Manipulate the thickness of anisotropic nanoparticles using self-assembly bilayer systems.

• Determine the growth mechanisms for tabular nanoparticles.

• Perform preliminary studies on porosity of anisotropic particulate materials synthesized by the self-assembly route.

• Find a scheme to infiltrate the microporous anisotropic particulate matrices such that unique properties might be demonstrated.
Chapter 2

Background

2.1 Introduction

The synthesis of anisotropically shaped particles and investigation of their optical and electronic properties have gained attention because of their potential applications. From a fundamental scientific understanding, nanoparticles with tailored architecture (such as core-shell) may demonstrate unique properties including quantum confinement, nonlinear optical response, blue shift, etc. Devices assembled from nanoparticles can be used in fields such as photonics, electronics, chemical sensors, photochemical processing and cosmetics. 1 Particles with core-shell structure often exhibit improved physical and chemical properties compared to their single-component counterparts, and hence are potentially useful in a broad range of applications. 2 In this thesis research, the starting materials for studying the intrinsic optical properties of the fine particles are $\alpha$-Fe$_2$O$_3$ (hematite), tabular SiO$_2$ and Ag/SiO$_2$ nanocomposites. Hematite demonstrates strong absorption in the entire visible spectrum, 3 and its apparent color is determined to a large degree by particle size. 4 Ferric ions (Fe$^{3+}$) have also been widely used as a near infrared luminescent activator in a number of matrices. 5, 6, 7 Concentrated Fe$^{3+}$ ions with octahedral coordination show a lack of luminescence due to the so-called “concentration quenching” effect. 8 Nanosized silica and metal/silica nanocomposites have been
extensively studied due to their electronic, optical and catalytic properties. 9, 10 Unfortunately, the nanoparticle suspensions involved were most likely stabilized by surfactant coatings, which could affect the homogeneity and optical properties of the nanoparticles arrays in the subsequent processing steps. 1 Moreover, the state of dispersion for the nanoparticle suspensions was not completely understood. Therefore, processing of nanoscale stable suspension with less residual surfactant remains a challenge. 11 The objective of this research can be divided into two parts. The first part is to prepare well dispersed Fe₂O₃, SiO₂ and Ag/SiO₂ nanocomposites from nanometer to submicrometer sizes using hydrothermal synthesis, self-assembly bilayers and reverse micelle techniques. 12, 13, 14 The second part is to assess the optical properties of the synthesized particles thereby to optimize the parameters that determine the size, shape and optical properties of the desired particles. The following work will concentrate on studying the optical behavior of the as-synthesized particles, consisting of Raman spectroscopy and UV-vis diffuse reflectance spectroscopy on materials with fully characterized sizes and shapes combined with calculations based on absorption and dynamic light scattering theory. 15, 16 The interpretation of the data acquired could establish a fundamental understanding of the optical properties for particulate materials which may reflect the role of morphology as well as atomic scale structural disorder. These efforts may provide useful guidelines for prediction of the macroscopic optical appearance of particulate materials.
2.2 Optical Properties of Ferric Oxide (Hematite) Particles

Iron oxides are a group of common metal oxides which are abundant in nature and readily synthesized in the laboratory. There are sixteen types of iron oxides, among which $\alpha$-Fe$_2$O$_3$ is the most stable phase and the alternate name “Hematite” derives from the Greek word *haimatos* (blood), an illusion to its striking maroon color. Hematite particles are one of the most popular colored pigments that have been used in applications such as paints, cosmetics and catalysts for quite a long time. Hematite belongs to corundum structure, space group $R\bar{3}c$, in which central Fe$^{3+}$ occupies the center of the O$^{2-}$ octahedral groups. Even though naturally occurring hematite is widespread in rocks and soils, the variance of its morphology is quite limited. Through hydrothermal synthesis, however, the shape and size of hematite crystals were remarkably broadened. Matijevic *et al.* pioneered the morphological manipulation of monodispersed hematite particles via a forced hydrolysis process in very dilute solutions. More recently, Sugimoto *et al.* used a gel-sol technique to process elongated shaped hematite particles from concentrated solution. The well-known morphologies for hematite particles include isotropic (spheres, cubes, pseudocubes) and anisotropic forms (ellipsoids, peanut, platelets, polyhedra), all of which can be readily synthesized by changing complexing agents, ferric salt concentration, precursor pH and temperatures.

Optical properties of hematite particles were noticed to some extent to be shape and size-dependent over the past decades, but systematical comparison of optical properties with respect to particle morphology was not well established. In general, the
color of hematite powders was summarized as brownish red to iron-black in the mineralogy community. The color of colloidal hematite was noticed by Kerker et al. and by Hsu to be morphology dependent. Hund later compared the color of red \( \alpha-Fe_2O_3 \) particles with respect to parameters such as particle shape, size and size distribution. It was found that the scattering and absorption cross-section behave differently when hematite particle size is less than 1.0 \( \mu \)m. The color purity is sensitive to particle size and shape. However, the studies were limited to small hematite particles (< 1.0 \( \mu \)m) with needle-like and cubic shapes. By performing theoretical calculations and experimental determination on ellipsoidal hematite particles deposited as thick films, Ryde and Matijevic revealed that the color purity of nonspherical particles depends on their specific dimensional characteristics, and the relationship of the particle morphology to optical properties appears to be quite complicated. However, the optical properties, particularly the color of hematite, have not been systematically compared on a fundamental basis. It is essential to measure the spectroscopic behavior of hematite so as to obtain better insight of the optical properties. Diffuse reflectance spectra were a proven technique for hematite and therefore received extensive studies from ultraviolet to near infrared region. The spectra of hematite typically consist of three distinct regions: crystal field transitions at near infrared wavelengths (1200 to 700 nm), strong absorption at visible wavelengths (700 nm to 400 nm), and intense ligand to metal charge-transfer (LMCT) transitions from 400 to 200 nm.

In the spectral range where crystal field transitions are the dominant mechanism, a characteristic absorption peak for hematite is associated with the \( ^6A_1 \rightarrow ^4T_1 \) transition at
850 nm. Adjacent to this broad band is a shoulder band at around 775 nm, caused by the $^6A_1 \rightarrow ^4T_2$ transition. These transitions are generally spin-forbidden would be expected to be weak, but in hematite their intensities are enhanced due to magnetic coupling of two neighbor $Fe^{3+}$ ions in the crystal structure. 35, 36, 37 Other crystal field transitions observed between 400 to 700 nm were assigned based on the Tanabe-Sugano diagram (Figure 2-1) for $d^6$ ions by Baily, 31 Marusak 3 and Sherman. 34 In the ultraviolet region, most of the transitions occurred due to the ligand to metal charge-transfer (LMCT). Discrepancies of band assignments were found between these ill-defined bands. This may be due to increased light scattering at shorter wavelengths. 34, 17

Figure 2-1: The Tanabe-Sugano diagram for $d^6$ ions. Note the ground state for $Fe^{3+}$ is $^6A_1$, B and C are the Racah constants. Left to the turning point is for high spin state, which is the case of $\alpha-Fe_2O_3$. 35 (Diagram by J. S. Berkes, MRL monograph, 1968).
Raman scattering of electromagnetic radiation by hematite was extensively studied in the past few decades. The spectra measured under different conditions could provide complementary structure information to that from infrared spectra. The Raman active lines of hematite were calculated based on group theory and confirmed experimentally. There are 2 $A_{1g}$ modes and 5 $E_g$ modes. The pressure dependence of Raman active modes was also explored first by Massey et al. and recently by Shim. Although the Raman spectra of hematite predicted by group theory has been well understood and utilized to identify crystal phase behavior between various forms of iron oxides, an ambiguity regarding the origin of a peak at $1320 \text{ cm}^{-1}$ still exits. Hart and Martin attributed this to a two-magnon scattering process while McCarty, Massey and Shim proposed a resonance enhanced two-phonon process.

The Luminescent emission of Fe$^{3+}$ doped compounds is well known. A number of materials were proved to be suitable hosts for Fe$^{3+}$ ions. Generally Fe$^{3+}$ activator replaces Al$^{3+}$ at concentrations of only a few mole percent. The Fe$^{3+}$ ion appearing in tetrahedral sites shows emission wavelength in the deep red to near infrared depending somewhat on specific values of $D_q$ and the Stokes shift, with AlF$_3$ an exception. For the Fe$^{3+}$ ion locates in octahedral site, the fluorescent emission is shifted deeper into the infrared. More recently, luminescence reported in nanocrystalline $\alpha$-Fe$_2$O$_3$ in the visible-range was proposed to be due to surface states.
2.3 Optical Properties of Silica-Based Nanocomposite

The interest in colloidal nanoparticles stems from their unique properties (optical, electrical, mechanical and chemical) that demonstrate size dependence. Following Faraday’s seminal experiments on optical properties of gold nanoparticles, the knowledge of nanoparticles has been continuously expanded and enriched both fundamentally and practically. More recently, intense effort has been placed on the production of composite nanoparticle with a core-shell architecture. The core-shell structured nanocomposites consist of a metallic or semiconductor quantum dot that capped with a number of materials having distinctly different characteristics than the core material. The uniformly coated shell provides enhancement to the core along with passivation and extra functionalities. Particularly for silica capped metallic quantum dot nanocomposites, the optical nonlinear response appears to be enhanced by size quantization and local field enhancement at the surface plasmon resonance.

The optical properties of colloidal nanoparticle have been of interest for centuries. Mie had developed a fundamental theory to describe the optical properties for spherical particle, complementing classical Rayleigh scattering. The Mie theory has remained an important explanation for most colloidal particle with approximately spherical geometry. However, with the development of more complicated nanoparticle systems, especially the presence of high aspect ratio nanoparticles, the optical anisotropy due to asymmetric shape should no longer be ignored. Colloidal Ag nanoparticles is one of the materials demonstrate unique optical properties as a result of shape effect. The surface plasmon resonance of spherical Ag nanoparticles is at around
400 nm, however, it is split into three peaks (335, 430 and 670 nm) for trigonal Ag nanosized prism. This experimental observation has been explained by a more specific electrostatic theory that takes shape and size into consideration. 50

The optical properties for metal-doped glasses having composite geometry were first considered by Maxwell-Garnett. 51, 49 The original Maxwell-Garnett model assumed that the embedded particles were spherical with uniform size (Figure 2-2). The size of the inclusion was much smaller than the typical spacing between inclusions. Similar models were also developed later to describe the composite materials by Genzel and Martin 52 for nonabsorbing medium, and by Neeves 53 for nanospheres suspened in nonlinear medium. However, a more useful approach is to express the average polarization in the inclusion under an applied electric field, 49, 52, 1 which is defined by Equation 2.1

$$4 \pi P = f (\varepsilon_i - 1) E_i + (1 - f) (\varepsilon_m - 1) E_m$$  \hspace{1cm} (2.1)

Where P is the average polarization, $\varepsilon_i$ the dielectric constant for inclusion, $\varepsilon_m$ dielectric constant for medium, $f$ volume fraction inclusion, $E_i$ and $E_m$ are the electric field in the inclusion and medium, respectively.

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Figure 2-2: The Maxwell-Garnett composite geometry. The dielectric constant of the inclusion is $\varepsilon_i$, and $\varepsilon_m$ is the medium dielectric constant. It assumed that the inclusion particles are spherical and uniform in size. 51
From the above equation an expression for the effective dielectric constant $\tilde{\varepsilon}$ can be derived in Equation 2.2

$$\tilde{\varepsilon} = \varepsilon_m \frac{\varepsilon_i (1 + 2f) + 2\varepsilon_m (1 - f)}{\varepsilon_i (1 - f) + \varepsilon_m (2 + f)}$$  \hspace{1cm} (2.2)

Taking Equation 2.2 to the lowest order in the fill fraction, the effective dielectric constant $\tilde{\varepsilon}$ is simplified to Equation 2.3

$$\tilde{\varepsilon} = \varepsilon_m + 3\varepsilon_m \cdot f \frac{\varepsilon_i - \varepsilon_m}{\varepsilon_i + 2\varepsilon_m}$$  \hspace{1cm} (2.3)

The refractive index of the composite materials can now be calculated using the Maxwell relation ($\varepsilon = n^2$) that connects the dielectric constant to the index of refraction.

The unique optical properties of SiO$_2$ coated core-shell nanocomposites originated from the core and the SiO$_2$ shell enhancement.\cite{54, 55} For a metallic core, this enhancement displays in the surface plasmon resonance. For example, the Maxwell-Garnett model was applied to understand the dipole coupling of the surface plasmon mode in Au for a thin film deposited by Au/SiO$_2$ nanoparticles. The transmitted color of this thin film exhibits size dependence of the core and the shell.\cite{56} Quantum size effect is observed in Au/SiO$_2$, Ag/SiO$_2$ and CdS/SiO$_2$ nanocomposites. The absorption of the CdS quantum dots is improved after silica coating.\cite{1} More recently, the principle of surface enhanced Raman scattering has been used to improve the Raman output of a SiO$_2$ coated Au or Ag nanocomposites so that it can be used as a Raman tagging system in biological application.\cite{57}

In addition to the spherical core-shell nanocomposites, a continuous SiO$_2$ matrix can also be utilized as a host material for creating heterogeneous structures with desired
properties. The SiO$_2$ substrate is chemically inert and can be loaded with guest species including metals, polymers and semiconductors. The cluster geometry can be well defined by the host microstructure. A number of nanoparticles with interesting electrical, optical and catalytic properties have been successfully embedded into mesoporous (pore size between 2 ~ 50 nm) and microporous (pore size less than 2 nm) SiO$_2$ frameworks. 58 There are a variety of shapes for SiO$_2$ matrix that may be used for host-guest inclusion, including isotropic and anisotropic particles such as spheres, fiber, and rod. However, information on formation mechanisms and crystal structural details of the cluster and physical properties of the hybrid materials are still inadequate. Besides, the inclusion of noble metal clusters such as Au, Pd and Pt in the microporous SiO$_2$ could lead to a distinct type of nanocomposites with unique functionalities. 59, 60

2.4 Conclusions

The intention of this thesis research is the fundamental understanding of optical properties of particulate materials down to nanoscale, and the study of their macroscopic morphology that may have impact on optical properties. It is necessary to address several issues so that the accomplishment of this goal is feasible. Therefore submicron size hematite particles with various morphologies were synthesized and their optical properties carefully compared using numerical techniques (Chapter 3). With these findings from a model submicron scale system, an extension will be applied to the nanosized particles. The optical properties of core-shell structured Ag/SiO$_2$ nanocomposites demonstrate size dependence, but dispersion of the nanocomposites
needs to be improved. To fulfill this prerequisite, a number of conventional methods were studied and agglomeration states for the suspension were determined (Chapter 4). The familiarity with the conventional methods eventually enables a dispersion scheme to be developed for silica-based nanoparticles using HPLC (Chapter 5). Further investigation of nanosized anisotropic SiO$_2$ particles was carried out using the knowledge on self-assembly bilayer systems. Infiltration of micropores may lead to new physical properties and open up potential applications in relevant fields (Chapter 6).

2.5 References


Chapter 3
Synthesis and Optical Properties of Hematite Particles

3.1 Introduction

Iron oxide (α-Fe₂O₃, hematite) particles have attracted much interest for many years due to their various geometrical shapes and unique optical and magnetic properties. 1, 2 From the materials synthesis point of view, different shapes of hematite particles have been obtained by carefully controlling processing parameters. 3 Hydrothermal synthesis was found to be an effective approach to manipulate the size and shape of the hematite particles. 2, 4, 5 For example, Ozaki et al. 2 prepared platelet-like hematite particles by introducing ethylenediaminetetraacetate (EDTA) into a Teflon-liner autoclave containing ferric hydroxide precursor. The particles formed single magnetic domains. A systematic study on growth mechanism of hematite particles produced by hydrothermal treatment was reported by Sugimoto and coworkers. 3, 4 It was found that adsorption of ions such as Cl⁻, SO₄²⁻ and PO₄³⁻ plays an important role in the nucleation and growth of hematite. Peanut-like, cubic or spindle-like particles were obtained in the presence of various ions.

As a traditional pigment being used in many applications, the optical properties of hematite have been studied extensively. 1 However, most work done in this regard did not provide enough information on particle size and shape related to macroscopic optical properties. One of the striking optical properties for hematite is its color, which was
known for years but not studied in detail until the work by Kerker et al., Hsu et al. for colloidal hematite, with Hund, Ryde and Matijevic who correlated the color to particle size and shape (cubes, spheres and needles). More recently, Katsuki and Komarneni extended this effort to the nanosize scale by comparing the colors of hematite particles generated from microwave synthesis. According to the optical absorption study of hematite thin films by Marusak et al. α-Fe₂O₃ strongly absorbs over the entire visible spectrum range. However, questions remain on the effect of particle size and shape on the optical absorption and scattering behavior of hematite pigments.

