Nanosynthesis Techniques of Silica-Coated Nanostructures

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Additional information is available at the end of the chapter

Abstract

Core-shell nanomaterials are fast-emerging hybrid nanocomposites in area of nanotechnology, materials science and biochemistry, which are fast attracting research attention. Nanostructured nanomaterials are utilized in wide industry fields such as electronics, biopharmaceutical, biomedicine, optics and biocatalysis. Owing to the additional exterior shell-coating material, the primary core material's functionality, biocompatibility, chemical stability and colloidal dispersibility can be greatly enhanced. Silica, in particular, is found to be an excellent exterior shell-coating material, has been widely researched for the synthesis of core-shell nanocomposite materials. So far, there have been numerous publications devoted to silica-coating techniques using hydrophobic silanes, such as tetraethylorthosilicate (TEOS) or tetramethyl orthosilicate (TMOS), via the classic Stober method. Recently, there has been strong interest in the use of water-soluble silanes such as MPTMS (3-(mercaptopropyl)-trimethoxysilane), MPTES (3-(mercaptopropyl)-triethoxysilane), MTMS (3-(methyltrimethoxysilane)) and sodium silicate for water-based silica-coating techniques have gained much attention, due to the fast-growing need to focus on process simplicity, large-scale fabrication and environmental-friendly synthesis techniques of silica-based core-shell nanomaterials. Hence, this chapter focuses on the recent development on silica-coating techniques for colloidal nanoparticles, particularly on water-based techniques and morphologies. In summary, we emphasize the importance of advanced nanomaterials in today's world and envisage there will be more breakthrough research on aqueous silica-coating techniques for silica-encapsulated core-shell nanomaterials.

Keywords: silica-shell coatings, core-shell nanomaterials, aqueous one-pot synthesis

1. Introduction

Core-shell nanomaterials are considered as highly functional hybrid nanomaterials with dual properties, originating from either core or shell materials. Core-shell nanomaterials have been widely researched due to its extraordinary ability to exhibit distinctive properties of both core and shell materials combined to deliver a wide spectrum of industry applications and requirements. Core-shell nanomaterials are commonly applied in different industries such as biomedical, bio-electronics, pharmaceutical applications, bio-catalysis, photoluminescence imaging, creating photonic crystals, etc. Especially for bioscience and medical research, the core-shell particles are mainly used for cell detection, bioimaging, targeted drug delivery, controlled drug release and bioengineering applications [1].

The benefits of an exterior shell-coating on a core particle are that surface reactivity and thermal stability can be greatly enhanced, while colloidal stability and dispersibility are vastly improved. Core-shell nanostructure itself can allow controlled release of center material, reduced usage of precious materials, hollow-core templating, etc. Hollow particles can be prepared using as a template by utilizing core-shell nanoparticles and after removing the core either by dissolution or calcination. These hollow-core nanoparticles are useful for various applications such as biocatalytic agent, biosupports, bioadsorbents, super light-weight structure, miniature vessels and thermal/electric insulative materials [1].

Silica is one of the most widely researched as exterior shell-coating material for encapsulating all sorts of core nanomaterials. Silica coating of nano-sized metals, semiconductors, magnetic and ceramic nanomaterials can enhance its large surface area, quantum confinement and photocatalytic, optical and magnetic properties. Silica is often chosen as the ideal shell material to encapsulate core nanomaterials in order to modify its exterior surface properties. Silica is also a favorite choice for core-shell nanostructures to enhance colloidal stability. The main advantages of silica as an excellent candidate for shell-encapsulation material predominantly lies in its exceptionally good colloidal stability, especially in water-based media, easy controllability of the synthesis, chemical inertness, controlled porosity, high processability and optical transparency. Silica possesses other advantages such as (i) lower Van der Waals interactions compared to bare core particles (Hamaker constant is smaller for core-shell) and (ii) charged molecules that can be grafted onto silica shell at silica/water interfaces under alkaline conditions. Thus, silica shell can provide effective steric-hindrance and electrostatic protection on its core material, as well as function as excellent dispersant to provide electrostatically stable colloids. Furthermore, silica shell allows core nanoparticle to be biocompatible and easily bioconjugated with functional groups, which is necessary for biomedical, diagnostic and therapeutic applications (magnetic resonance imaging, MRI) [2].

