SILICA NANOPARTICLES, SYNTHESIS, MODIFICATION AND THEIR APPLICATIONS IN THE FABRICATION OF POLYPYRROLE-BASED SILICA NANOCOMPOSITES

MOHAMMAD JAFARZADEH

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by

MOHAMMAD JAFARZADEH

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DEDICATION

To my family

And

To my love; Elnaz

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LIST OF SYMBOLS, ABBREVIATIONS AND NOMENCLATURE

Symbols	Descriptions
AFM	Atomic Force Microscopy
α_{OH}	Silanol number
APTES	3-aminopropyltriethoxysilane
APTMS	3-aminopropyltrimethoxysilane
BET	Brunauer-Emmet-Teller
BJH	Barett-Joyner-Halenda
CNT	Carbon nanotube
CP/MAS NMR	Cross-polarization magic angle spinning NMR
D_a	Apparent density
ΔH	Enthalpy
δ_{OH}	Silanol concentration
DSC	Differential Scanning Calorimetry
EDX	Energy dispersive X-ray
eV	Electron volt
FD	Freeze drying
FTIR	Fourier transform infrared
HD	Heat drying
λ_{max}	Lambda maximum
LO	Longitudinal optical
N_A	Avogadro number (6.022×10^{23})
NBOHC	Non-bridging oxygen hole center
NMR	Nuclear magnetic resonance
ν	Stretching vibration
ODC	Oxygen deficient centers
Oxi	Oxidant
PAni	Polyanilline
PL	Photoluminescence
PSD	Particle size distributions
Py	Pyrrole

Symbols	Descriptions
PPy	Polypyrrole
R	$[H_2O]/[TEOS]$ ratio
R′	$[H_2O]/[TEOS+APTES]$ ratio
R_a	Roughness
SEM	Scanning electron microscopy
σ	Standard deviation of particle size
STE	Self-trapped exciton
T	Temperature (°C)
TEM	Transmission electron microscopy
TEOS	Tetraethylorthosilicate
TGA	Thermogravimetric analysis
TMS	Tetramethylsilane
TO	Transverse-optical
Ts	*p*-toluenesulfonic acid
UV-Vis	Ultraviolet-visible
XRD	X-ray diffraction

SINTESIS, PENGUBAHSUAIAN NANOZARAH SILIKA SERTA PENGGUNAANNYA DALAM PEMFABRIKAN SILIKA NANOKOMPOSIT BERASASKAN POLIPIROL

ABSTRAK

Kajian ini menerangkan tentang pengubahsuian penyediaan silika zarah nano secara sol-gel. Keupayaan untuk mengawal saiz dan taburan zarah didapati bergantung pada mod campuran reaktan dan teknik pengeringan. Campuran tetraetoksilana (TEOS) dan etanol, diikuti dengan penambahan air (Mod - A) menghasilkan serbuk mono serakan dengan purata saiz zarah 10.6 ± 1.40 nm dan taburan saiz yang sempit. Selanjutnya, teknik pengeringan kering beku (FD) meningkatkan lagi kualiti serbuk tersebut berbanding dengan penggunaan teknik pengeringan haba (HD). Serbuk ini terdiri daripada struktur teratur silika nano zarah dengan tahap kecutan yang rendah, saiz dan isipadu liang yang lebih besar serta entalpi endoterma yang besar (ΔH_{FD} = - 688 J g^{-1} vs. ΔH_{HD} = - 617 J g^{-1}), yang memudahkan lagi pelepasan keluar air terjerap. Sehubungan ini, suatu kaedah mudah dan pantas dalam menyediakan silika organo terubah suai dalam julat saiz nano dengan kumpulan amina hujung secara kondensasi bersama telah dilakukan. Nano silika terubah suai organo terdiri daripada serbuk amorfus dengan saiz zarah ~ 60 nm, mono sebaran yang baik dan pengagregatan yang rendah. Kecacatan struktur bagi nano zarah silika organo terubah suai telah dikaji melalui penyerapan optik dan fotopendarcahaya dalam julat ultra ungu vakum (VUV), UV boleh nampak dan hampir IR. Analisis Raman juga menunjukkan ciri-ciri optik berkaitan kecacatan permukaan. Nano zarah silika tersedia (bersaiz ~ 10 nm) telah ditukar secara pasca pengubahsuaian kepada saiz baru 11-13 nm, tetapi dengan pengagregatan lebih tinggi dan kehadiran organosilana swakondensi. Kandungan spesis organik dengan kefungsian amino dicerap bagi silika terubah suai, menghasilkan