Luminescent materials activated by transition metal ions generally exhibit concentration quenching at concentrations of a few mole percent. However, the expected effect was not observed in the case of small α-Fe₂O₃ particles. Fe³⁺ has the d⁵-electron configuration. It is isoelectronic with the well-known activator Mn²⁺ but the higher charge shifts Dq to higher values and thus the luminescent ⁴T₁ → ⁶A₁ transition shifts to lower wavenumbers. Fe³⁺ is frequently used as a luminescent dopant. Compounds exhibiting Fe³⁺ emission include LiAlO₂, LiGaO₂, LiAl₆O₈, LiGa₅O₈, AlF₃, KAlSi₅O₈, Zn₂SiO₄, ZnS, CuGaS₂, CuAlS₂, LiGa₅O₈, AlF₃, KAlSi₅O₈, Zn₂SiO₄, ZnS, CuGaS₂, CuAlS₂, LiGa₅O₈, AlF₃ and phosphate glasses. There are several common themes to these compounds. One is that the Fe³⁺ activator replaces Al³⁺ at concentrations of only a few mole percent. The other is that (except for AlF₃) the Fe³⁺ appears in tetrahedral coordination with its emission wavelength in the deep red to near-infrared depending somewhat on specific values of Dq and the Stokes shift. The few examples known of emission of Fe³⁺ on octahedral sites include AlF₃ and some phosphate glasses.
Emission from octahedral Fe\(^{3+}\) is shifted deeper into the infrared, often at or beyond the cutoff for the detectors used in the spectrometers. A report on nanocrystalline Fe\(_2\)O\(_3\) luminescence described visible-range emission which was ascribed mainly to surface states. \(^{27}\)

The intent of this chapter is to prepare hematite particles with controlled shape and size via hydrothermal synthesis and to determine the optical properties as a function of size and shape. Another emphasis will be on a weak near infrared luminescence of the submicrometer trigonal corundum-type structured Fe\(_2\)O\(_3\) particles with Fe\(^{3+}\) coordinated by face-sharing octahedra. The objective is to achieve a fundamental understanding of the mechanisms behind the pigment coloration.

### 3.2 Experimental Procedure

#### 3.2.1 Synthesis of Hematite Platelets

The typical procedure used to prepare hematite platelet particles initially reported by Matijevic \(^2\) is summarized in Figure 3-1. Amorphous Fe(OH)\(_x\)O\(_y\) precipitates were first obtained by mixing 2 mL 0.5 M FeCl\(_3\) (FeCl\(_3\)·6H\(_2\)O, Aldrich Chemical Co., Milwaukee, WI) with 6 mL 4 M NaOH (J. T. Baker, Phillipsburg, NJ) aqueous solution, and 8 mL 0.2 M EDTA (Aldrich Chemical Co., Milwaukee, WI). Two mL 2 M NaCl (J. T. Baker, Phillipsburg, NJ) was added up to a total solution of 18 mL. The highly alkaline suspension was then transferred into a 23 mL stainless steel acid digestion bomb (Parr Instrument, Moline, IL) lined with Teflon and heat treated at 180 °C for more than 6 h. The precipitated particles were washed with 0.001 M HNO\(_3\) (J. T. Baker, Phillipsburg,
Figure 3-1 Flow sheet for hydrothermal synthesis of hematite platelet. Procedure was described by Matijevic et al. \(^2\) for platelet and Sugimoto et al. \(^4,28\) for pseudocube and peanut-like particles.
NJ) solution 3 times followed by deionized water 5 times (specific conductivity = 0.4×10^{-7} S/m). The particles were redispersed in DI water with a result of pH 6.0. The final suspension of Fe₂O₃ platelet particles had a purple color.

3.2.2 Synthesis of Polyhedron Hematite Particles

The procedure to prepare polyhedron Fe₂O₃ particles is different from the method to prepare platelets. The Fe(OH)ₓOᵧ precursor was first obtained by mixing 200 mL 0.5 M FeCl₃ with 600 mL 0.5 M NaOH and aged at room temperature overnight. The precipitate was centrifuged at 1500 rpm for 5 minutes and the Fe(OH)ₓOᵧ gel was collected and dispersed in DI water. The pH of the suspension was adjusted to pH 12.0 with a total volume of 480 mL. The final suspension was transferred to a 600 mL hydrothermal vessel and heated at 180°C for 10 hours with a continuous stirring rate of 150 rpm. The product was washed and redispersed in a manner similar to that used for hematite platelets.

3.2.3 Synthesis of Anisotropic Hematite Particles

Using the same starting chemicals, pseudocubic and peanut-like hematite particles were prepared following the protocol described by Sugimoto. Initially, 10 mL 2 M FeCl₃ was directly mixed with 9 mL 6 M NaOH with the solution diluted to a total volume of 20 mL by DI water. After stirring for 5 minutes, the solution was transferred to the 23 mL Teflon-lined hydrothermal vessel and heat treated at 100°C for 8 days. For
peanut-like particles, 1 mL of 0.6 M Na$_2$SO$_4$ stock solution (Aldrich Chemicals Co. Milwaukee, WI) was used instead of DI water.

### 3.2.4 Characterization

The morphology of the hematite particles was determined by scanning electron microscope (SEM, Hitachi S-3000H, Tokyo, Japan). Phase identification was done by X-ray diffraction (Scintag, Inc., Cupertino, CA, Cu Ka with a wavelength of 1.5418 Å). The surface charge of the hematite particles in aqueous was determined by Zeta PALS Analyzer based on the dynamic light scattering principle (Brookhaven Instruments Co., NY).

The shape of the hematite particles is strongly determined by the processing techniques and the parameters involved. Figure 3-2 shows the morphology of Fe$_2$O$_3$ particles hydrothermally treated at 180°C and 100°C, respectively. If the Fe(OH)$_x$O$_y$ precipitates were aged first prior to hydrothermal treatment, the growth of platelet hematite particles is believed to proceed through a dissolution-recrystallization mechanism from β-FeOOH. The basal plane diameter of the platelets in Figure 3-2 is about 3 μm and the thickness is around 0.5 μm, giving an aspect ratio of 6. The platelet particles possess a pseudohexagonal shape. The basal plane is the {0001} face and the side plane is the {0112} face according to Sugimoto. The characteristic shape of the platelet was formed due to stronger adsorption of OH$^-$ to the {0001} faces thereby retarding the growth in this direction. The growth rate on {0112} is relatively fast resulting in a tabular shape. The formation of hematite polyhedra was primarily due to
Figure 3-2 SEM micrograph of hematite particles prepared by hydrothermal synthesis.

(a) Platelets, 180°C, 6h, with 0.2 M EDTA; (b) Polyhedra, 180°C, 10h; (c) Pseudocube, 100°C, 8 days; (d) Peanut-like, 100°C, 8 days, with 0.6 M Na$_2$SO$_4$. 
the lack of preferred growth direction in the recrystallization step. In the case of pseudocubic hematite, the adsorption of Cl or chloro ferric complexes on the \{01 \bar{1}2\} faces is responsible for the restrained growth in the directions normal to the \{01 \bar{1}2\} faces. The presence of sulfate retarded the growth of crystal planes parallel to the c axis and forced the hematite particles to form an elongated peanut shape. A detailed discussion on the growth mechanisms for anisotropic hematite particles is postulated by Sugimoto 3 and Liu 29 elsewhere.

The XRD pattern shows that at a 3-hour heat treatment, both goethite (JCPDS ICDD 29-713) and hematite (JCPDS ICDD 33-664) are present, which is confirmed by SEM analysis. Goethite particles convert to hematite platelets with longer reaction time. XRD data for the 6-hour sample shows a pure hematite phase. No additional phase transformation is disclosed at longer holding times, which suggests the heating time for preparation of hematite particles should be no less than 6 hours. A complete comparison of the XRD patterns showed single-phase hematite for all morphologies (Figure 3-3). The diffraction lines for the platelets were very sharp while those for the polyhedra pseudocubic and peanut-like particles were somewhat broadened indicating less crystallinity.

To further modify the particle shape, samples were hydrothermally treated at 24 and 48 hours under the same conditions, respectively as for the 3 and 6 hours runs. According to the SEM observations, the particle shape was similar to those obtained at 6 hours (Figure 3-2), which indicates that longer heating times does not change the shape of the platelet. Previous studies show that different ions such as Cl\(^+\) and SO\(_4\)\(^{2-}\) can
Figure 3-3  X-ray diffraction patterns for hematite particles. Note increased diffraction line widths in the sequence platelets → polyhedra → pseudocubes and peanut-like. Hematite phase JCPDS ICDD 33-664.
strongly determine the shape of hematite particles. The residual Cl\(^{-1}\) ions in the system may play a role in the evolution of hematite platelet particles during hydrothermal treatment.

The isoelectric point (IEP) of hematite particles dispersed in DI water exhibits morphology dependence (Figure 3-4), a similar effect was observed by Bell et al. in the system of glycothermally synthesized α-Al\(_2\)O\(_3\) particles. Hematite platelets show an IEP around pH 8.2, while the IEP for polyhedron particles is shifted to pH 10.6. The difference of cation to anion ratio on a specific crystal planes was ascribed to the origin of this shift.

A commercially available hematite powder obtained from The Estee Lauder Corporation was used in the study of optical properties for hematite pigments. The particle size of The Estee Lauder sample was determined to be 0.5 \(\mu\)m with a random morphology and high purity (99.9%).

### 3.3 Optical Properties

#### 3.3.1 Color

The apparent color of Fe\(_2\)O\(_3\) particles significantly depends on phase, size and possibly the shape of particles. Hematite particles with a size around 0.3 \(\mu\)m have a strong maroon color, while platelet particles show a purple color with particle size about 3 \(\mu\)m. For a more precise comparison of the apparent color of the hematite particles, Munsell color notation was utilized. The Munsell notation uses hue (position of color in the spectrum, red, green, blue, etc.), lightness (on a scale ranging from black to white)
Figure 3-4 Zeta potential of hematite particles as a function of pH. The pH of the Fe$_2$O$_3$ aqueous suspensions were adjusted with 0.1 M HNO$_3$ and 0.1 M NaOH. The isoelectric point (IEP) is pH 8.2 for platelet and pH 10.6 for polyhedron. Error bars are the 95% confidence interval.
and saturation (the purity of the hue going from the grey to the pure color) to identify color using the notation hue value/chroma (H V/C) (Figure 3-5). It is interchangeable with other color systems such as the CIE (International Commission on Illumination) system through computer-aided transfer. Hematite particles were dried on a glass slide and compared with the Munsell color chips (Table 3-1). Hematite platelet particles (3 µm × 0.5 µm) have a purple color (10R 4/1), while the Munsell color notation for hematite polyhedra clearly depends on particle size. The hue, value and chroma change as the particle size increases.

3.3.2 Reflectance Spectra

Diffuse reflectance spectra of hematite particles were obtained by a Perkin Elmer Lambda 900 UV-vis-NIR spectrometer with BaSO₄ used as a reference material. The reflectance of hematite particles were also evaluated by means of a Datacolor SF 600 CT spectrophotometer (Estee Lauder, NY), a 31-point measurement was taken in the visible region from 400 to 700 nm.

The effect of particle size and shape on the color of hematite is illustrated by the reflectance spectra from 400 to 700 nm (Figure 3-6). The hematite particles have a very low reflectance from 400 to 570 nm. A rapid increase of reflectance occurs at about 570 nm. The slope of the curve depends on the particle size and shape involved. Polyhedron particles generally show higher reflectance than platelets when the incident wavelength is higher than 570 nm, and the degree of increase is strongly related to particle size for the same geometrical shape. Smaller polyhedron particles usually display a steep rise in
Figure 3-5 Munsell color notation. The cylindrical coordinates of the Munsell color notation (top left), the hue notation (top right) and the 3D view of the Munsell color space consist of color chips (bottom). (Figures from Munsell, a division of Gretag Macbeth, LLC.)
Table 3-1 Munsell color notation of hydrothermally synthesized hematite particles

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Parameters</th>
<th>Size (µm)</th>
<th>Shape</th>
<th>H V/C</th>
<th>Color chip</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hematite</td>
<td>180°C, 6h</td>
<td>3.0 × 0.5</td>
<td>Platelet</td>
<td>10R 4/1</td>
<td><img src="color1" alt="Color Chip" /></td>
</tr>
<tr>
<td>Hematite</td>
<td>180°C, 24h</td>
<td>3.0 × 0.5</td>
<td>Platelet</td>
<td>10R 4/1</td>
<td><img src="color2" alt="Color Chip" /></td>
</tr>
<tr>
<td>Hematite</td>
<td>180°C, 10h</td>
<td>0.2</td>
<td>Polyhedron</td>
<td>7.5R 4/8</td>
<td><img src="color3" alt="Color Chip" /></td>
</tr>
<tr>
<td>Hematite</td>
<td>180°C, 10h</td>
<td>0.3</td>
<td>Polyhedron</td>
<td>5R 4/2</td>
<td><img src="color4" alt="Color Chip" /></td>
</tr>
<tr>
<td>Hematite</td>
<td>180°C, 14h</td>
<td>0.5</td>
<td>Polyhedron</td>
<td>5R 4/8</td>
<td><img src="color5" alt="Color Chip" /></td>
</tr>
<tr>
<td>Hematite</td>
<td>180°C, 20h</td>
<td>1.0</td>
<td>Polyhedron</td>
<td>5R 5/8</td>
<td><img src="color6" alt="Color Chip" /></td>
</tr>
<tr>
<td>Hematite</td>
<td>As-received</td>
<td>0.5</td>
<td>Random</td>
<td>5R 5/8</td>
<td><img src="color7" alt="Color Chip" /></td>
</tr>
</tbody>
</table>

Note: The Munsell notation uses hue (H), value or lightness (V) and chroma or purity of color (C) to identify color using the notation hue value/chroma (H V/C). Hue basically refers to the spectral colors red (R), yellow (Y), green (G), blue (B), purple (P) and their intermediates. Value changes from 0 (black) to 10 (white). Chroma increases from 0 in steps of one, the higher the C value, the purer the color.
Figure 3-6 Reflectance spectra of hematite particles in the visible spectrum. The reflectance of hematite increases as particle size decreases from 570 to 700 nm, and platelets show lower reflectance than that of polyhedra.
reflectance from 550 to 600 nm that gives the particles their red color. A near-flat reflectance curve for platelets accounts for the purple color observed since most incoming light was absorbed by the material.

Diffuse reflectance spectra of $\alpha$-Fe$_2$O$_3$ particles are presented in Figure 3-7. Based on the data obtained in this work and on literature available regarding the optical absorption spectra of hematite, $^{11, 34, 35, 36, 37}$ the observed peaks can be assigned as following:

(1) The near infrared range from 700 nm to 1200 nm. This is a relatively low absorption region occupied by recognizable crystal field bands. A distinct band observed at 850 nm (11765 cm$^{-1}$) in polyhedron and 3 $\mu$m platelet hematite particles is due to the $^6A_1 \rightarrow ^4T_1$ ligand field transition. Marusak and coworkers $^{11}$ observed this band at 11560 cm$^{-1}$, while Tandon and Gupta $^{34}$ reported a value of 11630 cm$^{-1}$. In this work, only one broad band was recorded for the polyhedron and platelet hematite in the wavelength range from 700 nm to 900 nm. However, this broad band is split into two bands for pseudocubic and peanut like particles. As shown in the inserted figure, the two bands occur at about 820 nm and 890 nm, respectively. The peak at 890 nm most likely corresponds to the $^6A_1 \rightarrow ^4T_1$ transition, and another spin forbidden transition from $^6A_1 \rightarrow ^4T_2$ may give rise to the band at 820 nm (12195 cm$^{-1}$), as was recorded in hematite thin films at 12900 cm$^{-1}$ by Marusak et al. $^{11}$ even though the assignment is not certain. Although these bands can be assigned to crystal field transition, their intensities are much higher than that expected for purely crystal effects.
Figure 3-7 Diffuse reflectance spectra of hematite particles prepared by hydrothermal synthesis. (a) Polyhedra; (b) As-received; (c) Peanut-like; (d) Pseudocube; (e) Platelet. Note the shift of optical absorption edge at about 570 nm when particle morphology varies. The single broad band at 850 nm is split into two bands (820 and 890 nm) for pseudocube and peanut-like hematite particles. Baseline is obtained by a standard BaSO$_4$ sample. Rs-reflectance of BaSO$_4$, Rh-reflectance of hematite.
(2) Visible spectrum from 400 nm to 700 nm. There is a significant shape dependence of the spectra. Three poorly-defined absorption bands at 650 nm (15385 cm$^{-1}$), 535 nm (18691 cm$^{-1}$) and 470 nm (21276 cm$^{-1}$) were observed in this region. The first two bands at 650 nm and 535 nm are believed to arise from spin-forbidden ligand field transitions and have been observed previously by Marusak et al. 11 and Sherman, 36 even though the band assignment given by them was not identical. The third absorption band at 470 nm is assigned to the spin-flip transition among the $2t_{2g}$ states. 11, 35 Sherman observed this band at 430 nm and assigned it to the $^6A_1 \rightarrow ^4E$ transition. 36 However, two of these bands shift to longer wavelengths in the anisotropic particles, similar to the so-called “red shift”. Consequently, this shift increases the wavelength of each band by a value of about 40 nm, so that absorption bands were observed at 570 nm (17544 cm$^{-1}$) and 510 nm (19608 cm$^{-1}$), respectively. The complete set of observed transitions and assignments are summarized in Table 3-2.