However, the simple large-scale production and environmental-friendly fabrication of silica-coated core-shell nanomaterials currently remain a great challenge/bottleneck for practical commercialization [3]. The effective growth of homogenous silica shells on core nanoparticles faces problems of low chemical compatibility between both components [4]. Most existing silica-coating methods are dependent upon prior priming the surface of core material with

coupling agents, surfactants or polymers. The purpose of surface priming is to increase the compatibility of the core surface with silica, while providing particles with sufficient colloidal stability, so that colloids can be transferred into alcohol-based medium and classical Stober method [5] (using hydrophobic TEOS or TMOS in ethanol-water medium under alkaline conditions) is applicable for growing uniform silica shells on metal cores. A seminal publication on silica-coating gold nanoparticles was published by Liz-Marzán et al. [6]. Liz-Marzán et al. proposed silica-coating gold colloids in ethanol medium using a modified Stöber process. To achieve this, the authors surface-primed the nanoparticles with ATPMS before stabilizing the gold colloids by silica coating with a thin silica layer using sodium silicate in water medium, so that they can be stably transferred into ethanol medium. Since Liz-Marzán's pioneering work in 1996, many research studies have been carried out to simplify and shorten the tedious multiple steps procedure [7].

Recently, there has been an increasing number of studies on aqueous synthesis techniques of silica-coating nanoparticles due to its process simplicity, large scalability and environmental friendliness. The key advantage of synthesizing silica in aqueous solution will be that the problem of poor colloidal stability of core nanoparticles in alcohol mediums, due to reduced surface charges, can be resolved and, thus, obviates any need to perform tedious surface stabilization procedures [7]. Essentially, any aqueous synthetic route will allow users to overcome a key challenge of colloidal instability faced by existing silica-coating techniques, which occurs when metal colloids are transferred into organic solvents such as ethanol or isopropanol for silica coating via classic Stober synthesis techniques.

Water-based techniques enable scale-up production of silica-coated nanomaterials by harnessing the excellent colloidal stability of water-soluble nanoparticles in aqueous medium. The water solubility of silane precursors presents a highly attractive property to directly coat nanoparticles with silica in few simpler steps. Another advantage of an aqueous synthesis is that it promotes green chemistry in material synthesis through the use of inexpensive, non-toxic and ecologically friendly solvents such as water, in place of toxic solvents such as ethanol or isopropanol. By adopting a water-based silica-coating strategy, users can stably produce large quantities of core-shell nanostructures via simpler one-pot synthetic route. Essentially, by using water-soluble silane precursors, a water-based technique will allow fast and extensive silica coating of nanoparticle cores within a shorter time; without any need for transfer into alcoholic medium, dialysis or a change in reaction mixture, which are necessary for existing techniques such as Stöber process or reverse microemulsion techniques. A general synthetic route promotes green chemistry through sustainable material synthesis through the use of an inexpensive, non-toxic and ecologically friendly water medium, in place of organic toxic solvents such as ethanol or isopropanol. Furthermore, another important advantage of aqueous silica coating is that it is relatively neutral pH and lack of alcohol, thus being more suitable for encapsulating sensitive biomaterials such as enzymes and cells [8]. Aqueous silica-coating techniques are relatively straightforward processes that are less toxic, more cost-efficient and more environment-friendly. Hence, aqueous silica-coating techniques are not only less complex but also highly upscalable for commercial/industrial productions. These are the key reasons that motivated this chapter into summarizing the latest developments of new water-based techniques for direct silica coating of core nanoparticles.