kehidrofobiaan permukaan yang lebih banyak yang dapat meningkatkan lagi keserasian dan serakan silika organo terubah suai menjadi matriks polimer dalam pemfabrikatan nano komposit. Akhir sekali, sistem teras kelompang nano komposit silika-polipirola dengan saiz zarah 60-70 nm telah disintesiskan melalui pempolimeran penyebaran oksidatif menggunakan silika tulen dan silika terubah suai yang disediakan sebelum ini. Zarah-zarah tersebut menunjukkan tahap sebaran lebih tinggi dan pengagregatan lebih rendah tanpa menggunakan sebarang penstabil cas dan sterik. Prapengubahsuaian permukaan silika menunjukkan kesan ketara terhadap keberkesanannya sementara jumlah pembebanan jisim polipirola pada permukaan silika terubah suai mengakibatkan kekonduksian elektrik yang tinggi berbanding silika tulen. Kaedah penyediaan berdasarkan mod pra-endapan pirola atau $FeCl_3.6H_2O$ sebagai zat pengoksidaan merupakan satu lagi faktor penting terhadap keberkesanan pembebanan jisim polipirola pada permukaan silika terubah suai. $FeCl_3.6H_2O$ ialah agen pengoksidaan yang lebih berkesan bagi pempolimeran pirola berbanding dengan penggunaan satu lagi agen biasa iaitu $(NH_4)_2S_2O_8$. Penambahan *p*-toluena sulfonat sebagai bahan dop anion semasa proses pempolimeran telah meningkatkan lagi kekonduksian polipirola.

SILICA NANOPARTICLES, SYNTHESIS, MODIFICATION AND THEIR APPLICATIONS IN THE FABRICATION OF POLYPYRROLE-BASED SILICA NANOCOMPOSITES

ABSTRACT

A modified preparation of silica nanoparticles via sol-gel process is described. The ability to control the particle size and distribution is found to be highly dependent on mixing modes of the reactants and drying techniques. The mixture of tetraethoxysilane (TEOS) and ethanol followed by addition of water (Mode-A) produce monodispersed powder with an average particle size of 10.6 ± 1.40 nm and a narrow size distribution. The freeze drying technique (FD) further improves the quality of the powder compared to heat drying (HD). The powder consists of a well-order structure of silica nanoparticles with low shrinkage, bigger pore size and volume and large endothermic enthalpies (ΔH_{FD} = - 688 J g^{-1} vs. ΔH_{HD} = - 617 J g^{-1}), leading to easy escape of physically adsorbed water. Then, an easy and swift pathway in the preparation of organo-modified silica in nanosize range with amine terminal group via co-condensation method has been obtained. The organo-modified nanosilica consists of amorphous powder with particle size of ~ 60 nm, highly monodispersed and low aggregation. Structural defects in organo-modified silica nanoparticle have been studied via optical absorption and photoluminescence in the range of vacuum ultraviolet (VUV), UV visible, and near-IR. Raman analysis also demonstrates the surface defect-related optical properties. Post-modification of as-prepared silica nanoparticles (~ 10 nm in size) are converted into organo-functionalized silica with new size of 11-13 nm, but with higher aggregation and existence of self-condensed of organosilanes. Higher organic species content with amino functionality is observed for *in-situ* modified silica, leading to more surface hydrophobicity that can improve the compatibility and

dispersion of organo-modified silica into polymeric matrix in nanocomposite fabrication. Finally, the core-shell system of silica-polypyrrole nanocomposite with particle size of 60-70 nm has been synthesized via oxidative dispersion polymerization using pure silica and modified silica which was previously prepared. The particles demonstrate higher dispersion and lower aggregation without employing any charge and steric stabilizers. Pre-surface modification of silica shows significant effect on efficiency of polypyrrole deposition while the amount of mass loading of polypyrrole on the surface of modified silica compared to that in pure silica leading to higher electrical conductivity. The preparation method based on the mode of pre-deposition of pyrrole or $FeCl_3.6H_2O$ as oxidant is another important factor on efficiency of mass loading of polypyrrole on the surface of modified silica. Addition of *p*-toluene sulfonate as anion dopant during polymerization process has highly enhanced the conductivity of polypyrrole.

CHAPTER 1:
INTRODUCTION

1.1 Nanoparticles

Nanostructures or nanoscale materials are any solid materials that have a nanometer dimension. Nanoparticles are generally considered to be a number of atoms or molecules bonded together with a radius of < l00 nm. These nanosize solid particles could be nanocystalline, an aggregate of crystallites, or a single crystallite. The physical, chemical, and electronic properties of nanoparticles depend strongly on the number and type of atoms that make up the particle. It is found that color, reactivity, stability, and magnetic behavior all depend on the particle size. In some instances, an entirely new behavior, which is not seen in the bulk, has been observed such as magnetism in clusters that are constituted from nonmagnetic atoms (Wang, 2000; Poole & Owens, 2003; Köhler & Fritzsche, 2004; Rao *et al.* 2004; Sarid *et al.* 2004; Schmid, 2004; Rao & Cheetham, 2006). There are some preparation methods for nanoparticles such as laser evaporation, radio frequency (RF) plasma, thermolysis and chemical methods (Sarid *et al.*, 2004; Sharma *et al.*, 2004; Skandan & Singhal, 2006).