(3) Ultraviolet region from 200 to 400 nm. Three weak absorption features superimposed on a very intense background can be identified at 330 nm (30303 cm$^{-1}$), 290 nm (34483 cm$^{-1}$) and 230 nm (43478 cm$^{-1}$). Very little detail can be resolved. These bands have been attributed to ligand-to-metal charge transfer between the $O_{2p}$ orbitals to the Fe$^{3+}$ $2t_{2g}$ and $3e_g$ orbitals. 11

(4) Absorption edge. The optical gap obtained from the diffuse reflectance spectra of hematite polyhedra is about 2.22 eV (560 nm) and 2.14 eV (580 nm) for platelet particles. The agreement is good with the band gap reported in literature. 38, 39, 40 The origin for the shift between the two particle sizes is not clear at the present time.
Table 3-2 Summary of the absorption bands and assignments in hematite, $\alpha$-$\text{Fe}_2\text{O}_3$

<table>
<thead>
<tr>
<th>This work (cm$^{-1}$)</th>
<th>Assignment</th>
<th>Marusak</th>
<th>Sherman</th>
<th>Tandon &amp; Gupta</th>
</tr>
</thead>
<tbody>
<tr>
<td>11765(P, T)</td>
<td>$^6\text{A}_1 \rightarrow ^4\text{T}_1$</td>
<td>11560</td>
<td>11000</td>
<td>11630</td>
</tr>
<tr>
<td>15385 (P, T)</td>
<td>$^6\text{A}_1 \rightarrow ^4\text{A}_1$</td>
<td>16670</td>
<td>15000</td>
<td>--</td>
</tr>
<tr>
<td>18691 (P) 17544 (T)</td>
<td>$^6\text{A}_1 \rightarrow ^4\text{E}$</td>
<td>18690</td>
<td>18180</td>
<td>--</td>
</tr>
<tr>
<td>21276 (P) 19608 (T)</td>
<td>$2t_{2g} \uparrow \rightarrow 2t_{2g} \downarrow$</td>
<td>20408</td>
<td>20800</td>
<td>21500</td>
</tr>
<tr>
<td>30303 (P, T)</td>
<td>$1t_{1u} \downarrow \rightarrow 2t_{2g} \downarrow$</td>
<td>31750</td>
<td>27780</td>
<td>28570</td>
</tr>
<tr>
<td>34483 (P, T)</td>
<td>$1t_{1g} \downarrow \rightarrow 3e_g \downarrow$</td>
<td>38900</td>
<td>34480</td>
<td>34480</td>
</tr>
<tr>
<td>43478 (P, T)</td>
<td>$6t_{1u} \downarrow \rightarrow 3e_g \downarrow$</td>
<td>44840</td>
<td>--</td>
<td>43290</td>
</tr>
</tbody>
</table>

Note: P = polyhedra, T = platelet, pseudocube and peanut-like.

The spectra were acquired by scanning a layer of hematite particles deposited on an Aluminum sample holder with BaSO$_4$ used as a reference material.

The vibrational terms A, E, T are defined by group theory.
3.3.3 Raman Spectra

A Bomem DA3+ FT Raman spectrometer was employed to measure the Raman scattering of hematite. Excitation was by a 600 mW YAG laser source with a wavelength of 1064 nm. InGaAs was used as the detector. Raman spectra of platelet particles were also obtained with a microRaman spectrometer using an Ar-Kr gas laser with a power of 200 mW.

Raman spectra were measured on commercial hematite powder by McCarty et al. 41 at ambient conditions, and by Shim et al. 42 at high pressure. Seven Raman active lines were observed and assigned based on a group theory calculation. Hematite belongs to R̃3c space group with a corundum type structure. 1 Based on group theory predications, there should be seven Raman active vibrational modes which include 2 A1g modes and 5 Êg modes. The present spectra are shown in Figure 3-8. Although there still exist some differences regarding the position and intensity of each Raman-active line, the general trend is that the seven vibrational modes span from about 220 cm\(^{-1}\) to 620 cm\(^{-1}\). There are two strong Raman lines, one A1g mode at 225 cm\(^{-1}\) and one Êg mode at 293 cm\(^{-1}\). Table 3-3 summarizes the vibrational bands and assignments on this work in comparison with the results reported in literature. 43, 44 Hematite platelet particles have somewhat different spectra from polyhedron particles in response to incoming 1064 nm excitation. Seven Raman lines were observed in hematite platelets, with the vibrational frequencies in good agreement with literature. However, the spectral profile changes in the hematite polyhedron as size decreases. Six Raman lines were observed. The intensity
Figure 3-8 Raman spectra of hematite particles prepared by hydrothermal synthesis. The excitation was by a 0.6 W YAG laser source ($\lambda = 1.064 \, \mu m$).

Note platelets show higher scattering intensity than that of polyhedra.
Table 3-3 Assignment of vibrational modes for hematite particles

<table>
<thead>
<tr>
<th>Mode (cm(^{-1}))</th>
<th>Platelets</th>
<th>Polyhedra</th>
<th>Shim</th>
<th>Massey</th>
</tr>
</thead>
<tbody>
<tr>
<td>A(_{1g})</td>
<td>226</td>
<td>226</td>
<td>224</td>
<td>228</td>
</tr>
<tr>
<td>E(_g)</td>
<td>247</td>
<td>247</td>
<td>243</td>
<td>246</td>
</tr>
<tr>
<td>E(_g)</td>
<td>292</td>
<td>293</td>
<td>290</td>
<td>294</td>
</tr>
<tr>
<td>E(_g)</td>
<td>298</td>
<td>299</td>
<td>297</td>
<td>300</td>
</tr>
<tr>
<td>E(_g)</td>
<td>412</td>
<td>413</td>
<td>408</td>
<td>412</td>
</tr>
<tr>
<td>A(_{1g})</td>
<td>493</td>
<td>--</td>
<td>496</td>
<td>496</td>
</tr>
<tr>
<td>E(_g)</td>
<td>614</td>
<td>616</td>
<td>609</td>
<td>614</td>
</tr>
</tbody>
</table>

Note: The Raman spectra were acquired by scanning the hematite particles deposited on a zero background glass slide under ambient condition.

The A\(_{1g}\) mode at 496 cm\(^{-1}\) was not observed in the case of hematite polyhedra.
of the vibrational bands decreases as frequency increases, which eventually leads to a low intensity of the $A_{1g}$ mode at 493 cm$^{-1}$ and the $E_g$ mode at 614 cm$^{-1}$.

Raman spectra of Fe$_2$O$_3$ prove to be very sensitive to excitation wavelength (Figure 3-9). The line shapes and band intensities for platelet particles were significantly dependent on excitation wavelength. When the laser line changes from blue (457 nm) to green (514 nm), the Raman active modes remain the same except a slight decrease of intensity. However, when yellow line (568 nm) and red line (647 nm) were used, the Raman spectra are quite different in many features. With 568 nm excitation, the peak at about 1320 cm$^{-1}$ was strongly enhanced and there was enhanced intensity for all Raman lines. The Raman spectra become most sharp and intense when excited by the red line, although the peak at 1320 cm$^{-1}$ completely disappeared. The low intensity for the Raman spectra under blue and green can be expected due to the strong absorption of incoming radiation with a wavelength shorter than the optical absorption edge of hematite, which is around 570 nm for platelet particles. The red line, 647 nm, falls exactly on the optical absorption edge so that the great intensity enhancement is due to resonance scattering. However, the explanation to the wavelength response behavior of the peak at 1320 cm$^{-1}$ is still unclear. Although this band had been observed previously, ambiguity still exists about its origin. Martin proposed a two magnon scattering process. Other work by McCarty, Massey et al., and Shim and Duffy support a resonance-enhanced two-phonon scattering process. The very sharp frequency response shown in Figure 3-6 suggests that a specific electronic transition along the optical absorption edge is responsible for the resonance coupling. The fundamental mode would be 660 cm$^{-1}$ and would be connect to an IR-active vibration.
Figure 3-9 Raman spectra of hematite platelet particles with various excitation wavelengths. Spectra acquired by a microRaman spectrometer using an Ar-Kr gas laser with an output of 200 mW. The intensity enhancement in 568 and 647 nm excitations is due to resonance Raman scattering (Absorption edge of hematite platelet is 580 nm).
3.3.4 Luminescent Spectra

Luminescence of all types of hematite particles was excited using a Nd:YAG laser producing 600 mW power at 1064 nm in combination with a BOMEM DA$^{3+}$ Fourier transform Raman spectrometer. The InGaAs detector has an effective cutoff at 1650 nm so the abrupt decrease in intensity at the low frequency end of the spectra probably represents the sensitivity limit of the detector. The hematite powders were placed between two pieces of zero-background glass slides and properly aligned before each scan.

Emission spectra of the as-prepared particles are shown in Figure 3-10. Some sense of the intensity of the broad band emission may be obtained by comparison with the sharp, high wavenumber bands which are the Raman lines of hematite. There are three overlapping broad bands with relative intensities that depend on the morphology of the Fe$_2$O$_3$ particles. All spectra were deconvoluted to three overlapping Gaussian lines and the fits were used to determine the wavenumber at the band maximum (Table 3-4).

There are at least four possibilities for the source of the weak infrared emission: (i) an intrinsic emission of Fe$^{3+}$ in the Fe$_2$O$_3$ host structure. (ii) A band edge or defect emission from the hematite structure (iii) an emission from impurities in the Fe$_2$O$_3$. (iv) an emission from adsorbed impurities on the particle surfaces arising from the synthesis process.

To evaluate the possible adsorption of luminescent surface species, the platelet particles were annealed at a series of temperatures. Temperatures as high as 1000 °C...
Figure 3-10 Emission spectra of hematite particles as synthesized. (a) platelets, (b) polyhedra, (c) pseudocubes. Band A = 7994 cm⁻¹, Band B = 7225 cm⁻¹, and Band C = 6686 cm⁻¹ for polyhedra. Deconvoluted with PeakFit®.
Table 3-4 Emission band wavenumbers determined by fitting observed spectra. Fitting error standard deviation = 50 cm\(^{-1}\).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Band A (cm(^{-1}))</th>
<th>Band B (cm(^{-1}))</th>
<th>Band C (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Platelets, 25(^\circ) C</td>
<td>8212</td>
<td>7391</td>
<td>6717</td>
</tr>
<tr>
<td>Platelets, 500(^\circ) C</td>
<td>8188</td>
<td>7367</td>
<td>6698</td>
</tr>
<tr>
<td>Platelets, 1000(^\circ) C</td>
<td>8188</td>
<td>7367</td>
<td>6698</td>
</tr>
<tr>
<td>Polyhedra</td>
<td>7994</td>
<td>7225</td>
<td>6685</td>
</tr>
<tr>
<td>Pseudocubes</td>
<td>7977</td>
<td>7338</td>
<td>6696</td>
</tr>
<tr>
<td>E-L 25(^\circ) C</td>
<td>8236</td>
<td>7395</td>
<td>6737</td>
</tr>
<tr>
<td>E-L 300(^\circ) C</td>
<td>8174</td>
<td>7395</td>
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<td>E-L 500(^\circ) C</td>
<td>8185</td>
<td>7395</td>
<td>6702</td>
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<tr>
<td>E-L 700(^\circ) C</td>
<td>8169</td>
<td>7394</td>
<td>6707</td>
</tr>
<tr>
<td>E-L 1000(^\circ) C</td>
<td>8064</td>
<td>7411</td>
<td>6717</td>
</tr>
</tbody>
</table>

E-L = Estee Lauder
should volatilize surface species. However, the annealed particles, in fact, produced a more intense luminescence than the unannealed particles (Figure 3-11). It seems unlikely that simple adsorbed species are the source of the luminescence.

A chemical analysis (X-ray fluorescence, The Mineral Lab, CO) of the platelet particles (Table 3-5) reveals several potential activators. Mn$^{2+}$ is a classical activator, but, especially in the annealed particles, should be in the form of Mn$^{3+}$ in solid solution in the Fe$_2$O$_3$. Ni$^{2+}$ is a known activator with an emission in the near infrared. The emission from the $^3T_{2g} \rightarrow ^3A_{2g}$ transition in MgO:Ni$^{2+}$ is near 8000 cm$^{-1}$ at 15 K. The Ni$^{2+}$ emission exhibits strong thermal quenching and at most only a very weak emission would be expected at 300 K. Because the low temperature literature spectra exhibit considerable fine structure, it is not easy to compare these spectra with the broad band emission observed in the present investigation.

To obtain an independent comparison, a sample of small particle Fe$_2$O$_3$ used in the cosmetic industry was obtained from the Estee Lauder Corporation. It also exhibited a similar weak infrared luminescence (Figure 3-12). An unexpected result is that this sample also gave a more intense luminescence after the powder had been annealed at high temperature. The bands shift to lower wavenumber with higher temperature anneals. The Estee Lauder Fe$_2$O$_3$ was of higher purity than the synthesized material (Table 3-5).

The evidence from the annealing experiments and from the comparison of spectra of Fe$_2$O$_3$ from different sources seems to eliminate possibilities (iii) and (iv). The observed luminescence appears to be an intrinsic property of Fe$_2$O$_3$.

If the emission is from Fe$^{3+}$ in an octahedral site in Fe$_2$O$_3$, it should arise from the usual $^4T_{1g} \rightarrow ^6A_{1g}$ transition. In single crystal Fe$_2$O$_3$ this transition has been identified at
Figure 3-11 Emission spectra of hematite platelet particles after annealing at the specified temperatures. (a) unannealed, (b) 500°C, 3h, (c) 1000°C, 3h. Band A = 8212 cm$^{-1}$, Band B = 7391 cm$^{-1}$, and Band C = 6717 cm$^{-1}$ for unannealed particles. Deconvoluted with PeakFit®.
**Table 3-5** Chemical composition of platelet (Plat.) and Estee Lauder (E-L) Fe$_2$O$_3$ determined by X-ray fluorescence analysis.

<table>
<thead>
<tr>
<th>Minor Elements</th>
<th>Plat.$^a$</th>
<th>E-L$^a$</th>
<th>Detection Limit</th>
<th>Trace Elements</th>
<th>Plat.$^b$</th>
<th>E-L$^b$</th>
<th>Detection Limit</th>
</tr>
</thead>
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<tr>
<td>Na$_2$O</td>
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<td>V</td>
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<td>10</td>
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<tr>
<td>MgO</td>
<td>Nd</td>
<td>nd</td>
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<td>Cr</td>
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<td>42</td>
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<td>Nd</td>
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<td>0.03</td>
<td>Co</td>
<td>75</td>
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<td>10</td>
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<tr>
<td>SiO$_2$</td>
<td>Nd</td>
<td>nd</td>
<td>0.03</td>
<td>Ni</td>
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<td>76</td>
<td>10</td>
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<td>P$_2$O$_5$</td>
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<td>0.05</td>
<td>Cu</td>
<td>38</td>
<td>38</td>
<td>10</td>
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<td>0.05</td>
<td>Zn</td>
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<td>Cl</td>
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<td>nd</td>
<td>10</td>
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<td>Fe$_2$O$_3$</td>
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<td>99.94</td>
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<td></td>
<td></td>
<td></td>
<td>Zr</td>
<td>nd</td>
<td>nd</td>
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<td></td>
<td></td>
<td>Rb</td>
<td>nd</td>
<td>nd</td>
<td>10</td>
</tr>
<tr>
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<td></td>
<td></td>
<td></td>
<td>Y</td>
<td>nd</td>
<td>nd</td>
<td>10</td>
</tr>
</tbody>
</table>

“Not detected”, nd, is specified for those elements with concentrations less than the detection limit. (a) Concentrations in weight percent. (b) Concentrations in parts per million.
Figure 3-12 Emission spectra of commercial small particle hematite after annealing at various temperatures. (a) unannealed, (b) 300°C, 3h, (c) 500°C, 3h, (d) 700°C, 3h, (e) 1000°C, 3h. Note the weak Raman scattering peaks from 9400 cm$^{-1}$ to 8900 cm$^{-1}$.
The absorption coefficients of both the $^4T_{1g}$ and $^4T_{2g}$ spin-forbidden transitions is two to three orders of magnitude higher than what would be expected from pure crystal field transitions. Magnetic coupling between adjacent Fe$^{3+}$ ions is claimed to be responsible for this effect. The larger absorption coefficient of these bands would enhance pumping by the Nd:YAG laser ($9400 \text{ cm}^{-1}$) but the emission is at a wavelength where Fe$_2$O$_3$ is relatively transparent.

Assigning the Fe$_2$O$_3$ emission bands to the $^4T_{1g} \rightarrow {}^6A_{1g}$ transition requires Stokes shifts of 3553, 4374, and 5048 cm$^{-1}$ respectively for the three observed bands. The values are large but not impossible. There is also the problem of explaining why the emission appears as three separate bands with relative intensities that vary between the different particle morphologies. Furthermore, the shifts in emission wavenumber with temperature of annealing must be explained (Table 3-4). The obvious wavenumber shift after 1000 °C annealing might be an indication of improved crystallinity at high temperature.

The effective absorption edge for Fe$_2$O$_3$ is near $15,500 \text{ cm}^{-1}$ (645 nm) where the absorption coefficient begins to abruptly increase from about $2000 \text{ cm}^{-1}$ for the two crystal field bands to values in excess of $10^5 \text{ cm}^{-1}$ in the visible region of the spectrum. The observed emission bands, therefore seem to occur at too low a wavenumber to be due to exciton or electron/hole recombination at the absorption edge. The role of defects cannot be discounted. Fe$_2$O$_3$ is known to be slightly non-stoichiometric. A distribution of oxygen vacancies near the emitting Fe$^{3+}$ ions or deep traps could be responsible for the observed multiband structure of the luminescence spectrum.
3.4 Conclusions

Phase pure hematite particulate pigments with various sizes and shapes were prepared via hydrothermal treatment of Fe(OH)\textsubscript{x}O\textsubscript{y} gel at designed conditions depending on the morphology required. Platelet-like hematite particles (3 µm × 0.5 µm) were obtained with the presence of EDTA at pH 12, while the absence of EDTA will form hematite polyhedra. The perceived colors of the pigments vary with particle size and shape. The apparent color of hematite particles changes from maroon (5R 4/2) to purple (10R 4/1) as particle size increases from 0.2 µm to 3 µm based on the Munsell color notation. A “red-shift” of the absorption bands for hematite particles were observed in platelet particles, in comparison with polyhedron-like hematite particles. The Raman band intensities of hematite particles exhibit a significant dependence on particle size, excitation source and vibrational frequency as revealed. The E\textsubscript{g} mode at 614 cm\textsuperscript{-1} was significantly reduced as particle size decreases to 0.5 µm.

A weak near infrared fluorescence emission was observed in phase pure hematite polycrystal particulate powders. The as-synthesized hematite particles were stable during high temperature annealing, while the spectral intensity was significantly enhanced. The possible origins responsible for the near infrared luminescence were discussed.

3.5 References


Chapter 4

Synthesis and Optical Properties of Ag/SiO$_2$ Nanocomposites

4.1 Introduction

Nanoscale composite particles with a core-shell structure have gained extensive interest due to their unique properties and potential applications in electronics and photonics. 1, 2, 3, 4 A substantial literature is available on the subject of silica-coated metallic quantum dot nanocomposite particles in recent years due to their flexibility and versatility. 2, 3, 5, 6 The nanocomposites are promising as building blocks to form 2D or 3D structures via a number of techniques such as Langmuir-Blodgett method (LB), self-assembly 7, 8 and electrophoretic deposition (EPD). 9 Optical properties of nanoscale particles are often quite different from those of bulk materials. 10 Particularly for nanocomposites which in many cases consist of a metallic core and an insulator shell, the quantum size effects and local field enhancement at the surface plasmon resonance could significantly contribute to the optical nonlinear response. 2

Core-shell structured nanocomposite particles were first synthesized and reported by Mulvaney et al. (Au/SiO$_2$, 11 Au/SnO$_2$ 12 and Ag/SiO$_2$ 13 ) and by Adair et al. (Ag/SiO$_2$, 3 CdS/SiO$_2$ 2 and Pt/SiO$_2$ 14 ). Most SiO$_2$ coated nanocomposite particles with a core-shell architecture fall into two categories based on the synthetic method used. The approach developed by Liz-Marzan and Mulvaney et al. involved the modification of metal cluster surfaces with a silane coupling agent 3-aminopropytriethoxysilane (APS,
NH₂C₃H₆Si-(OC₂H₅)₃) before the formation of the silica shell. The silane coupling agent APS is used as an adhesion promoter between the vitreophobic metal cluster core and the SiO₂ shell. The Au/SiO₂ nanoparticles were deposited via a layer-by-layer technique to form a macroscopic thin film. However, the state of dispersion for the nanocomposite suspension was not examined and possible residual surfactant may be present in the self-assembly thin film, which could affect the homogeneity and optical properties of the 2D nanoparticle arrays. Using a microemulsion as a nanoreactor, Li and Adair et al. successfully coated metallic and CdS clusters with silica via a simple hydrolysis and condensation of tetraethoxysilane (TEOS) in cyclohexane /Igepal /water tertiary system. The coating of the silica shell is very uniform with a tunable thickness of both the core and the shell due to the confined water droplets in oil. Unfortunately, agglomeration is an issue when the protective surfactant is removed using conventional washing protocols such as centrifugation. The core-shell nanocomposites were also used to prepare metal/SiO₂/polymer double coating nanocomposites, and then selective dissolution of the SiO₂ layer leads to a novel metal/polymer nanocomposites with a movable metal core.

The unique optical properties of the SiO₂ coated core-shell nanocomposites originated from the metallic core and the dielectric shell enhancement. A number of theoretical models were developed to understand the optical properties of colloidal metal particles, and a detailed review is discussed in Chapter 2. The size and shape effect on the color of nanoparticles were studied by Schatz et al. and Pileni et al. for Ag nanoprisms, and by Mulvaney et al. for Au/SiO₂ nanocomposite thin films. More recently, the SiO₂ coated Au or Ag nanocomposites were examined as a Raman tagging
system using the surface enhanced Raman scattering effect. Photonic crystals assembled with Au/SiO$_2$ nanocomposites (50 nm Au and 80 nm SiO$_2$) exhibit optical absorption related to the metal core and the SiO$_2$ shell thickness. Unfortunately, most of the nanocomposites generated from colloidal approaches requires the presence of a surfactant or polymeric species to stabilize the nanoparticle suspension. The role of the dispersant in the optical properties of the nanocomposite devices is not well understood.

In this chapter, the preparation of Ag/SiO$_2$ nanocomposites using the Igepal/cyclohexane/water reverse micelle system was discussed. A number of conventional washing techniques were examined in order to generate well-dispersed Ag/SiO$_2$ nanocomposite dispersion. This effort leads to the application of high performance liquid chromatography (HPLC) in SiO$_2$ based nanocomposite dispersion. Optical properties of the Ag/SiO$_2$ nanocomposite were studied on the HPLC generated suspension.

### 4.2 Experimental Procedure

#### 4.2.1 Synthesis of Ag/SiO$_2$ nanocomposites

The method used to prepare Ag/SiO$_2$ nanocomposite particles was outlined in detail by Li et al., all chemicals involved were used as received. Nonionic surfactant poly (oxyethylene) nonylphenyl ether (Igepal CO-520), cyclohexane, silver nitrate, tetraethoxysilane (TEOS), silane coupling agent 3-aminopropyltriethoxysilane (APS), hydrazine and NH$_4$OH (28–30%) were all purchased from Aldrich Chemicals Co. (Milwaukee, WI). Dehydrated ethanol (200 proof, Pharmca Products Inc. Brookfield, CT) and glacial acetic acid (J. T. Baker Chemicals) were used without further
purification. All aqueous stock solutions were prepared with deionized water (specific conductivity = 0.4×10^{-7} S/m).

The reverse micelle was formed by mixing 10 ml of cyclohexane and 4 ml of Igepal CO-520 followed by the addition of a prescribed amount of 0.01 M AgNO₃ aqueous solution under vigorous stirring according to the R ratio. The Ag⁺ ions were reduced to metallic Ag by adding a drop of hydrazine into the microemulsion. An appropriate amount of TEOS was added to coat the metal cluster based on the H ratio, and a drop of NH₄OH aqueous solution was introduced as a catalyst to ensure the hydrolysis of TEOS in an alkaline pH regime. The microemulsion was sealed and allowed to settle 24 hours for the completion of the SiO₂ coating under stirring. The complete process is shown schematically in Figure 4-1.

4.2.2 Washing and Recovery

Reverse micelle microemulsions containing Ag/SiO₂ nanocomposite particles were first treated with APS-ethanol solution. The surfaces of the Ag/SiO₂ nanocomposite particles are positively charged (~30 mV) at a pH lower than pH 7.0 due to the surface graft of APS. The microemulsion was broken using 50 ml 0.02 M acetic acid/ethanol stock solution with rigorous stirring to maintain pH below pH 7.0. The suspension was further processed with ethanol using a number of washing techniques including centrifugation, sedimentation, Soxhlet extraction and filtration. The residual concentration of surfactant Igepal CO 520 was monitored by UV-vis spectra. Using the Beer-Lambert law, a calibration curve for Igepal CO 520 was constructed by measuring
Figure 4-1 Flow sheet of Ag/SiO$_2$ nanocomposite suspension obtained from reverse micelle synthesis and washing with various methods. (Modified from Li, et al. $^3$)
the absorbance at 280 nm as a function of concentration. All the measurements were conducted at pH 6 Igepal/ethanol solutions.

4.2.3 Characterization

The zeta potentials of Ag/SiO$_2$ nanocomposite suspensions were measured by a ZetaPALS Analyzer based on dynamic light scattering (Brookhaven Instruments Co., NY). The pH was adjusted by 0.1M HNO$_3$ and 0.1M KOH aqueous solutions. The morphology and dispersibility of Ag/SiO$_2$ suspensions were first examined with an AFM (MultiMode, Digital Instruments) using the Tapping Mode$^\text{TM}$. The samples for AFM experiments were prepared by placing drops of Ag/SiO$_2$ suspension on a freshly cleaved mica substrate and spin coating the substrate at 1500 rpm for 30 seconds. Image analysis was performed on a high-resolution transmission electron microscope (HRTEM) (HF 2000, Hitachi, Japan and JEOL 2010F, Tokyo, Japan). A drop of freshly prepared suspension was placed on a carbon film supported on a copper grid and dried over night in vacuum oven. A state-of-the-art Malvern Nanosizer (Malvern Instruments, UK) was used to determine the state of dispersion for Ag/SiO$_2$ suspension. The pH of the Ag/SiO$_2$ nonaqueous suspensions were measured with a Sentron pH meter (Argus IP 65 ISFET probe, Sentron Inc., WA) calibrated against standard aqueous buffer solutions.
4.3 Dispersion of Ag/SiO$_2$ Nanocomposites

4.3.1 Centrifugation

The state of dispersion for Ag/SiO$_2$ nanocomposites washed and redispersed with centrifugation is shown in Figure 4-2, for the sample with R=2, H=100 and X=1, the primary particle size by TEM is $30 \pm 1.2$ nm. The collective particle size distribution measured by dynamic light scattering is 233 nm. Using the average agglomeration number (AAN) concept developed by Adair et al., the AAN of the Ag/SiO$_2$ suspension is calculated by taking the volume ratio of the light scattering size (DLS) to the microscopic size (TEM). For centrifugation protocol, the AAN is estimated to be 468, indicating a significantly aggregated suspension. This degree of aggregation is consistent with the TEM observation.

4.3.2 Sedimentation

The Ag/SiO$_2$ nanoparticles were washed via sedimentation and redispersion after APS coating. The resulting nanocomposite suspension has a bimodal distribution according to the light scattering analysis, with a primary mode at around 25 nm and a secondary mode at 2 $\mu$m (Figure 4-3). Compared to the particle size from TEM, the AAN is estimated to be 921. Although the AAN is high relative to that of centrifugation, the dispersion may further be improved by using filtration to remove the nanocomposite agglomeration. However, the sedimentation washing procedure is usually time-consuming even though the protocol requires little instrumentation.
Figure 4-2 Ag/SiO$_2$ nanocomposites suspension (R=2, H=100, X=1) washed with centrifugation. TEM analysis (top), particle size distribution by dynamic light scattering (bottom). Average agglomeration number (AAN) is 468.
Figure 4-3 Ag/SiO$_2$ nanocomposites suspension (R=2, H=100, X=1) washed with sedimentation. TEM analysis (top), and particle size distribution by DLS (bottom). The AAN is 921.
4.3.3 Soxhlet Extraction

Soxhlet extraction offers a pathway to wash and extract materials in a continuous manner, which improves the efficiency of the washing solvent. Therefore, Ag/SiO$_2$ nanocomposites were washed and collected with a Soxhlet extractor. The washing solvent was heated to its boiling point and evaporated from the solvent reservoir, then condensed down to the thimble which contains as-prepared Ag/SiO$_2$ nanoparticles, and finally flowed back into the reservoir. A washing cycle takes about 40 minutes. Figure 4-4 shows a TEM image as well as particle size distribution of the Ag/SiO$_2$ particles washed with Soxhlet extractor. The AAN is determined to be around 106, which is confirmed by the TEM analysis. A portion of the Ag/SiO$_2$ nanoparticles displays particle size less than 10 nm, which may be caused by the dissolution of the SiO$_2$ shell during washing.

4.3.4 Filtration

This washing method follows the protocol reported by Tan et al. for SiO$_2$ coated nanoparticles. The microemulsion is broken and coagulated with acetone, and then the particles are filtered (2 µm filter, Millipore, Bedford, MA) and washed with acetone and ethanol three times. The particle size distribution measured by dynamic light scattering is bimodal, and the agglomerate size about 250 nm (Figure 4-5). The AAN for Ag/SiO$_2$ nanocomposite ethanol suspension is about 318. The agglomeration is likely to occur because of the coagulation induced by acetone, which allows nanoparticles to come into contact, and sinter via neck formation. This is an irreversible process for
Figure 4-4 Ag/SiO$_2$ nanocomposites suspension (R=2, H=100, X=1) washed with Soxhlet extraction. TEM analysis (top) and particle size distribution by DLS. The AAN is about 106.
Figure 4.5 Ag/SiO$_2$ nanocomposites suspension (R=2, H=100, X=1) washed with filtration. The AAN is 318, and the primary particle size of 30 nm is used based on TEM analysis. Washing based on Tan’s protocol.$^{22,23}$
nanoscale particles. Therefore, improving the stability for nanoscale dispersion does not involve any of the usual separation and washing approaches. 28

4.4 Optical Properties of Ag/SiO$_2$ Nanocomposites

4.4.1 UV-vis Spectra

The UV-vis spectra of optical properties of Ag/SiO$_2$ nanocomposites are shown in Figure 4-6. A characteristic absorption band observed at 410 nm for both samples (R=2, H=100, X=1 and R=8, H=300, X=10) is attributed to the surface plasmon resonance of Ag quantum dots. 3, 17 This peak is in the ultraviolet regime for bulk Ag metal, whose electron concentration is much higher than that of the Ag clusters. 29 Therefore, the shift of this peak to the visible spectrum is primarily due to the decrease of electron concentration in Ag quantum dots. 2, 29 The same “red shift” is common in most metals as a consequence of the size quantization. A very weak absorption band found at around 280 nm is most likely due to the APS molecules attached to the surface of the Ag/SiO$_2$ nanocomposites.

4.4.2 Refractive Index

The refractive index for Ag/SiO$_2$ nanocomposite materials was calculated using equation 2.3 discussed in Chapter 2. A dielectric constant of 2.10 (n = 1.45) is used for amorphous SiO$_2$, 30 and the Ag/SiO$_2$ nanocomposites are treated as perfect spheres. The ratio of effective dielectric constant to that of SiO$_2$ (\(\frac{\varepsilon_i}{\varepsilon_m}\)) is plotted against the diameter
ratio of Ag core to SiO$_2$ shell (D$_c$/D$_s$) and illustrated in Figure 47. The effective dielectric constant increases as the Ag core diameter increases, reaching a finite value of 4$\varepsilon_m$ when D$_c$ = D$_s$ is satisfied. The boundary condition for Dc/Ds is anywhere from 0 to 1 because of the core-shell architecture leading to a finite effective dielectric constant ranging from $\varepsilon_m$ to 4$\varepsilon_m$. Hence, the refractive index of the Ag/SiO$_2$ nanocomposites can have values between 1.45 ($n_m$) (amorphous SiO$_2$) and 2.90 (2$n_m$). It is important to mention the limitation of this calculation, which is primarily based on the Maxwell-Garnett model at low fill fraction. 2, 10 The upper limit for effective dielectric constant (4$\varepsilon_m$) may never be satisfied in reality, because that is the case for pure Ag nanoparticles, where equation 2.3 needs to be replaced with a specific model dealing with metals in electric fields. 2, 17, 31

4.5 Conclusions

AgSiO$_2$ nanocomposites were prepared using cyclohexane/Igepal/water reverse micelles as a nanoreactor. The resulting nanocomposites were coated with APS and several conventional methods were employed but failed to generate stable Ag/SiO$_2$ dispersion. The “red shift” was observed in the Ag/SiO$_2$ nanocomposites, whose surface plasmon resonance peak is around 410 nm. The refractive index of Ag/SiO$_2$ nanocomposites was estimated using the modified Maxwell-Garnett theory.
Figure 4-6 UV-vis spectra of Ag/SiO$_2$ ethanol/water suspensions. Note the absorption band at about 410 nm is due to the surface plasmon resonance of Ag quantum dots. The APS surface coating is responsible for the weak band at 280 nm.
Figure 47 Effective dielectric constant of Ag/SiO$_2$ as a function of core-shell ratio. Note the Maxwell-Garnett model is simplified at low fill fraction. A dielectric constant of 2.10 is used for amorphous SiO$_2$ shell. The refractive index can be obtained using $\varepsilon = n^2$. 
4.6 References


Chapter 5

Dispersion of SiO$_2$-Based Nanocomposites with High Performance Liquid Chromatography (HPLC)

5.1 Introduction

Synthesis and patterning of nanoparticles has become one of the most popular topics in recent research activities. 1 Unfortunately, most of these nanoparticles generated through colloidal approaches require large quantities of surfactant or polymeric species to ensure the stability of the nanoparticle suspension. 2 The trade off is obvious because surfactant additives will be transferred to the subsequent process steps and could have a negative impact on the homogeneity of the arrays assembled from the nanoparticles. Therefore, it is important to develop a protocol that can produce nanoparticle suspensions with less or no dispersant addition.

Dispersion essentially starts with washing of freshly prepared nanoparticles in a chemical synthetic method. However, washing and dispersion of nanoparticles are always a challenge because of the strong van der Waals attraction between neighboring particles. For this reason, nanoparticle suspensions were stabilized with surface coatings of surfactant, which could effectively balance the interaction forces with increasing repulsion potential created by surfactant molecules. However, the content organic dispersants should be minimized in order to achieve better performance for these nanoparticle-based devices. Four conventional methods were applied to disperse Ag/SiO$_2$
nanocomposites in Chapter 4, but none of those could produce well-dispersed nanoscale dispersion. Utilizing the concept of protective dispersion initially proposed by Zsigmondy, Kimel and Adair were able to make stable aqueous suspensions of 8 nm ZrO$_2$ nanoparticles.

High performance liquid chromatography (HPLC) is a promising alternative to wash and disperse nanocomposite particles simultaneously. The initial inspiration for washing and dispersion of nanoparticles by HPLC stems from the separation of Fullerenes C$_{60}$ and C$_{70}$ originally reported by Hawkins et al. and Cox et al. using functionalized silica as the stationary phase. The physical shape of Fullerenes and silica nanoparticles are quite similar, but with typical silica nanoparticles (~ 20 nm) significantly larger than Fullerenes (~ 1 nm). Both systems have accessible surface sites that can be functionalized. Therefore, it was hypothesized that a separation and dispersion scheme could be established for metal/SiO$_2$ nanocomposites by selecting a suitable stationary phase and modifying the HPLC procedures to accommodate the silica nanoparticles.