1.2 Silica nanoparticles

Silica is an inorganic polymer [$(SiO_2)n$] formed via condensation of silicic acid as a fully hydrolyzed monomer [$Si(OH)_4$]. Silica is generally used as a short convenient designation for “silicon dioxide” in all its crystalline, amorphous, and hydrated or hydroxylated forms (Iller, 1979). Silica has two different functional groups on its surface; silanol (Si—OH) and siloxane (Si—O—Si) groups. These two groups

substantially influence the surface properties and subsequently the application properties. The fully hydroxylated surface of silica generally has ~ 4.6 silanol groups per nm^2 which results in the hydrophilic character of products (Brinkmann *et al.*, 2006). There are various methods for the preparation of nanosilica, among them, the well-known / used is sol-gel technique.

1.2.1 Sol-gel technique

The synthesis of silica by sol-gel technique involves the evolution of inorganic network (Si-O-Si) through the formation of a colloidal suspension (sol) and gelation of the sol, forming a network in a continuous liquid phase (gel) (Brinker & Scherer, 1990). At the functional group level, three reactions are generally used to describe the sol-gel process: hydrolysis, alcohol condensation, and water condensation. This general reaction scheme can be seen as follows;

Hydrolysis

$$\equiv Si\text{-}O\text{-}R + H_2O \rightarrow \equiv Si\text{-}OH + R\text{-}OH \quad (1)$$

Water condensation

$$\equiv Si\text{-}OH + HO\text{-}Si\equiv \rightarrow \equiv Si\text{-}O\text{-}Si\equiv + H_2O \quad (2)$$

Alcohol condensation

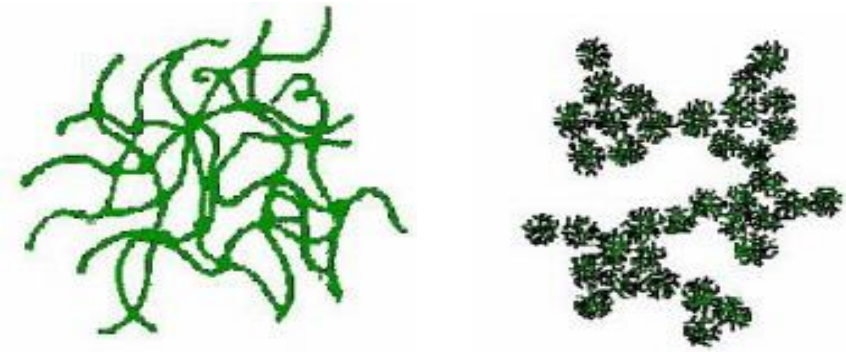
$$\equiv Si\text{-}O\text{-}R + HO\text{-}Si\equiv \rightarrow \equiv Si\text{-}O\text{-}Si\equiv + R\text{-}OH \quad (3)$$

Under most conditions, condensation commences before hydrolysis is completed. However, parameters such as pH, $[H_2O]/[TEOS]$ molar ratio (R), and catalyst can force the completion of hydrolysis before the condensation begins. Additionally, since water and alkoxide are immiscible, a mutual solvent such as an alcohol is utilized. Thus, in the presence of this homogenizing agent i.e. alcohol,

hydrolysis is facilitated due to the miscibility of the alkoxide and water (Brinker, 1988, 2006). As the number of siloxane bonds increases in the condensation process, the individual molecules are bridged and jointly aggregated in the sol. When the sol particles aggregate, or are inter-knited into a network, a gel is formed. The gel is dried by means of low temperature treatments (25-100 ^{o}C) or under a supercritical condition and is converted into dense ceramics (xerogel) or extremely low-density material called "aerogel", respectively (Hench & West, 1990). Upon drying, trapped volatiles (water, alcohol, etc.) are driven off and the network shrinks. It should be emphasized that the addition of solvents and certain reaction conditions as a serious drawback may promote esterification and depolymerization reactions according to the reverse of equations (1), (2), and (3) (Celzard & Marêché, 2002; Coltrain & Kelts, 2006).

In morphological aspect point of view, sol-gel polymerization occurs in three stages: (a) Polymerization of monomers to form particles, (b) Growth of particles, and (c) Linking of particles into chains, and subsequently networks that extend throughout the liquid medium, thickening into a gel. Within the context of these stages, many factors affect the resulting silica network, such as, pH, temperature and time of reaction, reagent concentration, catalyst nature and concentration, [H_2O]/[TEOS] molar ratio (R), aging temperature and time, and drying techniques (Iller, 1979). Thus, by controlling these factors, it is possible to control nucleation and the growth of particle as well as to avoid any undesirable phenomenon such as aggregation and agglomeration.

However, the sol-gel process under acid-catalyzed conditions yields primarily linear or randomly branched polymers which entangles and forms additional branches in gel. On the other hand, the reaction under base-catalyzed conditions yields more highly branched clusters which does not interpenetrate prior to gelation and thus behave as discrete clusters (Brinker & Scherer, 1990) (Figure 1.1).