This chapter demonstrates the washing and dispersion of the Ag/SiO$_2$ nanocomposites by the HPLC technique. The Ag/SiO$_2$ ethanol/water suspension was characterized by TEM and dynamic light scattering methods. The average agglomeration number (AAN) for the Ag/SiO$_2$ nanocomposites suspension is calculated. The Ag/SiO$_2$ suspensions obtained via surface grafting with APS and HPLC washing exhibit good stability at room temperature. Such particles provide an ideal precursor for the fabrication of electro-optic devices by self-assembly or electrophoretic deposition (EPD) approaches.
5.2 Experimental Procedure

5.2.1 Washing with HPLC

Reverse micelle microemulsions containing Ag/SiO$_2$ nanocomposite particles were first treated with APS-ethanol stock solution (1 w/o, 15 g of APS mixed with 15 mL anhydrous ethanol, 0.15 mL glacial acetic acid and 0.75 µL DI water). The surfaces of the Ag/SiO$_2$ nanocomposite particles are positively charged (~30 mV) at a pH lower than pH 7.0 due to the surface grafting of APS. The microemulsion was mixed with 50 ml 0.02 M acetic acid/ethanol stock solution with rapid stirring to maintain pH below pH 7. Then the suspension was pumped into the HPLC system (Waters Delta Prep 3000 HPLC system, Milford, MA). An empty HR 5/5 column was purchased from Amersham Pharmacia Biotech (Piscataway, NJ). The column was packed with 20 µm APS treated spherical silica (Stellar Phases, Inc. PA) at a rate of 2 mL/min. The terminal end of the column was connected to a UV-vis spectrum detector set at a wavelength of 405 nm, the wavelength of the surface plasmon peak of the Ag quantum dot core. Dehydrated ethanol was pumped through the HPLC system as the washing solvent and the nanocomposites were collected with ethanol-water solution (volume ratio 7:3). A fraction collector was utilized to collect elute from the HPLC column during the entire washing procedure. A sketch of the configuration for the HPLC system is shown in Figure 5-1.

5.2.2 Characterization

The zeta potentials of Ag/SiO$_2$ nanocomposite suspensions were measured by a ZetaPALS Analyzer based on the dynamic light scattering principle (Brookhaven
Figure 5-1 Schematic setup of the HPLC system for washing and dispersion of Ag/SiO$_2$ nanocomposites ethanol/water suspension based on the size exclusion chromatography. The UV-vis detector wavelength is set at 405 nm for Ag/SiO$_2$ nanocomposites. The size of the HPLC column is HR 5/5 (5 × 50 mm).
Instruments Co., NY). The pH was adjusted by 0.1M HNO$_3$ and 0.1M KOH aqueous solutions. The morphology and dispersibility of Ag/SiO$_2$ suspensions were first examined with an atomic force microscope (AFM) (MultiMode, Digital Instruments) in Tapping Mode$^\text{TM}$. The samples for AFM experiments were prepared by placing drops of Ag/SiO$_2$ suspension on a freshly cleaved mica substrate and spin coating the substrate at 1500 rpm for 30s. Image analysis was performed on a high-resolution transmission electron microscope (HRTEM) (HF 2000, Hitachi, Japan and JEOL 2010F, Tokyo, Japan). A drop of freshly prepared suspension was added on a carbon film supported on a copper grid and dried over night in vacuum oven. A state-of-the-art Malvern Nanosizer (Malvern Instruments, UK) was used to determine the state of dispersion for Ag/SiO$_2$ suspension. The morphology of as-received SiO$_2$ microspheres was obtained by a scanning electron microscope (SEM, Hitachi S-3000H, Japan). The surface structure of SiO$_2$ microspheres was examined by AFM after a washing and dispersion cycle. All the pH measurements were carried out with a Sentron pH meter (Argus IP 65 ISFET probe, Sentron Inc., WA) calibrated against standard aqueous buffer solutions.

5.3 Results and Discussion

5.3.1 Morphology of Ag/SiO$_2$ Nanocomposites

Figure 5-2 shows the morphology of Ag/SiO$_2$ nanoparticles derived from water-in-oil reverse micelle synthesis with conventional washing protocols. The formation mechanism and chemical kinetics of nanoparticles in the cyclohexane/Igepal/water reverse micelle system have been discussed in detail by Arriagada and Osseo-Asare. 7, 8
Figure 5-2  Morphology of Ag/SiO$_2$ nanocomposites (R=2, H=100, X=1) washed with conventional method. TEM images show the core-shell structure (top and insert). Particle size distribution obtained from TEM image on the top. $D_{50} = 30$ nm, $SD = 1.2$ nm (with 95% confidence interval).
The size and shape of the particles generated from the reverse micelle synthesis depends on the molar ratio of water to surfactant, R, and the ratio of water to TEOS, H. The general trend for the growth of Ag/SiO\(_2\) nanocomposites is that the silver core diameter is proportional to R while silica shell thickness decreases as H increases. For example, R = 2, H = 100 and X = 1 ([NH\(_4\)OH] to [TEOS]), the diameter of the Ag/SiO\(_2\) nanocomposite particles obtained through reverse micelle synthesis is about 30 ± 1.2 nm and the silver quantum dot is about 5 ± 0.6 nm (± 95% confidence interval). The SiO\(_2\) layer thickness is about 12 nm. The conventional methods used to wash and collect as-synthesized nanocomposite particles did not prevent agglomeration induced by the van der Waals forces between particles, as clearly illustrated in the TEM images. Detailed comparison of these methods was made in Chapter 4.

There is insufficient data to identify the formation step of the agglomeration during the entire synthesis. However, nanocomposite particles trapped in the reverse micelle should not agglomerate due to the protective layer of surfactant. In many cases surfactants were applied to modify the surfaces of nanoparticles to obtain monodispersed suspensions, which would be used as ideal precursors for creating nanoparticle-based devices. Therefore, the hypothesis was that washing out the surfactant layer could induce agglomeration. To minimize the agglomeration during the synthesis of Ag/SiO\(_2\), it is important to wash and disperse nanoparticles simultaneously.
5.3.2 HPLC Washing

The HPLC system was employed to wash and disperse nanocomposite particles in order to produce well-dispersed Ag/SiO$_2$ suspensions. Figure 5-3 shows the morphology of silica microspheres used as stationary phase in the HPLC system. The silica particles are uniform spheres with a mean particle size of 20 µm and a pore size of 65Å (surface area 425 m$^2$/g). A random packing density of 57% was obtained when the silica microspheres were dry-packed in the HPLC column. This generates a column porosity as high as 43%, which could form multiple micro-channels for nanoparticles to migrate during HPLC operation. The silica microspheres were treated with APS to produce positive charges to prevent the positively charged Ag/SiO$_2$ nanoparticles from sticking on the surface of stationary phase silica. Thus, control of the surface charge on the microspheres is a critical step in the HPLC washing to produce well-dispersed nanoparticles.

The spectrum shown in Figure 5-4 reflects the washing process of Ag/SiO$_2$ in the HPLC column. Elute of Ag/SiO$_2$ from the HPLC column took about 3 minutes when the extraction solvent (ethanol/water, volume ratio 7:3) was being pumped at 2 mL/min. The spectral intensity increased significantly at the onset point where Ag/SiO$_2$ nanocomposite particles pass through the detector, and a stable suspension was continuously collected at the HPLC terminal. The HPLC spectrum appeared to be a relatively narrow band with a high intensity (recorded as voltage because of the HPLC detection setup) accompanied by a secondary shoulder observed in the range of the washing cycles, which was the basis for collecting well-washed Ag/SiO$_2$ suspension. Deconvolution of the spectrum by
The SiO$_2$ microspheres were treated with APS (90 g SiO$_2$ mixed with 0.336 mL APS, 1.5 mL glacial acetic acid, 7.5 mL DI water and 150 mL ethanol, keep stirring overnight and dried at 70°C). The surface area is 425 m$^2$/g with average pore size of 6.5 nm (Data courtesy of Stellar Phase, Inc.).
Figure 5-4 HPLC spectrum of Ag/SiO$_2$ ethanol/water suspension (R=2, H=100, X=1) washed with the HPLC system. Spectrum acquired at 405 nm (surface plasmon resonance of Ag quantum dots) by a UV-vis detector. The washing solvent is an ethanol/water solution (volume ratio 7:3), and the flow rate is 2 mL/min. The spectrum was deconvoluted by PeakFit$^\text{®}$, the central positions of the peaks are 95.1, 112.2 and 150.7 s.
PeakFit® yields three discrete peaks (area ratio of the three peaks is 1.1:1.8:1, and the central positions of the peaks are 95.1 s, 112.2 s and 150.7 s), which may correspond to the resolution of the HPLC column for individual Ag/SiO₂ nanocomposite particles and their aggregates (doublets, triplet, etc.). It suggests that the concentration of Ag/SiO₂ nanoparticles must be very high based on the Beer-Lambert law. The entire washing procedure takes about 45 minutes, including an actual eluent collection time of about 3 minutes. This is much more efficient than conventional washing procedures such as centrifugation and sedimentation which can require days to weeks. The profile of the spectra suggests that the majority of the Ag/SiO₂ nanoparticles travel through the HPLC column with a constant rate, which allows nanoparticles to continuously move inside the interstitial channels and thereby reduces the chance that particles will aggregate and deposit on the surface of stationary SiO₂ microspheres. However, the asymmetrical profile of the spectra also indicated that a small number of Ag/SiO₂ nanoparticles need a longer time to go through the column due to the variation of particle size, as related to the principle in chromatography that smaller particles tend to take more time to elute. This could be an indication that a few doublet, triplet or even larger clusters were formed in the washing process along with individual Ag/SiO₂ nanoparticles.

Figure 5-5 shows the morphology of Ag/SiO₂ nanoparticles washed by the HPLC method. According to the UV-vis analysis from 200 to 600 nm, the Ag/SiO₂ nanoparticles were free of surfactant within instrumental detection limits because the characteristic 280 nm absorption band for Igepal CO-520 is not present. The zeta potential, +30 mV, firmly indicates robust surface grafting with APS even after the HPLC washing. The average size of the Ag/SiO₂ nanocomposite particles remains the
Figure 5-5 Morphology of Ag/SiO$_2$ nanocomposites ethanol/water (7:3 vol) suspensions washed with HPLC.

Digital images: suspension A, R=2, H=100, X=1, suspension, $D_{50} = 30$ nm, SD = 1.2 nm.

B, R = 8, H = 300, X = 1, $D_{50} = 20.3$ nm, SD = 1.5 nm. (With 95% confidence interval).

TEM images show the size, core-shell architecture and state of dispersion of the suspensions A and B.
same as determined by TEM prior to the HPLC washing, with a Ag core of 5 ± 0.6 nm and overall diameter around 30 ± 1.2 nm (R=2, H=100, X=1). An average size of 20.3 ± 1.5 nm is observed for R=8, H=300 and X=1 after HPLC washing. Besides the individual nanoparticles, nanoscale clusters formed by two, three or four particles were also observed in HRTEM. Aggregates with continuous inter-particle connections are not found. This implies that the HPLC method breaks the nanoparticulate aggregates down to a size that allows the nanoparticles to penetrate through the interstitial channels. These observations support the conclusions drawn from the previous HPLC spectral analysis.

An AFM image of Ag/SiO\textsubscript{2} ethanol/water suspension (R=2, H=100, X=1) spin-coated onto a freshly cleaved mica substrate is shown in Figure 5-6. At a spin rate of 1500 rpm, nanoparticles were found sparsely distributed on the surface of mica. Further analysis indicated that the mean particle size is around 60 nm, which derives an average agglomeration number of about 2 if the particle size of 30 nm in HRTEM was taken as the primary unit. Furthermore, the Ag/SiO\textsubscript{2} suspension treated with HPLC turned out to be very stable as experimentally confirmed by sedimentation tests over a span of one month.

The state of dispersion of Ag/SiO\textsubscript{2} ethanol/water suspension was determined by the dynamic light scattering method. The hydrodynamic size distribution of the Ag/SiO\textsubscript{2} nanocomposite particles is presented in Figure 5-7 (R=8, H=300 and X=1). An overall collective average size of 18.6 ± 1.5 nm was found for the Ag/SiO\textsubscript{2} nanocomposite particles with a narrow monomodal distribution. The light scattering result is in agreement with the particle size measured by TEM (20.3 ± 1.5 nm). The AAN for the
Figure 5-6 AFM images of Ag/SiO$_2$ nanocomposites (R=2, H=100, X=1) suspension obtained with the HPLC washing. Images obtained by Tapping Mode$^{\text{TM}}$. The samples were prepared by placing a drop of the Ag/SiO$_2$ ethanol/water suspension on a freshly cleaved mica substrate and spin coat at 1500 rpm for 30 s. The 3D image shows the aggregate size about 60 nm.
Figure 5-7 Particle size distribution of Ag/SiO$_2$ nanocomposites (R = 8, H = 300, X = 1) measured by dynamic light scattering (DLS) and TEM image analysis. $D_{50} = 18.6$ nm, SD = 1.5 nm for DLS, the particle size from TEM image analysis is $20.3 \pm 1.5$ nm (30 particles were counted). Note the close match between DLS and TEM analysis.
HPLC washed sample is around 1.0. Thus, Ag/SiO$_2$ nanocomposite particles are well dispersed in ethanol/water co-solvent after HPLC washing, because light scattering is more precise in revealing the collective state of dispersion for a colloidal suspensions that TEM. The consistency between dynamic light scattering data and TEM size analysis indicates that the hydrodynamic effect is compressed, which reflects the presence of ions in the as-prepared suspension. Determination of ionic strength in suspension is essential for further investigation in order to understand the mechanisms of HPLC dispersion.

5.3.3 APS Grafting

Silane coupling agents are frequently used to modify the surface of silica-based particles. Table 5-1 summarizes some of the silane coupling agent utilized for a number of applications. APS is one of the most widely used silane coupling agents. The effectiveness of APS surface grafting is illustrated in Figure 5-8. Ag/SiO$_2$ nanoparticles without an APS coating has a weak negative zeta potential when pH is higher than pH 2 in ethanol-water solutions. The zeta potential curve becomes flat with a plateau reached above pH 7.0 at a maximum value of about -30 mV. However, the APS grafted SiO$_2$ nanoparticles gained relatively high surface charge and positively charged. In the acidic region below pH 7.0, the APS coated Ag/SiO$_2$ nanocomposites show zeta potentials as high as 30 mV, but a significant APS concentration effect is not observed. By contrast, the SiO$_2$ microspheres exhibit noticeable increase of zeta potential when the APS concentration reaches 1.5 w/o (Figure 5-9). This is likely due to the high surface
Table 5-1 Silane coupling agents for surface modification of SiO₂ based particles

<table>
<thead>
<tr>
<th>Name</th>
<th>Structure</th>
<th>pH window</th>
<th>Remarks</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>3-aminopropyl-trimethoxysilane (APS)</td>
<td>( \text{H}_2\text{NC}_3\text{H}_6\text{Si} - )</td>
<td>2.0~9.0</td>
<td>Modify the surface of SiO₂</td>
<td>Plueddemann¹</td>
</tr>
<tr>
<td></td>
<td>( (\text{OCH}_3)_3 ) (or ( \text{OC}_2\text{H}_5 ))</td>
<td></td>
<td></td>
<td>Mulvaney², Mann³</td>
</tr>
<tr>
<td>3-aminopropyl-silsesquioxane</td>
<td>( \text{H}_2\text{N}_8(\text{CH}_2)_2\text{O}_12\text{Si}_8 )</td>
<td>2.0 ~ 6.5</td>
<td>Surface coating of SiO₂ and Ag</td>
<td>Caruso⁴</td>
</tr>
<tr>
<td>3-glycidoxypropyl-trimethoxysilane (GPS)</td>
<td>( \text{H}_2\text{NC}_6\text{H}_1\text{O}_2\text{-} )</td>
<td>&lt; 9.0</td>
<td>Modify SiO₂ surfaces</td>
<td>Schmidt⁵</td>
</tr>
<tr>
<td></td>
<td>( \text{Si}(\text{OCH}_3)_3 )</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Trimmethoxysilylpropyldiethylenetriamine (DETA)</td>
<td>( \text{H}_2\text{N}_3\text{C}_7\text{H}_12\text{-} )</td>
<td>6.8</td>
<td>Surface coating of SiO₂</td>
<td>Tan⁶</td>
</tr>
<tr>
<td></td>
<td>( \text{Si}(\text{OCH}_3)_3 )</td>
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<tr>
<td>3-trimethoxysilylpropyloxysuccinic anhydride</td>
<td>( \text{C}_8\text{H}_11\text{O}_3\text{-}\text{Si} - )</td>
<td>&gt; 8.0</td>
<td>Surfaces coating of SiO₂</td>
<td>Hemplemann⁷</td>
</tr>
<tr>
<td></td>
<td>( (\text{OCH}_3)_3 )</td>
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</table>

Figure 5-8 Zeta potential of Ag/SiO\textsubscript{2} nanocomposites (R = 2, H = 100, X = 1) ethanol/water suspensions as a function of pH and APS concentration. Note the conversion of negative to positive charge after the addition of APS. The pHs of the suspensions were measured using a Sentron pH meter calibrated against standard aqueous buffer solutions. Error bars are the 95% confidence interval.
Figure 5-9 Zeta potential of SiO$_2$ microspheres as a function of pH and APS concentration. The average size of SiO$_2$ is 20 µm with a surface area of 425 m$^2$/g and 6.5 nm average pore size. The SiO$_2$ microspheres were dispersed in ethanol/water (7:3 vol) solution. The pHs of the suspension were measured by a Sentron pH meter calibrated against standard aqueous buffer solutions. Error bars are the 95% confidence interval.
area (425 m²/g) and the nature of the SiO₂ microsphere surfaces associated with their manufacture procedures. A detailed discussion of the graft mechanism can be found elsewhere. 15, 20, 21, 22 The main reaction was described as follows:

\[
3 \text{Si}-\text{OH} \text{(surface)} + \text{NH}_2\text{C}_3\text{H}_6\text{Si(OC}_2\text{H}_5\text{)}_3 \rightarrow (\text{Si-O})_3\text{-SiC}_3\text{H}_6\text{NH}_2 + 3 \text{C}_2\text{H}_5\text{OH}
\]  

Equation 5.1 implies that the silane groups on the surface of Ag/SiO₂ nanocomposite particles were replaced by siloxane groups and ethanol was released as a consequence of the Si-O bond formation. This configuration was exclusively desired in which the amine group tail is oriented toward the solvent and protonates at pH < 7.0. 15, 20 As a result, positive charge could be readily accomplished in an acidic pH regime owning much to the positively charged amine groups from APS. The zeta potential measurements indicate that surface charge for the treated samples is unanimously positive at pH < 7.0. A further decrease in pH to below pH 6 rapidly increases zeta potential to a plateau value of around +30 mV, supporting the theoretical interpretation.

The importance of surface grafting of both Ag/SiO₂ nanocomposites and SiO₂ microspheres with APS can also be seen from Figure 5-10, which shows the AFM image of an untreated SiO₂ particle after the HPLC washing. The HPLC column was easily blocked in the washing process prior to surface grafting of Ag/SiO₂ with APS. This can be explained if the surface morphology revealed in Figure 5-10 is taken into account. A 3D view of the silica microsphere indicated that the previously smooth surface was significantly compromised due to the interaction with Ag/SiO₂ nanocomposites. The morphology of silica microspheres prior to the HPLC washing was uniformly spherical.
Figure 5-10 AFM image of Ag/SiO$_2$ nanocomposites (R = 2, H = 100, X = 1) aggregation formed on the surface of a SiO$_2$ microsphere. APS surface coating only applied to Ag/SiO$_2$ nanocomposites (average size 30 nm), the SiO$_2$ were used without further treatment (average size 20 µm). SiO$_2$ particles from a blocked HPLC column were placed on a freshly cleaved mica substrate.
with a very low surface roughness according to SEM (Figure 5-3) and AFM observations. However, the surface was fouled during HPLC washing and agglomerations of Ag/SiO₂ nanocomposite particles were observed to attach on surface of the large silica spheres. One of the aggregates stuck on the silica microsphere was about 0.5 µm across, and must therefore consist of at least 150 individual nanocomposite particles if the primary particle size is 30 nm. There are a number of mechanisms for the aggregation of Ag/SiO₂ nanocomposites on the surface of SiO₂ microspheres that are not well understood. However, the Coulombic interaction between APS grafted Ag/SiO₂ nanocomposite particles and negatively charged spherical SiO₂ microspheres plays a significant role in the evolution of agglomeration. As the HPLC washing was carried out in weak acidic pH regime (pH 5.0 ~ 7.0), the nanocomposites gain positive charge because of the APS coating, while SiO₂ microspheres were negatively charged in this pH range. 23, 19 When two oppositely charged particles approach each other, the tendency to aggregate is enhanced due to electrostatic attraction. This is very likely the mechanism of the blocked column that caused the initial washing and collection attempts with HPLC to fail. Therefore, the same surface grafting was applied to SiO₂ microspheres in order to control the surface potential and thereby eliminate particle agglomeration. This protocol proved to be the critical step for HPLC washing of Ag/SiO₂ nanocomposite particles based on size exclusion chromatography. Stable suspensions of Ag/SiO₂ nanocomposite particles in ethanol/water solvent were routinely produced once this principle was precisely followed.
5.3.3 Washing Solvent

In addition to the surface modification with APS for both mobile and stationary phase, the selection of a proper extraction solvent is also critical to successful operation. The Ag/SiO$_2$ nanocomposites remain clustered in the upper part of the HPLC column when DI water, pure anhydrous ethanol, isopropanol and acetone solvents were used. When a ethanol/water cosolvent (ethanol : water = 7 : 3 vol) was pumped in, the clusters started to migrate downward and eventually elute out of the column. The mechanism for this experimental observation is not known at present. However, it is proposed that the ability of the surfactant to dissolve in the solvent is critical. Poor solvents for the surfactant lead to agglomeration because of phase separation.

5.3.4 Suspension pH

Suspension pH is an important parameter that must be controlled in preparing well-dispersed Ag/SiO$_2$ nanocomposite dispersions. This is illustrated by Figure 5-11. At pH 2.8, the Ag/SiO$_2$ nanocomposite suspension shows considerable agglomeration based on the TEM and dynamic light scattering analysis, the AAN is about 15 due to the bimodal particle size distribution. In the alkaline regime with a measured pH of 9.7, the dissolution of SiO$_2$ shell leads to the formation of Ag metal core contact and a small particle size. The poorly dispersed suspension shows an AAN of 0.02, which indicates the damage of the nanocomposite architecture. A well-dispersed Ag/SiO$_2$ nanocomposite suspension can be obtained when the pH is adjusted to around pH 6.0. Dynamic light scattering data of this sample suggests that the particle size distribution is
**Figure 5-11** The effect of pH on the state of dispersion for Ag/SiO$_2$ nanocomposites ethanol/water suspensions ($R = 8$, $H = 300$, $X = 1$). The TEM images were taken by placing a drop of the suspension on a lacy carbon grid and dried at 25 °C. Note the dissolution of SiO$_2$ shell at pH 9.7 which gives rise to the bimodal distribution.
monomodal, which is consistent with the TEM analysis. The corresponding AAN is around 1, indicating a well-dispersed suspension under pH 6.0.

5.3.5 Column Length

One of the parameters that affect the efficiency of HPLC washing is the length of the column. More washing solvent and time are required for a longer length of column. Three types of HPLC columns with specific size dimension were studied, columns HR 16 (16 × 500 mm) and HR 10/10 (10 × 100 mm) were too long for the Ag/SiO$_2$ nanocomposites to elute. In contrast, the short column HR 5/5 (5 × 50 mm) is suitable for Ag/SiO$_2$ dispersions. The total accessible pore volume (V) to nanoparticle with size $R_0$ can be expresses by Equation 5.2

$$V = \pi \cdot (R_p - R_0)^2 \times (L - R_0)$$

(5.2)

Where $R_p$ is the pore radius, and $L$ is the pore length. For Ag/SiO$_2$ nanocomposites, the condition $L >> R_0$ is satisfied, the total volume $V$ is proportional to $L$. Hence, larger pore length $L$ increases the washing time. For instance, assume the pores are composed of octahedral interstices, $R_p$ is 4.1 µm (0.414 of the radius of SiO$_2$ microsphere), $R_0$ is 20 nm for Ag/SiO$_2$ nanocomposites. Using equation 5.2, the estimated pore volume $V$ is $2.7 \times 10^{-5}$ mL for $L = 500$ mm (HR 16 column, assume the octahedral interstices form straight channels) and $2.7 \times 10^{-6}$ mL for $L = 50$ mm (HR 5/5). Therefore, the washing time of long column length ($L = 500$ mm) is approximately an order of magnitude higher than that of short column length ($L = 50$ mm).
5.4 Conclusions

The silane coupling agent APS effectively reacted with Ag/SiO$_2$ nanocomposite particles, thereby increasing the surface charge of Ag/SiO$_2$ nanoparticles to ensure that the Ag/SiO$_2$ nanocomposite particles can diffuse through the positively charged spherical SiO$_2$ stationary phase matrix during HPLC operation. Size exclusive chromatography based on this principle eliminates agglomeration and deposition of Ag/SiO$_2$ nanocomposite on the silica microspheres. Therefore, elute dispersion generated by the HPLC method demonstrates excellent homogeneity and stability with the zeta potential up to +30 mV. The resulting ethanol/water suspension is an ideal precursor for colloid chemistry based “bottom-up” nanoscale assembly for macroscopic devices. Processing parameters such as surface modification of both mobile and stationary phases, solvent, suspension pH and column dimension are of great importance to the HPLC dispersion. In the separation process, this approach could be extended to many similar nanoparticulate systems where surfactant-free dispersion is a major concern.

5.5 References


Chapter 6

Synthesis and Infiltration of Tabular SiO₂ Nanoparticles

6.1 Introduction

Shape control has significant relevance in the fabrication of nanoscale particulate materials, which could add extra variable in tailoring the properties of nanoparticles. Self-assembly bilayer is one of the templates that demonstrate sufficient control of nanoparticle morphology. Short-chain amines are known to be able to form bilayer structures with water due to the amphiphilic nature of the organic molecules, and therefore have been used as templates to prepare anisotropic nanoparticles.

Flanigen et al. reported a highly hydrophobic crystalline silica through hydrothermal treatment of tetrapropylammonium and silica. The resulting silicalite molecular sieve has a pore volume up to 33% with a pore size about 0.6 nm. The formation of the silicalite was attributed to the enhancement of silica solubility in water and the clathration of silica to assemble into a framework. It was noticed by Sun and Ying that short hydrocarbon chain amine molecules such as hexylamine and heptylamine can be used as molecular templates to direct the growth of amorphous microporous silica and transition metal oxide molecular sieves. The microporosity was developed in the calcinations of dried powders for most SiO₂ based zeolites. Further studies on the synthesis of hexagonal microporous silica using hexylamine as template molecules was successful according to Eswaramorthy. The pore size was in the range of 1.3-1.5 nm.
The surface area observed for silica calcined at 400°C was 800 m²/g, which includes the contribution from an undetermined portion of mesopores. It is also feasible to engineer the pore structure via molecular imprinting of 3-aminopropyltriethoxysilane as demonstrated by Katz and Davis. Bulk SiO₂ powder can be designed to have a uniform pore size and microporosity after selective molecular imprinting, which could make the microporous silica accessible to a wide range of functional molecules. The effect of surfactant templates to the microporous silica pore structure was studied by Lu and Brinker et al., it was found that template-derived microporous silica consists of two type of pores, the smaller primary pores and larger secondary pores. The primary porosity decreases as the template ligand concentration increases while template concentrations above 25 vol% could induce a partial collapse of the silica network during template pyrolysis. A similar dual type of pore distribution was reported by Kooli for hydrothermally synthesized silica with the presence of tetramethylammonium hydroxide (TMAOH). The resulting micropore sizes were 0.88 nm and 1.56 nm after 500°C calcination. In most synthesized silica zeolites, the microporosity is usually high with a uniform pore size distribution and the silica networks demonstrate good crystallinity based on XRD patterns.

Silica powders with high surface area and uniform pores have emerged as one of the few host materials for creating heterogeneous structures with appealing properties as well as scientific significance. Functional guest species such as metal, polymer and semiconductor clusters were loaded into the chemical friendly versatility SiO₂ matrix, the resulting composites could exhibit unique physical properties. A number of mesoporous and microporous SiO₂ nanocomposites with interesting electrical,
optical and catalytic properties have been successfully fabricated. Mesoporous SiO$_2$ nanoparticles were extensively studied due primarily to their organized pore structure with dimensional size from 2 to 50 nm. Mesoporous SiO$_2$ matrices are also used as sacrificial templates to synthesize metallic nanowires and nanoparticles. 19, 20, 21 Even though microporous SiO$_2$ powders have been long known as ideal molecular sieves in catalytic science, 22, 23 infiltration of the microporous SiO$_2$ matrix with guest species was sparsely reported. Bogomolov et al first utilized the microporous zeolites as templates to make quantum confinement nanoclusters, 24 since then inclusion chemistry of molecular sieves have become increasingly attractive. The guest quantum clusters were confined in the host framework via arrested precipitation or reduction, which was carried out by ion exchange to the cages or channels of the matrix. The host structure provides a better quantum well barrier to define the cluster geometry. Therefore, selection of the matrix is very important. Typical matrix materials include silicate and phosphate molecular sieves. The guest species embedded into the host channels include Se, Te, 24 Idione, 17, 18 Mercury halides compounds 17 and CdS. 24 The unique properties associated with these host-guest compounds are investigated.

Based on this background, the octylamine/water self-assembly bilayer system was extended to synthesize tabular SiO$_2$ nanoparticles via a proposed template-directed agglomeration mechanism. The resulting microporous silica zeolite shows extraordinary large surface area after high temperature pyrolysis. The tabular SiO$_2$ nanoparticles were infiltrated with palladium through a simple solution chemistry route. The goal is to achieve some insight into the self-assembly bilayer synthesis and insertion chemistry of the microporous SiO$_2$ matrix.
6.2 Experimental Procedure

6.2.1 Synthesis of Tabular SiO₂ Nanoparticles

All chemicals involved in the synthesis were reagent grade and used as-received without further purification. Tetraethoxysilane (TEOS) (99+%, Aldrich Chemical Co.) was used as the source for SiO₂. Octylamine (99%), amylamine, polyethylamine and triethoxyl boronate were purchased from Aldrich Chemical Co., while ethanol (94.4%, 200 proof), nitric acid and glacial acetic acid were obtained from J. T. Baker Chemicals. Deionized water was used (specific conductivity = 0.4 × 10⁻⁷ S/m) for all experiments.

The procedure used to prepare tabular SiO₂ nanoparticles is based on the method developed by Yener for the octylamine/water bilayer system. 4 A modified flow sheet describing the synthesis of silica is shown in Figure 6-1. The lamellar bilayer structure was formed by mixing a defined amount of octylamine and deionized water. The pH of the bilayer was adjusted with 2.0 M nitric acid aqueous solution to pH 11.0. The total amount of water was determined by R (molar ratio of [water]/[octylamine]). After the pH adjusted bilayer was formed, a known amount of TEOS (with 3 at% triethoxyl boronate) was transferred to the mixture based on M (molarity of TEOS in the aqueous layer). Hydrolysis and condensation of TEOS was allowed to proceed overnight.

6.2.2 Washing and Recovery

The self-assembly bilayer was broken with 1% (w/o) PEI/ethanol stock solution dispersant (3 w/o), followed by the addition of 2M acid/ethanol solution (CH₃COOH/ethanol or HNO₃/ethanol). The amount of acid/ethanol solution was determined from a
**Figure 6-1** Flow sheet for the synthesis and dispersion of tabular SiO$_2$ nanoparticles. Modified from Yener.\textsuperscript{4} Note the R ratio ([water]/[octylamine]) determines the thickness of the bilayer, which controls the size of the tabular SiO$_2$ nanoparticles. The weight ratio of octylamine to amylamine is 25:1.
pre-established titration curve (the pHs of the tabular SiO$_2$ nonaqueous suspension were measured with a Sentron pH meter calibrated against standard aqueous buffer solution). After shaking for 15 minutes, the suspension was transferred to a separation funnel. The supernatant was discarded and the translucent suspension was collected and washed repeatedly. UV-vis spectra (Pharmacia LKB ultrospec III spectrophotometer with a scan range from 200 nm to 900 nm) were acquired as a function of washing to ensure the removal of surfactants. The final suspension was about 30 ml (1.6 mg/mL SiO$_2$) with pH close to 6.0 and a zeta potential of +15 mV. The final product was vacuum dried at room temperature until a constant weight was reached. Calcination of the resulting silica powder was carried out at various temperatures for 2 hours in air.

6.2.3 Infiltration with Palladium

The as-synthesized tabular SiO$_2$ nanoparticles were first calcined at 700°C for 2h to obtain maximum porosity and surface area. The infiltration of SiO$_2$ with Pd was carried out following the flow sheet outlined in Figure 6-2. In a typical infiltration cycle, an aqueous suspension of SiO$_2$ was obtained by mixing 1 g of tabular SiO$_2$ powder with 200 mL deionized water. The suspension was then adjusted to pH 6.4 and stirred at ambient condition for another 30 minutes. Afterward 5 mL of 0.04 M Pd(NO$_3$)$_2$ solution was added into the suspension and vigorously stirred for another 30 minutes during which the suspension was shielded from light. To obtain metallic Pd, 0.5 mL hydrazine hydrate was added and the reaction was allowed to proceed overnight. Complete saturation of the micropores may take up to 3 infiltration cycles.
Figure 6-2 Flow sheet for the infiltration of tabular SiO$_2$ nanoparticles with Pd. This procedure is repeatable depending on the target Pd content in SiO$_2$ matrix. Note the Pd$^{2+}$ ions are light sensitive.
The Pd-infiltrated SiO$_2$ nanoparticles were first centrifuged at 3000 rpm for 5 minutes. The solid particles were collected and redispersed in DI water. This procedure was repeated three times to remove any possible excess Pd$^{2+}$ ions and residual Pd particles. The final product was vacuum dried at room temperature until a constant weight was reached.

### 6.2.4 Characterization

The morphology of the tabular SiO$_2$ nanoparticles was analyzed with TEM (JEOL-2010F at 200KV, Tokyo, Japan). Chemical composition of the Pd infiltrated SiO$_2$ nanoparticles was obtained with energy dispersive X-ray spectroscopy (EDS) attached to the electron microscope. The thickness, face diameter and aspect ratio of the tabular SiO$_2$ nanoparticles were measured by AFM (Digital Instruments, Multi mode III,) under the tapping mode. Structural analysis for tabular SiO$_2$ nanoparticles was conducted with XRD (Scintag pad V, Cu K$_\alpha$ 1.5418Å) and FTIR (Nexus-670 FTIR, ThermoNicolet USA). The chemical composition of the tabular SiO$_2$ nanoparticles was determined by direct current plasma atomic emission spectroscopy (DCP)(SMI III, Spectrametrics, Inc., USA). Thermogravimetric analysis (TGA) (TA Instruments, TA 2050, USA) and differential scanning calorimetry (DSC) (TA Instruments, SDT 2960, USA) were used to study the thermal stability of powders at elevated temperature. Specific surface area and microporosity of the tabular SiO$_2$ nanoparticles were analyzed with multipoint BET (Micromeritics, ASAP 2020, USA). Adsorption isotherms were measured at liquid nitrogen temperature 77 K and adsorption-desorption data were automatically processed.
using a density functional theory to obtain pore size distribution. The porosity of tabular SiO$_2$ was also measured with a using a multipoint BET facility (Micromeritics Gemini 2370, Atlanta, GA). The sample was vacuum degassed at 200$^\circ$C for 2 hours following a standard protocol for the Gemini series. The BET surface area data obtained for the microporous SiO$_2$ nanoparticles were significantly low due to possible exposure of degassed samples to the air during sample transfer.