A B

Figure 1.1 Particle growths under the (A) acidic and (B) basic sol-gel conditions. (Accessed on 14 May 2009, http://www.psrc.usm.edu/mauritz/solgel.html)

1.2.2 Applications of nanosilica

Silica powders can be represented by different functions in different applications, for example, reinforcing, stiffening and hardening of organic polymers, reducing adhesive between solid surfaces, increasing adhesion of adhesives, increasing viscosity in liquid, creating various optical effect, surfactant effect, absorbent, catalyst base, chromatographic column packing and biological application such as dental filling (Hench, 1998; Bergna, 2006; Falcone, 2006; Wang *et al.*, 2008; Yeoh *et al.*, 2009).

1.3 Modification process

In silica, where the siloxane groups are generally chemically inert, the reactivity of silanol groups allows some chemical surface modifications. Thus, the reaction with organosilanes can lead to hydrophobic silica. The attachment of silane coupling agent molecules to colloidal silica particles can prevent the aggregation of the particles due to the steric repulsion of grafted organic groups (Tertykh, 2004). The combination of the properties of organic and inorganic components lead to the preparation of hybrid materials that possess the enormous functional variation of organic chemistry with the advantages of a thermally stable and robust inorganic substrate. On the other hand, the adsorption phenomenon depends on the interaction between the surface of the adsorbent and the adsorbed species. The interaction may be due to, (1) chemical bonding, (2) hydrogen bonding, (3) hydrophobic bonding, (4) van der Waals force (Parida *et al.*, 2006).

Three pathways are available for synthesizing the modified hybrid materials based on organosilica units: (1) the subsequent modification of the surface of a purely inorganic silica material ("grafting"); (2) the simultaneous condensation of corresponding silica and organosilica precursors ("co-condensation") and (3) the incorporation of organic groups as bridging components directly and specifically into the pore walls by the use of bissilylated single-source organosilica precursors ("production of periodic mesoporous organosilica") (Hoffmann *et al.*, 2006).

1.3.1 Post-modification (grafting)

Grafting refers to the subsequent modification of the inner surface of mesostructured silica with organic groups. This process is primarily carried out by the reaction of

organosilanes with the free silanol groups of the surfaces. This method of modification has the advantage that the mesostructure of the starting silica is usually retained, whereas the lining of the walls shows a reduction in the porosity of the hybrid material. If the organosilanes react preferentially at the open pore during the initial stages of the synthetic process, the diffusion of further molecules into the center of the pores can be impaired, which can in turn lead to a nonhomogeneous distribution of the organic groups within the pores and a lower degree of occupation. In extreme cases (e.g., with very bulky grafting species), this can lead to a complete closure of the pores (pore blocking) (Vansant *et al.*, 1995; Hoffmann *et al.*, 2006).

1.3.2 *In-situ* modification (co-condensation method)

An alternative method to one-pot synthesize organic-functionalized mesoporous silica is the co-condensation method (Direct method). It is possible to directly prepare mesostructured silica by the co-condensation of tetraalkoxysilanes with terminal trialkoxyorganosilanes, leading to materials with organic residues anchored covalently to the pore walls. Since the organic functionalities are direct components of the silica matrix, pore blocking is not a problem in the co-condensation method. Furthermore, the organic units can generally and more homogeneously be distributed than in materials synthesized with the grafting process owing to the homogeneous distribution of different organic functionalities in the framework. However, the co-condensation method also has a number of disadvantages as well: in general, the degree of order of the products decreases with the increasing concentration of $(R'O)_3SiR$ in the reaction mixture, which ultimately leads to totally disordered products. An increasing proportion of $(R'O)_3SiR$ in the reaction mixture favors homo-condensation reactions—at the cost of cross-linking co-condensation reactions

with the silica precursors (Hoffmann *et al.*, 2006). Therefore, by controlling the amount of organosilanes, it could constrain any undesirable formation of homo-condensed product.

1.3.3 Incorporation modification

The synthesis of organic-inorganic hybrid materials by hydrolysis and condensation reactions of bridged organosilica precursors of the type $(R'O)_3Si\text{-}R\text{-}Si(OR')_3$ is known via sol-gel chemistry. The organic units in this case incorporate in the three-dimensional network structure of the silica matrix through two covalent bonds and thus are distributed totally homogeneously in the pore walls. These materials, which are obtained as porous aerogel and xerogels, can have large inner surface areas as well as high thermal stability but generally exhibit completely disordered pore systems with a relatively wide distribution of pore radii. This method is employed for the preparation of a new class of mesostructured organic-inorganic hybrid materials-periodic mesoporous organosilicas (PMOs) (Asefa *et al.*, 1999; Inagaki *et.al.*, 1999; Melde *et al.*, 1999). Recently, microwave heating was employed for the preparation of periodic mesoporous organosilica material with smaller and uniform particle size (Yoon *et al.*, 2008).