6.3 Tabular SiO$_2$ Nanoparticles

6.3.1 Removal of Surfactant

Figure 6-3 shows the UV-vis spectra of several SiO$_2$ suspensions after washing with ethanol stock solution. The first absorption peak at about 220 nm is due to the presence of octylamine and PEI, the second peak at 300 nm, however, is due primarily to Octylamine. As the washing procedure is repeated, the absorbance decreases. It is obvious that the concentration of octylamine is much higher in the supernatant within the same washing. After five times washing, the concentration of octylamine in SiO$_2$ suspension is lower than the detection limit of the UV-vis spectrometer, as can be seen from the spectra. To determine the concentration of octylamine in the SiO$_2$ suspension, a working curve for octylamine in a pH ~5.2 sodium acetate trihydrate buffer solution was established based on the absorption peak at 300 nm (Figure 6-4). In the range from 1 wt% to 5 wt%, the absorbance increases linearly as concentration of octylamine increases, therefore, the amount of residual octylamine in SiO$_2$ suspension can be determined by measuring the absorption spectra.
Figure 6-3 UV-vis spectra of tabular SiO$_2$ ethanol suspension as a function of washing. (A) 2$^{nd}$ wash, (B) 5$^{th}$ wash. Spectra were taken after phase separation of the SiO$_2$ suspension.

The peak of octylamine at 300 nm disappeared after 5 times wash in the silica suspension.
Figure 6-4 UV-vis spectroscopic calibration curve for octylamine in sodium acetate trihydrate buffer (pH 5.2), which was constructed by plotting the absorbance at 300 nm vs octylamine concentration. The detection limit for octylamine is ~1 wt%.

\[ A = 0.456C + 0.0965 \]

\[ R^2 = 0.995 \]
Specrochemical analysis performed on the thoroughly washed and calcined (800°C, 2h) tabular SiO₂ nanoparticles is summarized in Table 6-1. Impurities identified (detection limit = 0.005 wt%) include Ca, Al, K, Mg and Na, which are reasonable because the chemical precursors were used without further purification during the synthesis. However, the content of B is surprisingly low with respect to the target value of 3 at% (1.74 wt%). It is quite possible that B may be washed out from the SiO₂ matrix as a result of consecutive resin, further pursue is obviously require to rule in or rule out this possibility.

6.3.2 Morphology

Figure 6-5 shows the morphology of as-synthesized tabular SiO₂ (R=4.3, M=0.04, applied to the following discussion) nanoparticles observed using TEM. The state of dispersion for the particles is poor with considerable agglomeration. The average size of the particle aggregates is estimated to be in the range of 100~300 nm. The thickness of the tabular nanoparticles can not be obtained directly from the TEM images, but a distinct stack of discrete edges is shown in the TEM image, which is most likely due to several layers of platelet nanoparticles. The low particle contrast may also actually imply a thin nanoparticle in the Z direction, which can be well controlled during the particle synthesis as shown by Yener. 4, 27

The thickness of the tabular nanoparticles was measured with AFM using the cross section profile analysis method. 4 An average thickness of about 6.0 ± 0.9 nm (with 95% confidence interval) was observed for three randomly selected particles (Figure 6-6).
Table 6-1 Spectrochemical analysis of tabular SiO$_2$ nanoparticles. (R = 4.3. 800° C, 2h)

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<tr>
<td>B</td>
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</tr>
<tr>
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</tr>
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</tr>
<tr>
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</tr>
<tr>
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<td>0.01</td>
</tr>
<tr>
<td>Sr</td>
<td>&lt;0.005*</td>
</tr>
</tbody>
</table>

* Data from Direct Current Plasma (DCP) with a detection limit of 0.005 wt%.

SMI III, Spectrametrics, Inc.
Figure 6-5 TEM micrographs of tabular SiO$_2$ nanoparticles prepared from octylamine/water bilayer (R = 4.3, M = 0.04). Particle agglomeration was observed in the TEM analysis. The high magnification picture shows the edges of tabular SiO$_2$ nanoparticles.
Figure 6.6 AFM analyses of tabular SiO$_2$ nanoparticles prepared from octylamine/water bilayer (R = 4.3, M = 0.04). AFM sample prepared by spin coat a drop of SiO$_2$ ethanol suspension on a freshly cleaved mica substrate. Particle size analysis performed on three particles. (with 95% confidence interval).
Unfortunately, the face diameters of the SiO$_2$ nanoparticles were found to be quite different, ranging from 100 nm to 280 nm across the face for the three measured particles. However, this observation is not beyond expectation if the template microstructure is taken into account. Formation of the SiO$_2$ nanoparticles was achieved via hydrolysis of TEOS in the aqueous layer with a tunable thickness depending on the R ratio. At R = 4.3, the corresponding thickness of the aqueous layer is about 3 nm in the case of silver platelets, 4 which is considered to be smaller than that of TEOS. The difference in thickness may be ascribed to the swelling of the bilayer after the addition of TEOS solution, which is likely to increase the total volume of the aqueous layer. Another reason might be the specific growth mechanism associated with each precursor. The formation of Ag nanoscale platelets was proposed by Yener et al. 4 to be via a specific adsorption-reduction routine for the Ag$^+$ ions, owing to the strong affinity between Ag$^+$ ions and nitrogen end groups from the amphiphilic octylamine molecule. However, in the case of SiO$_2$, hydrolysis should take place in the aqueous layer because the TEOS monomers are randomly oriented and aggregation immediately leads to the evolution of SiO$_2$ nanoparticles, 2, 3 and thus a wider distribution of both face diameter and thickness compared with silver nanoscale platelets.

6.3.3 Structure Characteristics

The X-ray diffraction pattern of tabular SiO$_2$ nanoparticles is shown in Figure 6-7. A broad diffraction peak from 16 to 30 degrees indicates the amorphous nature of tabular SiO$_2$ calcined at various temperatures. 28 The absence of diffraction peaks at both low
Figure 6-7 XRD patterns of tabular SiO$_2$ nanoparticles prepared from octylamine/water bilayer (R = 4.3, M = 0.04). Calcined samples are at 700 and 900 °C for 2 hours. The broad band from 16 to 30 degrees indicates the formation of amorphous SiO$_2$. 
angle ($2\theta < 3$) and high angle ($2\theta > 30$) suggests that the tabular SiO$_2$ nanoparticles are essentially different from mesoporous silica or zeolite-like silica. The amorphous tabular SiO$_2$ nanoparticles are thermally stable up to 1000°C. At higher temperature the SiO$_2$ nanoparticles begin to sinter and significant shrinkage was observed.

To better understand the thermal stability of tabular SiO$_2$ nanoparticles, samples calcined at various temperatures were also analyzed by FTIR (Figure 6-8). The characteristic vibrational bands for SiO$_2$ were observed with band assignments are listed in a Table attached to Figure 6-8. The amorphous SiO$_2$ displays two vibrational modes at 1250 and 1050 cm$^{-1}$, which corresponds to the antisymmetric stretching vibrations of Si-O and Si-O-Si, respectively. A weak band at around 850 cm$^{-1}$ is assigned to the Q$^3$ Si-OH (Q$^n$-terminology is used in NMR, where n indicates the number of bridging bonds (-O-Si) tied to the central Si atom, Q$^3$ = single silanol) bonds in the tabular SiO$_2$ nanoparticles. The Q$^3$ Si-OH vibrational band was observed from 950 to 980 cm$^{-1}$ by a number of research groups in different forms of SiO$_2$ powders. The spectral profiles are clearly temperature-dependent as illustrated in Figure 6-8. At room temperature, the two characteristic peaks for Si-O bonds are much more overlapped and intense than those at 600 °C and 1200 °C. In fact the vibrational intensity for the three peaks decreases as thermal treatment temperatures increase. This is probably due to the partial collapse of the Si-O network and removal of OH groups upon calcination. The surface chemistry of amorphous SiO$_2$ is quite complicatedly relative to thermal decomposition temperature. Although the number of OH groups continues to decrease as a result of increasing temperature, complete removal of isolated surface OH groups is not
Vibrational mode

This work (cm$^{-1}$)  Vein et al$^{29}$ (cm$^{-1}$)  Zarzycki et al$^{31}$ (cm$^{-1}$)  Kooli et al$^{12}$ (cm$^{-1}$)

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<th>Vibrational mode</th>
<th>This work</th>
<th>Vein et al</th>
<th>Zarzycki et al</th>
<th>Kooli et al</th>
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<td>~1100</td>
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</table>

**Figure 6-8** FTIR spectra of tabular SiO$_2$ nanoparticles prepared from octylamine/water bilayer (R=4.3, M=0.04). Sample prepared by KBr pellets.

Si-O and Si-O-Si are antisymmetric stretching, Si-OH (Q$^3$) is a bending mode.

Q$^3$ = single silanol.
achieved until 1200 °C, beyond which the SiO\textsubscript{2} surfaces should be covered solely by siloxane (Si-O-Si) groups. These observations are consistent with the temperature-dependent FTIR spectra of the tabular SiO\textsubscript{2} nanoparticles.

**6.3.4 Thermal Stability**

Direct observation of the thermal stability for tabular SiO\textsubscript{2} nanoparticles was performed using TGA and DSC analysis. Continuous weight loss was observed from 25°C up to 800°C as shown by the representative TGA result in Figure 6-9. A precise determination of the weight loss point can be usually obtained with the first derivative of the TGA curve. At least five distinct weight loss maxima were present in the TGA of the tabular SiO\textsubscript{2} nanoparticles. The first peak at 100°C is related to the loss of moisture, adjacent to that is the burnout point for acetic acid at about 130°C. In the temperature range from 200 to 500°C, two peaks were identified and barely resolved. The one at 220°C is assigned to the elimination of external OH groups while the other at 280°C is most likely due to the removal of PEI dispersant. PEI should decompose around 300°C based on the TGA test of pure PEI dispersant. The final weight loss peak at 550°C is primarily ascribed to the removal of internal OH groups in the SiO\textsubscript{2} skeleton, whose condensation and elimination is normally reported to occur from 400 to 900°C. DSC on the same sample confirmed the TGA analysis and assignment of weight loss mechanisms.

Drying conditions are critical to the thermal decomposition of tabular SiO\textsubscript{2} nanoparticles (Table 6-2). Drying in a vacuum oven at 100°C, SiO\textsubscript{2} particles show a total weight loss of 34.3% over the tested temperature range of 25°C to 600°C. The major
Figure 6-9 TGA of the tabular SiO₂ nanoparticles prepared from octylamine/water bilayer (R = 4.3, M = 0.04). The derivative of TGA was used to determine the weight loss peaks and assigned to relevant chemical species (TGA curve obtained at 5 °C/min in air).
Table 6-2 The effect of drying conditions on weight loss and surface area of tabular SiO$_2$ nanoparticles ($R = 4.3$, $M = 0.04$).

<table>
<thead>
<tr>
<th>Drying conditions</th>
<th>Weight loss $&lt;200^\circ$C (%)</th>
<th>Weight loss $200\sim600^\circ$C (%)</th>
<th>Total weight loss (%)</th>
<th>Surface area (m$^2$/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>70$^\circ$ C in air 2h</td>
<td>25</td>
<td>50</td>
<td>75</td>
<td>N/A</td>
</tr>
<tr>
<td>100$^\circ$ C, vacuum 2h</td>
<td>17.2</td>
<td>17.1</td>
<td>34.3</td>
<td>N/A</td>
</tr>
<tr>
<td>200$^\circ$ C, vacuum 2h</td>
<td>7.5</td>
<td>17.4</td>
<td>24.9</td>
<td>293.8</td>
</tr>
<tr>
<td>500$^\circ$ C in air, 2h</td>
<td>9.8</td>
<td>3.0</td>
<td>12.8</td>
<td>745.3</td>
</tr>
</tbody>
</table>

Surface area measured by a Micromeritics Gemini 2370 BET instrument.
weight loss takes place at about 150°C, which is possibly due to the dehydration of SiO₂. The sample vacuum dried at 200°C shows more weight loss from 200°C to 600°C, which reflects the condensation of the internal OH groups. Major weight loss was found below 200°C for the sample dried at 500°C, which is likely due to the moisture sucked by the newly formed micropores. This is consistent with the high surface area (750 m²/g) observed in this particular drying condition.

6.3.5 Microporosity

The as-synthesized tabular SiO₂ nanoparticles demonstrate unique porosity as illustrated in Figure 6-10, which was achieved by liquid nitrogen adsorption under standard conditions. A type I adsorption isotherm curve was obtained for tabular SiO₂ nanoparticles, which indicates the sample calcined at 700°C for 2h is microporous. A rapid increase of the adsorption isotherm at extremely low relative pressure (P/P₀) regime (10⁻⁶ to 10⁻¹) suggests that a large number of micropores were present after calcination. A cumulative pore volume of 0.3 cm³/g is observed. The lack of a hysteresis loop on the adsorption-desorption isotherms and the shape of the curves suggest that the tabular SiO₂ nanoparticles possess uniform microporous structure.

The pore size distribution was therefore calculated from the adsorption isotherm results using density functional theory (Tarazona DFT model, cylindrical pores) (Figure 6-11). A significant fraction of the pores with an average pore size of 0.63 nm were found after calcining at 700°C, along with a very small portion of secondary pores less than 2 nm. No mesopores (> 2 nm) were developed in the tabular SiO₂ skeleton during heat
Figure 6-10 Adsorption isotherm of tabular SiO$_2$ nanoparticles prepared from octylamine/water bilayer (R=4.3, M=0.04, 700 °C, 2h). Data measured by Jeffery Kevin at Micromeritics using a Micromeritics ASAP 2020 at 77 K.
Figure 6-11 Pore size distribution of tabular SiO$_2$ nanoparticles prepared from octylamine/water bilayer ($R = 4.3$, $M = 0.04$, $700$ °C, $2h$). Data measured by Jeffery Kevin at Micromeritics using a Micromeritics ASAP 2020 at 77 K. Pore size distribution calculated by density functional theory (DFT, assume cylindrical pores, $V_p = 0.3$ cm$^3$/g) for microporous material.
treatment. This finding is consistent with the conclusion derived from the adsorption isotherm in Figure 6-10, which indicates a uniform microporous structure. However, it is surprising to observe that microporous SiO$_2$ nanoparticles consist completely of zeolite-like (10- and 12-membered rings) ultra-fine pores while still maintaining an amorphous structure according to XRD. The origin for this is not known presently, but possible reasons may include short chain octylamine templates and thermal decomposition of other organic species such as acetic acid and PEI. A role for octylamine in micropore formation is highly possible because its versatility in promoting the creation of pores has been well known for several decades. Flanigen et al first noticed the importance of alkylammonium in promoting the evolution of microporous silicalite under hydrothermal condition. The crystallization mechanism proposed ascribed much to the improved solubility of SiO$_2$ by alkylammonium in such a way that linked the structure of water and SiO$_2$ up to 200 °C. The findings by Sun and Ying, and by Rao et al. show that short chain amine is a powerful supramolecular template in directing the synthesis of metal oxide molecular sieves. Similar to the mechanism described by Sun, the micropores in the tabular SiO$_2$ nanoparticles may be formed through the interaction of octylamine and TEOS. Upon breaking of the self-assembly bilayer with ethanol, the amphiphilic octylamine molecules bonded to Si-O tended to self-assemble, forming a hydrophobic core. However, the following washing steps facilitate removal of the octylamine molecule thereby creating pores in the tabular SiO$_2$ matrices. Further condensation and shrinkage of the pores was achieved by vacuum drying and thermal calcinations. However, this hypothesis excludes the contribution from other chemical
species (such as OH, PEI and acetic acid) that may play a role as well in micropore development.

It is worth mentioning that the surface area of the tabular SiO$_2$ nanoparticles shows unusual stability against temperature (Figure 6-12). The surface area of tabular SiO$_2$ nanoparticles increases rapidly as the heating temperature increases from 200 °C to 500 °C, and reaches a maximum of 790 m$^2$/g at 600 °C (Note: the surface area data discussed in this section is based on the Gemini 2370 instrument with a limited vacuum capability and P/P$_0$ range, 0.1 ~ 0.3). The surface area then decreases with further heating and drops to about 4 m$^2$/g at 1200°C. In the range from 500 to 800°C, the surface area remains above a plateau value of 600 m$^2$/g. Using the average aspect ratio of 34 for tabular SiO$_2$ nanoparticles determined by AFM, the external surface area is calculated to be around 160 m$^2$/g. It is obvious that the internal surface area plays a major role in the formation of high surface area. The trend of BET surface area as a function of temperature is clearly shown in this plot, although the values are much lower than these obtained from other BET instruments (Micromeritics ASAP 2010 showed 1252 m$^2$/g, and ASAP 2020 showed 1158 m$^2$/g for the 700°C, 2h sample). The condensation of SiO$_2$ nanoparticles in the initial stage of calcination is believed to promote porosity while the shrinkage of micropores above 1000°C causes the surface area to decrease. However, the combination of high surface area and microporosity of tabular SiO$_2$ nanoparticles could be used as a superior supporting matrix for catalytic metal particles at high temperatures.
Figure 6-12 Surface area of tabular SiO$_2$ nanoparticles (R = 4.3, M = 0.04) as a function of temperature. Tabular SiO$_2$ powders were calcined at different temperatures for 2 hours, the surface areas were measured by a Gemini 2370 BET instrument. Error bars are the 95% confidence interval.
6.4 Pd Infiltrated SiO$_2$ Nanoparticles

6.4.1 Morphology and Structure

The morphology of the Pd-infiltrated tabular SiO$_2$ nanoparticles is illustrated in Figure 6-13. The distinct contrast change under bright field mode indicates insertion of Pd species. The dark areas in particle aggregates reflect a Pd-rich SiO$_2$ particulate matrix while the gray areas are more similar to pure SiO$_2$ aggregates. The overall size of tabular SiO$_2$ nanoparticles remains essentially constant even after Pd infiltration. This may actually imply a micropore-confined embedding process in the synthetic step. The average pore size of the open SiO$_2$ network was determined to be around 0.63 nm, with all accessible pores less than 2 nm based on BET analysis. Therefore, the size of the embedded Pd clusters should be most likely in the atomic length scale. However, the HRTEM analysis could not confirm this mainly due to the small size scale.