1.4 Nanocomposites

Many efforts have focused on the integration of a variety of nanoscopic materials into polymers and the impact of these composites on a broad spectrum of applications, from engineering plastics to electronic materials to biotechnology. Significant interest in the use of well-ordered nanoparticles as fillers within polymer materials are expected to provide access to new materials (known as organic-

inorganic nanocomposite) that combine the unique physical properties of the inorganic particles (rigidity, high surface hardness, high modules, strength, high thermal stability, UV-shielding property, and high refractive index, etc.) with the superior processibility of the polymers (flexibility, ductility, transparency, mouldability, low density, dielectric strength, etc.) (Ajayan *et al.*, 2003; Sill *et al.*, 2004; Koo, 2006).

Organic-inorganic nanocomposites, which are based on organic polymer and inorganic mineral exhibit the enhanced performance properties compared to conventional composites owing to the maximized interfacial contact between the organic and inorganic phases in comparison with bulk materials (Seo & Kim, 2005). However, it is very difficult to manufacture nanocomposites with the nanoparticles dispersed uniformly as nanoparticles have very high surface energies and are prone to agglomerating into larger particles during the preparation of the materials (Xu *et al.*, 2003). The most important approach that can be employed to solve the problems is a surface organo modification of nanoparticles in order to promote compatibility. Therefore, the properties of a composite material depend not only upon the properties of the individual component phases (matrix, filler, interphase), but also upon their interaction (Kashiwagi *et al.*, 2003). Owing to the poor compatibility between the organic matrix and inorganic fillers, some efforts are necessary in order to enhance the compatibility between the fillers and the hydrophobic polymer matrix during the preparation of nanocomposites (Y. -L. Liu *et al.*, 2003).

Generally, there are two typical types of interactions in organic-inorganic nanocomposites, depending on the strength or level of interaction between organic

and inorganic phases: one involving physical or weak phase interaction (e.g., hydrogen bonding, van der Waals forces) and another possessing a strong chemical covalent or ionic-covalent bond between the organic and inorganic phases (Chen *et al.*, 2005). These forces can strongly affect on physical, mechanical and thermal properties of nanocomposites.

1.4.1 Preparation methods of nanocomposites

To provide well dispersion of these organic-modified nanoparticles in a polymer matrix, there must be favorable interactions between the nanoparticle and the polymer. Several approaches have been investigated for this aim, such as (i) sol-gel process, (ii) *in-situ* polymerization, and (iii) direct solution blending (Yang & Nelson, 2004).

1.4.1.1 Sol-gel process for nanocomposites preparation

In sol-gel process, nanoscale particles of the inorganic material can be formed *in-situ* and the interaction between the inorganic compound and the polymer can be controlled in order to avoid the formation of voids between both materials. The inorganic moiety can be inserted into the polymer backbone by a reaction between functional groups of the polymer and the alkoxysilane monomers, or, the inorganic compound can be formed *in-situ* without covalent crosslinking with the polymer backbone (Gomes *et al.* 2005).

1.4.1.2 *In-situ* polymerization process for nanocomposites preparation

In *in-situ* polymerization, nanosilica particle is first dispersed into polymer precursors (monomers), and subsequently polymerization process is conducted.

Dispersing *in-situ* polymerization may be the most desirable method for preparing nanocomposites as the types of nanoparticles and the nature of polymer precursors can vary in a wide range, depending on the requirement (Xu *et al.* 2003).

1.4.1.3 Blending process for nanocomposites preparation

Although nanocomposites can be prepared by simply blending the nanoparticles with base polymers via high shear stirring or ball milling, the dispersing degree of nano-particles and the interfacial adhesion were obviously insufficient in order to obtain desirable material properties (Qi *et al.* 2006).

Among these three approaches, the *in-situ* polymerization method has the advantages of ease of handling, i.e. a relatively quick process, and usually offers better performance for the final products (Yang & Nelson, 2004).

1.4.2 Core-shell nanocomposites

Core-shell or nano-shell particles constitute a special class of nanocomposite materials. They can also be classified as hybrid nanostructures. In this system, the particles of one material are coated with a thin layer of another material using specialized procedures. They can show modified and improved properties than their single component counterparts or nanoparticles of the same size. Their properties can be modified into either constituting materials or core-to-shell ratio. The term of nanoshell is used especially when the thickness of the shell is ca. 1-20 nm. They are frequently referred as core-shell or core@shell particles (Caruso, 2001; Zhang *et al.*, 2004).

1.4.2.1 Preparation methods for core-shell nanocomposites

Preparation of nanoshell particles involves multistep synthesis procedure. It requires a highly controlled and sensitized synthesis protocol to ensure complete coverage of core particles with the shell materials. There are various methods to fabricate core-shell structure, e.g. precipitation, grafted polymerization, microemulsion, reverse micelle, sol-gel condensation, and layer-by-layer adsorption techniques. Although several methods have been established, it is still difficult to control the thickness and homogeneity of the coating. If the reaction is not properly controlled, it eventually leads to aggregation of the core particles, formation of separate particles of shell materials or incomplete coverage (Aguiar *et al.*, 1999; Li & Stöver, 2000; See *et al.*, 2005; Gong *et al.*, 2009).