The chemical composition analysis performed by EDS revealed the successful doping of Pd in the tabular SiO$_2$ matrix (Figure 6-14). It is worth noticing that three emission peaks were found for Pd with 200 KV energetic electron beam bombardment. The sharp peak at 2.9 KeV is from the L$_\alpha$ transition with the K$_\alpha$ and K$_\beta$ lines located at 21.2 and 24.3 KeV, respectively. The most intense peak is associated with Cu, an artifact from the TEM grid. Peaks from silica are also identified at around 1.8 KeV with a fairly weak intensity.

Figure 6-15 shows the powder diffraction pattern of Pd-infiltrated SiO$_2$ nanoparticles. It is generally quite similar to the XRD pattern of pure tabular SiO$_2$ nanoparticles except for four distinct peaks from the guest Pd species. Infiltration with Pd
Figure 6-13 TEM micrographs of Pd infiltrated tabular SiO$_2$ nanoparticles (R = 4.3, M = 0.04, 700°C, 2h) (micropore size ~ 6.3Å, surface area ~ 1158 m$^2$/g from Micromeritics ASAP 2020, infiltrated with Pd twice). Note lacey carbon coated copper grid was used for TEM analysis.
Figure 6-14 EDS spectrum of Pd infiltrated tabular SiO$_2$ nanoparticles (R = 4.3, M = 0.04, 700°C, 2h). Note that a lacey carbon coated copper grid was used for TEM analysis which contributes the strongest peak in the spectrum. The TEM was operated at 200 KV.
Figure 6-15 XRD of Pd infiltrated tabular SiO₂ nanoparticles (R = 4.3, M = 0.04). (scan rate at 2.0 degree/min). Tabular SiO₂ nanoparticles calcined at 700°C for 2h, infiltrated with Pd twice. Miller indices from JCPDS ICDD # 46-1043 (Pd) and # 46-1211 (PdO).
seems to have negligible impact to the amorphous nature of the SiO\textsubscript{2} matrix, because the broad peak at around 15~30 degrees remains the same after Pd infiltration. The diffraction peaks at 31.0 and 45.0 degrees are assigned to PdO, while the others are from metallic Pd at 40.0 and 46.5 degrees. The presence of PdO is unavoidable and its concentration in the SiO\textsubscript{2} matrix is currently not determined. Direct imaging of Pd clusters by high resolution TEM was impossible because the embedded clusters are likely to be less than 2 nm, which was determined largely by the size of the micropores in SiO\textsubscript{2} matrix. Therefore, the oxidation of Pd clusters under ambient conditions is expected due to the sub-nanometer scale of metallic Pd inclusions. This readily leads to the formation of PdO. However, possible palladium silicide compounds were not discovered in this work, which may be attributed to the inert interfacial interaction between Pd and Si cations at room temperature as well as the removal of silanol groups from calcined tabular SiO\textsubscript{2} nanoparticles. 36

The insertion of Pd into the micropores of tabular SiO\textsubscript{2} nanoparticles should reduce the porosity of the host and thereby affect the surface area of SiO\textsubscript{2}, which is exactly what is observed by BET analysis. The BET surface area for tabular SiO\textsubscript{2} nanoparticles prior to Pd infiltration is 748 m\textsuperscript{2}/g (with Gemini 2370), which is only about 65 \% of the result obtained with the Micromeritics ASAP 2020 (1158 m\textsuperscript{2}/g). The surface area for Pd infiltrated SiO\textsubscript{2} nanoparticles measured using the same protocol is about 649 m\textsuperscript{2}/g, a decrease of 13\%. A weight gain of 33 wt\% was observed on a 1g basis after two infiltration cycles. Standard ICP analysis also gives a Pd content of 27 ± 5 wt \%. Based on these findings, the spherical equivalent size of Pd clusters is estimated to be around 1.3 nm, which is reasonably consistent with the upper limit of micropore size for the
tabular SiO₂ host. Therefore, most of the Pd clusters that survived after washing are those that reside inside the micropores. A possible mechanism for the insertion of Pd clusters into the SiO₂ micropores may consist of a diffusion-reduction process. As Pd²⁺ ions approach the hydroxyl group-rich surface of SiO₂, the cations are first adsorbed and diffuse into the micropores under a concentration gradient until equilibrium is established. Upon the addition of hydrazine hydrate, reduction of Pd²⁺ takes place with those cations adjacent to the open terminals of the pores. Therefore, the micropores will be eventually blocked as reaction proceeds leaving some Pd²⁺ species trapped in the pores. The residual Pd²⁺ ions can bond with O²⁻ to form PdO as detected by XRD. Further pursuit of this work will focus on the infiltration mechanism, along with catalytic, electric and optical properties of the Pd clusters confined in the micropores.

6.4.2 Hydrogen Adsorption

The hydrogen adsorption isotherms of the Pd infiltrated tabular SiO₂ nanoparticles (33 wt% Pd) were shown in Figure 6-16. The hydrogen absorption increases as temperature increases. The samples were outgassed at 25°C, 50°C and 150°C for 2 hours before each measurement. For the adsorption isotherms carried out at 50 °C, the hydrogen uptake is less than 0.3 wt% (with respect to Pd), and a slight plateau which corresponds to the phase transformation of palladium hydride was observed at a hydrogen pressure of 50 mbar. A small increase of hydrogen concentration is occurred at 100°C operation, a adsorption maximum is about 0.42 wt% for the sample initially outgassed at 150 °C. However, these values are slightly lower than the typical maximum adsorption
Figure 6-16 Hydrogen adsorption on Pd infiltrated Tabular SiO$_2$ nanoparticles (R = 4.3, M = 0.04, 700 °C, 2h, infiltrated twice). Trials 1 to 3 are measured at 50 °C, and trials 4 to 5 are measured at 100 °C. Trial 1 is outgassed at 25 °C and 50 °C for 2 hours respectively, and trials 2 to 5 are outgassed at 150 °C for 2 hours. Hydrogen concentration was calculated with respect to the total amount of Pd (33 wt%) in SiO$_2$ matrix. Data courtesy of Kishore Srinivasan.
observed in bulk Pd, which is around 0.57 wt% for a 50 µm Pd powder. The reasons for this difference are not quite clear at this moment. A more accurate Pd concentration as well as the interface structure between Pd and SiO$_2$ matrix need to be established in order to account for the low solubility of hydrogen in the nanocomposite.

6.5 Conclusions

Microporous tabular SiO$_2$ nanoparticles with a thickness of about 6 nm (aspect ratio 10~50) were synthesized from the self-assembly octylamine/water bilayer at room temperature. The amorphous tabular SiO$_2$ nanoparticles show a stable high surface area at calcination temperatures up to 800 °C. Further increase of firing temperature leads to the collapse of SiO$_2$ skeleton, resulting the loss of microporosity. Fine micropores less than 2 nm were discovered after calcination at 700 °C for 2h with mode at 0.63 nm. The elimination of octylamine is proposed to be responsible for the formation of microporosity in the tabular SiO$_2$ nanoparticles.

Pd infiltrated SiO$_2$ nanocomposite particles were successfully prepared via a redox reaction in the micropores of a tabular SiO$_2$ matrix. The spherical equivalent size for the Pd clusters formed in the micropores is estimated to be around 1.3 nm with a total concentration of 33 wt%. The resulting Pd clusters in SiO$_2$ nanocomposite powder demonstrates a low hydrogen solubility compared to bulk Pd. A significant drop of porosity up to 13% for tabular SiO$_2$ nanoparticles was observed without enlarging the
size of amorphous SiO$_2$ nanoparticles. A measurable portion of Pd was oxidized but no palladium silicides were discovered at the synthesis temperature.

### 6.6 References


Chapter 7

Summary and Future Work

7.1 Summary of Research

Many physical properties such as the electrical and optical behavior of particulate materials are strongly related to their size dimension and shape geometry. These properties have been studied extensively for materials systems such as metals and ceramics. With the development of more complicated morphology toward smaller size domain, the understanding of optical properties of these materials is of great interest. The current research work is to synthesize and disperse particulate materials with various sizes and shapes, and to investigate how these parameters affect their optical activity.

7.1.1 Hematite Particles

Iron oxide hematite particles with various shapes (platelet, polyhedron, pseudocube and peanut-like) have been synthesized by hydrothermal treatment of a Fe(OH)$_x$O$_y$ precursor under various conditions. The size and shape of hematite particles can be adjusted by carefully controlling the processing parameters such as holding time, temperature and adsorption ions present in the system. The nearly monosized $\alpha$-Fe$_2$O$_3$ platelets possess face diameters of approximately 3 $\mu$m and a thickness of 0.5 $\mu$m under SEM. The apparent color of the particles changes as particle size and shape varies. Munsell color notation was employed to compare the colors of hematite particles with
various size and shape. Diffuse reflectance spectra show that a “red-shift” of 40 nm is observed in platelet, pseudocube and peanut-like particles compared to conventional particles. The band at 850 nm for the $^6A_1 \rightarrow ^4T_1$ transition was split in the pseudocubic and peanut-like particles. Raman spectra of the hematite particles also reveal that the vibrational modes of $\alpha$-Fe$_2$O$_3$ particles diminish as particle size decreases, and the dependence of vibrational band intensity to frequency is also observed. The spectral profiles demonstrate significant difference as excitation radiation lines changes from blue (457 nm) to red (647 nm).

A weak near infrared luminescence has been observed for fine-particle Fe$_2$O$_3$ when excited by 1064 nm radiation from a Nd:YAG laser. There are three broad luminescence peaks at 7994, 7225 and 6686 cm$^{-1}$, with intensities about ten times that of the Raman scattering. The relative intensities vary with particle morphology and with heat treatment. Overall band intensities increase by about a factor of ten for Fe$_2$O$_3$ that has been heated to 500 °C and then decreases again for material that has been heated to 1000 °C. The emission was assigned to the $^4T_{1g} \rightarrow ^6A_{1g}$ crystal field transition of octahedral Fe$^{3+}$. A large Stokes shift is associated with these transitions. Possible mechanisms responsible for the optical properties of hematite particles are postulated based on the findings of the experiments.

7.1.2 Ag/SiO$_2$ Nanocomposites

The dispersion and optical properties of silica-based Ag/SiO$_2$ nanocomposites have been investigated. Ag/SiO$_2$ nanocomposites with a uniform core-shell geometry
have been synthesized by reverse micelle techniques. The silver core is about 5 nm and the silica shell thickness is 10 nm when \( R = 2 \) (\( R = [\text{water}]/[\text{surfactant}] \)), \( H = 100 \) (\( H = [\text{water}]/[\text{TEOS}] \)) and \( X = 1 \) (\( X = [\text{NH}_4\text{OH}]/[\text{TEOS}] \)) are employed for the cyclohexane/Igepal/water tertiary system. The spherical nanocomposite particles were washed and collected using high performance liquid chromatography (HPLC) in order to remove the surfactant added during synthesis. Spherical SiO\(_2\) submicron particles were packed in the HPLC column as the stationary phase for the washing and dispersing of Ag/SiO\(_2\) nanocomposite particles. Surface modification of Ag/SiO\(_2\) nanocomposites and SiO\(_2\) microspheres with APS enhanced the charge of the nanoparticles and improved the efficiency of washing with HPLC. Dynamic light scattering (DLS), transmission electron microscope (TEM) and spin coat/atomic force microscope (AFM) analysis revealed that well-dispersed Ag/SiO\(_2\) stable suspensions in ethanol-water mixed solvent were successfully obtained after HPLC washing. The parameters pertinent to the HPLC washing protocol for nanocomposite particles were discussed.

### 7.1.3 Tabular SiO\(_2\) Nanoparticles

Amorphous tabular SiO\(_2\) nanoparticles were synthesized from the self-assembled octylamine/water bilayer via a template-directed growth mechanism. Morphology of the tabular SiO\(_2\) nanoparticles was analyzed by transmission electron microscope (TEM) and atomic force microscope (AFM) for the as-synthesized powders. The tabular SiO\(_2\) nanoparticles demonstrated well-defined thickness (4~6 nm) with a quite large face diameter (100~300 nm), which leads to a wide distribution of aspect ratio based on AFM
analysis. High surface area up to 1158 \text{m}^2/\text{g} were readily obtained with a very uniform micropore size of about 0.63 nm after thermal treatment at 700°C for 2 hours.

Metallic Pd clusters were embedded into the host matrix of microporous tabular SiO$_2$ nanoparticles via a solution reduction of Pd(NO$_3$)$_2$ by hydrazine hydrate. The infiltration of 33 wt% Pd leads to a 13% porosity loss of tabular SiO$_2$ nanoparticles. The presence of Pd in the SiO$_2$ matrix was demonstrated by EDS spectroscopy and by X-ray diffraction. The metallic guest species presumably reside in the accessible micropores with an estimated size about 1.3 nm. A portion of PdO was identified and related to the reduction process. Preliminary studies on hydrogen storage of the Pd infiltrated SiO$_2$ nanoparticles were performed.

7.2 Future Work

7.2.1 Luminescence of Hematite

The optical properties of Fe$_2$O$_3$ including color, reflectance spectra, Raman scattering and luminescence were carefully explored in terms of particle size and shape. There still exist at least two uncertainties for this particular pigment, the scattering peak at 1320 cm$^{-1}$ and the origin of the near infrared luminescence.

Five discrete laser lines in the visible spectrum have been applied to excite the hematite particles and different spectra profiles were recorded. However, the current findings offer inadequate information regarding the mechanism associated with the band at 1320 cm$^{-1}$. The two-magnon scattering and the two-photon scattering arguments were proposed decades ago, however, current results seem to be in favor of the photon
coupling theory. This argument could be further clarified if a continuous laser line is available as excitation sources and the spectra profile can be consecutively constructed. A precise onset wavelength of this band could be determined and one of the two coupling mechanisms may be ruled out.

The near infrared emission intensity is weak and occurs at an unusual wavelength. This could be a result of defect or deep traps in the hematite particles. To test this hypothesis, the Fe$_2$O$_3$ powder should be annealed under O$_2$ atmosphere with various oxygen concentrations. Changes in emission intensity could be expected if the luminescence is due to structure defect. 2 Obviously, this is a critical experiment with plenty of significance that would help to understand and utilize the infrared luminescence in hematite.

7.2.2 Dispersion of Ag/SiO$_2$ Nanocomposites

Dispersion at the nanoscale is still a challenging issue for many colloidal particles to fulfill the need in nanodevices fabrication. 3 With the scheme established from the dispersion of silica based nanocomposites, a similar approach can be applied to other materials where surfactant removal is required for dispersion.

The reason why ethanol/water cosolvent can drive the Ag/SiO$_2$ nanocomposites through the HPLC and produce a stable suspension is currently unknown. Molecular level segregation in a 7:3 molar ratio ethanol-water solution was observed. 4 The water molecules are believed to cluster in the mixture rich of hydrophobic ethyl groups. Other ethanol/water solutions with different ratio have been used in SiO$_2$ nanoparticle
There are also questions with regards to solids loading of the Ag/SiO$_2$ nanocomposites after HPLC washing.

### 7.2.3 Dispersion and Infiltration of Tabular SiO$_2$ Nanoparticles

Tabular SiO$_2$ nanoparticles were doped with 3 at % (1.7 wt %) triethoxyl boronate precursor during synthesis in order to lower the sintering temperature of SiO$_2$. However, the chemical analysis only provides 0.03 wt % boron, which indicates the loss of boron during particle processing. It is equally important to identify the source of the problem and modify the processing parameter. Control of the suspension pH is critical to minimize the solubility of B$^{3+}$ in the washing solvent. The dispersion of tabular SiO$_2$ nanoparticles remains a challenge due to the formation mechanism in the self-assembly bilayer.

The hydrogen adsorption concentration in the tabular SiO$_2$ nanoparticles with 33 wt% Pd is unexpectedly lower than that of bulk Pd. One of the possibilities is the content of Pd, because of the Pd infiltration method, some Pd might be deep in SiO$_2$ pores and unable to react with hydrazine, resulting in a low hydrogen adsorption volume. An optimal amount of Pd can be determined by measuring the hydrogen adsorption isotherm as a function of Pd concentration. The infiltration procedure should be modified so that the formation of PdO is eliminated. A possible reduction route is to add the reducing agent at a low temperature and then raise the temperature after a certain period of time. The redox reaction is expected to take place simultaneously in the SiO$_2$ matrix. A
uniform distribution of Pd clusters in the SiO$_2$ matrix could improve the hydrogen adsorption properties of the nanocomposites.

7.3 References


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