1.4.2.2 Application of core-shell nanocomposites

The coating of colloidal particles with shell offers the most simple and versatile way of modifying their surface, chemical, optical, magnetic, and catalytic properties. A variety of applications such as fluorescent diagnostic labels, catalysis, avoiding photo degradation, photoluminescence enhancement, photonic crystals creation, bio-conjugates preparation, chemical and colloidal stability have been found (Schärtl, 2000; Caruso, 2001; Zhong & Maye, 2001; Haag, 2004; Basinska, 2005).

1.5 Conducting polymers

Conductive polymers or organic metals are good conductors of electricity. Polymers with conjugated π-electron backbone can be doped to produce materials that exhibit electrical conductivities approaching those of metals. They have the electronic properties of a semiconductor as well as the mechanical properties of polymers. In

addition, conducting polymers offer advantages over metals and other semiconducting materials owing to their good mechanical properties, stability, ease of processing, and relatively low price (Carswell & Grady, 2004). Polyacetylene (PA), poly(*p*-phenylene) (PPP), poly(*p*-phenylene sulfide) (PPS), polypyrrole (PPy), polythiophene and polyaniline (PAni) have been identified as intrinsically conducting polymers. A number of different charge-transfer agents, known as dopants have been used to improve the conductivity of such polymers, such as AsF_5, I_2, and BF_3. The doping of conjugated polymers generates high conductivity by increasing the carrier concentration via oxidation or reduction with electron acceptor or donor, respectively (Vernitskaya & Efimov, 1997; Wallace *et al.*, 2003; Filocamo & Grinstaff, 2004). Figure 1.2 represents the structure of some common conducting polymers.

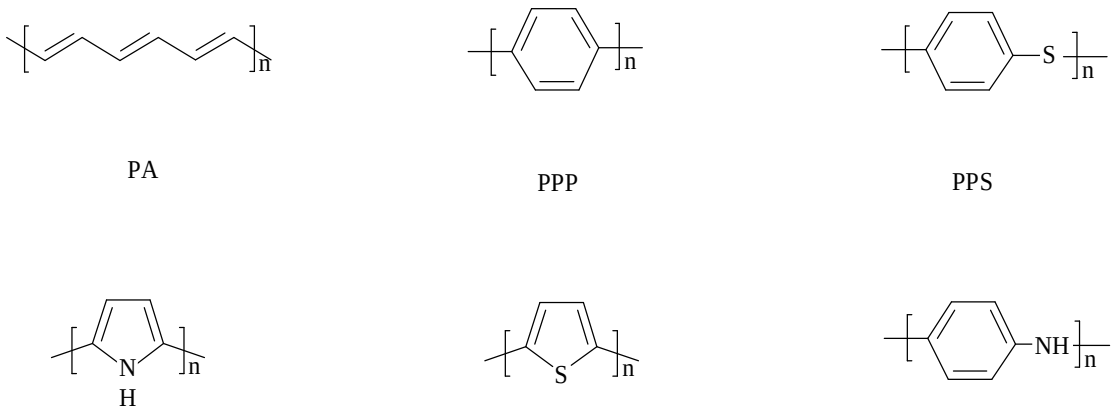


Figure 1.2 The structure of some conducting polymers

1.5.1 Polypyrrole

Polypyrrole (PPy) a promising conducting polymer has widely found of particular interest, owing to their high polarizability, superior conductivity, stability in the

oxidized state and interesting redox properties (Vernitskaya & Efimov, 1997). Polypyyrole is an inherently conducting polymer which contains one positive charge delocalized over three or four pyrrole residues in the polymer backbone. These positive charges are counter-balanced by anions (e.g. Cl^-, NO_3^-, SO_4^{2-} …), called ‘‘dopants,’’ that are incorporated during synthesis. PPy has stiff and inflexible polymer chains and can be considered to be a lightly cross-linked (Wallace *et al.*, 2003). PPy is generally amorphous structure that depends on the degree of polymerization where the color changes from yellow to the blue and ultimately, black. Apart from this, the structural ordering in polymeric layers can strongly affects on the conductivities (Vernitskaya & Efimov, 1997; Cho *et al.*, 2007).

1.5.2 Preparation methods of Polypyrrole

The simplicity of the synthetic procedures and availability of the initial monomers are attractive features of PPy. PPy as a high conductive and environmentally stable polymer, has been extensively synthesized via chemical and electrochemical (Electropolymerization) approach (Vernitskaya & Efimov, 1997; Cho *et al.*, 2007).

In chemical method, polypyrrole prepared by oxidation of the monomer with chemical oxidants has a form of black powder. Aqueous or anhydrous $FeCl_3$ and / or other salts of iron (III) and copper (II) are widely used as chemical oxidants. The yield and conductivity of the PPy are affected by a variety of factors such as solvent and oxidant, initial pyrrole/oxidant ratio, duration and temperature of the reaction (Vernitskaya & Efimov, 1997; Cho *et al.*, 2007). Figure 1.3 shows the schematic preparation of the PPy.

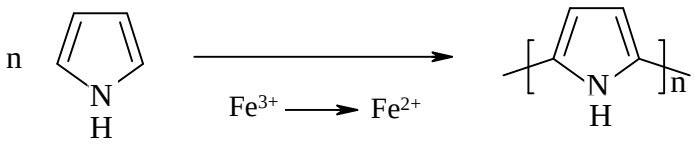


Figure 1.3 The oxidative polymerization of PPy.

1.5.3 Application of conducting polymers

The conducting polymers have found much interesting application in various areas such as energy storage devices (Yoneyama *et al.*, 1991), electrocatalysts, biosensors, photoluminescent and electroluminescent materials (Komaba *et al.*, 1998), artificial muscles, gas separating membranes, anticorrosive coatings, electromagnetic shields, materials for microlithography, electrophotography, etc (Vernitskaya & Efimov, 1997; Komaba *et al.*, 1998; Cho *et al.*, 2007). PPy is intensively colored (black) in the oxidized form while its reducing form shows transparent green that can be utilized in electrochromic switching application (Partch *et al.*, 1991). Soluble polypyrrole as the transparent anode can also be used in polymer light-emitting diodes (Gao *et al.*, 1996). Interestingly, polypyrrole actuator with a bioadhesive surface has been employed for accumulating bacteria from physiological media (Liu *et al.*, 2009).

1.5.4 Conducting polymer-inorganic nanoparticle composites

Conducting polymers are infusible in nature and generally insoluble in the usual solvents of which seriously limit its processability. Therefore, one method of overcoming the processability problem is to prepare the conducting polymers in colloidal form via dispersion *in situ* polymerization with deposition of polymer onto inorganic particle surface (Filocamo & Grinstaff, 2004; Cho *et al.*, 2007). Therefore,

conducting polymer-based inorganic composites seem to find more potential application compared to pure conducting polymers.

1.6 Problem Statements

Nanosilica, owing to excellent mechanical and optical properties, has potential application as a filler to polymeric system in the preparation of nanocomposites. The main disadvantages of the incorporation of the fillers to polymers are agglomeration of particles and formation of non-selective voids at the interface of the particles and the polymer matrix. Therefore, the nature of the interface between the organic and inorganic parts plays a crucial role. By introducing coupling agents or reactive groups onto the surface of nanoparticles, a good interfacial adhesion between inorganic and organic components can also be achieved.

Silica nanoparticle can be prepared via sol-gel process which is very sensitive towards the experimental conditions that affect the rate of hydrolysis and condensation reactions, e.g., the type and concentration of starting materials (alkoxides), H_2O/alkoxide ratio, catalyst nature and concentration/pH, nature of solvent, temperature, time of reaction, aging and drying method (Iller, 1979; Chu *et al.*, 1997; Meixner & Dyer, 1999; Colomer & Anderson, 2001; Enomoto *et al.*, 2005). There are several drawbacks in sol-gel process such as difficulty in controlling the particle size, aggregation and agglomeration, shrinkage and cracking, and reaction time. Some key parameters in the preparation of nanosilicas, such as, effect of feed rate, mixing mode and drying process have been expected to affect on the particle size as well as distribution and aggregation and agglomeration, shrinkage and cracking of the silica nanoparticles.

For modification of the surface of silica nanoparticles, two main methods are generally employed; post-modification and *in-situ* modification (co-condensation method) (Hoffmann *et al.,* 2006). Most of the literatures report the application of co-condensation method in the preparation and modification of mesoporous silica by using surfactant or polymeric compound as a template (Fowler *et al.*, 1998; Richer, 1998; Igarashi *et al.,* 1999; Macquarrie *et al.,* 1999; Macquarrie *et al.*, 2001; Etienne *et al.*, 2002; N. Liu *et al.*, 2003; Sadasivan *et al.*, 2003; Gibaud *et al.*, 2004; Shah *et al.*, 2004; Park & Ha, 2006). There are a few works on the preparation of nanoparticles via co-condensation method (Vandenberg *et al.,* 1991; Branda *et al.*, 2007). Although post-modification is commonly used for modification purpose but, there are some drawbacks in this method such as reduction of porosity by attaching organic group to the pore surface and wall, and blocking via diffusion of modifier into the pore for mesoporous silica (Hoffmann *et al.,* 2006), multiple reaction, time and energy consuming as well as the use of organic solvent (e.g. toluene) for silica nanoparticles (Avella *et al.,* 2006; Rahman *et al.*, 2007).

On the other hand, polypyrrole (PPy) as a promising conducting polymer has been widely found of particular interest, owing to their high polarizability, superior conductivity, stability in the oxidised state and interesting redox properties. Although simplicity of the synthetic procedures and availability of the initial monomers are attractive features of PPy, but, bulk polypyrrole is infusible, intractable and insoluble in common solvents leading to a serious limit on its processability (Perruchot *et al.,* 1998). One method of overcoming the processability problem is to prepare conducting polymers in colloidal form via oxidative dispersion *in-situ* polymerization with deposition of polymer onto inorganic or organic particle surface.

In many of cases, surfactant and water soluble polymeric overlayer are used for better dispersion of nanocomposite particles.

1.7 Research Objectives

The main objectives of this research are proposed as follows;

(a) To develop a modified sol-gel method in preparation of silica nanoparticles with controlling particle size, monodispersity, aggregation and agglomeration by focusing on feed rate of ammonia, order of mixing of starting material and drying process.

(b) To develop an organo-modification method for synthesizing of modified silica nanoparticles via *in-situ* modification (co-condensation method) by emphasizing on mass loading of modifier (organosilanes), solvent type and optical properties.

(c) To compare between *in-situ* and post-modification process by emphasizing on mass loading of modifier, physical properties (density, specific surface area, and porosity), morphological properties, optical properties and studying thin film preparation of modified silica.

(d) To establish a method in order to synthesize core-shell composite system in nanoscale with silica and modified silica nanoparticle as a core and polypyrrole as a conducting polymer shell by emphasizing on preparation method, pre-deposition mode of monomer (Py) or oxidant ($FeCl_3.6H_2O$ and / or $(NH_4)_2S_2O_8$), pre-deposition time, mass loading of PPy on the surface of substrate (silica and modified silica), oxidant type and dopant type.

1.8 Scope of the Study

This study investigates the synthesis of silica nanoparticles and their potential applications in the preparation of inorganic-organic conducting polymer nanocomposite particles using pre-chemical modification of silica surface and bulk. This research is divided into three parts: (i) synthesis of silica nanoparticles by emphasizing on the controlling parameters on aggregation and agglomeration, (ii) surface modification of silica by adopting two methods *in-situ* and post-modification technique by emphasizing the amount of modifier mass loading that affects on aggregation and agglomeration of particulate system and (iii) synthesis of core-shell system using silica and modified silica-PPy nanocomposite particles with expectation towards lower aggregation, higher monodispersity and higher conductivity.

In the first part, some effective parameters on particle size and dispersity with focusing on aggregation and agglomeration are described. Three key factors such as, effect of feed rate, mixing mode and drying process are used to control and reduce the undesirable phenomena, i.e. aggregation and agglomeration (feed rate and mixing mode), the control of particle size (feed rate and mixing mode), and shrinkage and cracking (drying process).

In the second part, co-condensation method is introduced in the preparation of organic-inorganic hybrid materials via *in-situ* chemical modification of silica particle. The effect of mass loading of modifier on particle size and distribution and gelling time of reaction is investigated. When methanol is used instead of ethanol as a solvent a significant effect on particle size and distribution can be expected. Photoluminescence, solid state UV and Raman spectroscopy are utilized in order to

study optical properties of *in-situ* modified silica in comparison with that in pure silica. In addition, a comparison study between *in-situ* modified and post-modified silica (prepared in non-aqueous and aqueous media) is done by emphasizing the organic content on the surface in which the dispersion of particle could be improved by reducing the aggregation and agglomeration. Specific surface area, porosity, density, morphological and optical properties, and thin film coating on glass slide are obtained in order to study comparative aspects.

In the last part, all particles prepared in former parts, silica, *in-situ* modified and post-modified (in non-aqueous and aqueous solvent) are used as substrate or nano-core for chemical deposition of polypyrrole (as nano-shell) in the preparation of core-shell nanocomposite systems. The effect of preparation method and mode of pre-deposition of monomer (pyrrole) or oxidant, deposition time, type of oxidant ($FeCl_3.6H_2O$ and $(NH_4)_2S_2O_8$), type of dopant (*p*-tosylate) on conductivity, particle size and distribution are studied.

1.9 Thesis layout

This thesis contains of 7 chapters. Chapter 1 provides a brief introduction to general aspects of silica nanoparticles, modification processes, conducting polymers, core-shell nanocomposites and objectives of this study. Chapter 2 consists of literature reviews, mainly on the synthesis of silica nanoparticles via sol-gel process, chemical modification of silica via co-condensation and post-modification method, and the synthesis of PPy and silica-PPy nanocomposites via dispersion polymerization. The materials, instruments, experimental procedures, and characterization techniques used in this research are described in Chapter 3. Chapters 4 to 6 are actually the

results and discussion chapters according to the research objectives. Chapter 4 describes the synthesis of silica nanoparticles via sol-gel process. Chapter 5 introduces the synthesis of organo-functionalized silica nanoparticle by co-condensation method with further study on optical properties. In addition, this chapter investigates a comparative study of *in-situ* and post-modification process based on physical, morphological, and optical properties. Chapter 6 demonstrates the preparation and characterization of silica and modified silica-PPy nanocomposite particle via oxidative dispersion polymerization. Finally, the thesis ends with the conclusion and recommendation for future work in Chapter 7.

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