	Pros	Cons
"Aqueous-based" silica-coating techniques	1. Facile one-step synthesis 2. Precisely controllable shell thickness 3. Shell growth is generally faster than non-aqueous routes 4. Functional groups may be intrinsically incorporated 5. Mild and less toxic, environmentally friendly 6. Most cost-effective and upscalable technique	1. May still require a small amount of acidic and/or basic catalysts 2. May require new surface functional groups. 3. Relatively new field, hence limited literature available. Generally applicable to hydrophilic core-materials only
"Solvent-based" silica-coating techniques	1. Shell thickness adjustable through reactant conditions 2. Extensively researched and mature technology 3. Mild, ambient temperature, low-pressure conditions 4. Nanometric resolution control of core/shell morphology 5. Structures and morphologies easily reproducible and tunable 6. Generally fast hydrolysis and condensation of silica	1. Complex reactions, multiple precursors, solvents, controls 2. Multiple reactants increase costs, time and environmental pollution, limited scale 3. Alcoholic and extreme pH conditions are cytotoxic 4. Processes to remove alcohol require evaporation and buffer solutions, increasing time, cost and complexity 5. Need surface functionalisation

Table 1. Pros & cons of aqueous and non-aqueous silica-coating routes.

Since water-based silica-coating of core-shell nanoparticles is a fast broadening field that is presently seeing remarkable developments, we summarized a collection of up-to-date work related to a variety of water-based silica core-shell nanomaterials and their synthesis techniques. In this chapter, four main types of aqueous synthesis routes related to water-soluble silane precursors have been widely used in recent publications, namely sodium silicate, MPTMS (3-(mercaptopropyl)-trimethoxysilane), MPTES (3-(mercaptopropyl-triethoxysilane) and MTMS (3-(methyltrimethoxysilane)). These silane precursors possess high water solubility. For example, the alkoxy group of MPTMS has been replaced with a sufficiently polar group. The substitution of the methoxy group in water-insoluble tetramethyl orthosilicate (TMOS) with a mercaptopropyl group ('MP') results in MPTMS that can be hydrolyzed in water prior to condensation to form core-shell structures at the nanoscale.

Table 1 summarizes the pros and cons of aqueous silica coating (using water-soluble silanes, namely sodium silicate, MPTMS, MPTES and MTMS) and solvent-based silica coating (using water-insoluble silanes, such as TEOS), which will be discussed in subsequent sections.

2. Sodium silicate-assisted silica coating

Silanization of diverse metal-core and semiconductor-core nanomaterial into core-shell systems has gathered much research attention due to enhancement of surface properties. Silica-shell encapsulation was useful in inhibiting particle growth, agglomeration and photo-induced

decomposition. For example, synthesizing silica coatings encapsulating gold nanoparticles with Raman-active dye molecules was proven to be useful as a surface-enhanced Raman scattering (SERS) nanoprobes. Inert and biocompatible silica-shell coatings are useful for bio-conjugation of quantum dots (QDs). Silica core-shell inhibits agglomeration of nanoparticles, hinders foreign biospecies from contaminating the nanoparticles' surface and aids to enhance the high photoluminescence for biosensing. Surface functionalisation of the silica outer shell with any various types of functional groups, such as carboxylate COOH, amine NH_2, phosphate, thiol SH and poly(ethyleneglycol) (PEG) groups, enables enhanced control in bioconjugation techniques [9].

A primary work on silica-coating gold nanoparticles was published by Liz-Marzán et al. [6] in 1996. The authors proposed silica-coating gold colloids in ethanol-based medium using a modified Stober process [5]. First, the gold colloidal surface must be activated with a surface-coupling agent, 3-aminopropyltrimethoxysilane (APTMS), to render the gold nanoparticle surface vitreophillic (that is receptive toward silica monomers or oligomers) before proceeding to coat them with water-soluble sodium silicate due to the low affinity between gold nanoparticles and sodium silicate. After APTMS treatment, the vitreophilic Au nanoparticles are coated with a thin inhomogenous silica shell (thickness < 2 nm) using sodium silicate in water at a low pH to stabilize the gold colloids, so that they can be stably transferred into alcoholic medium (**Figure 1**). However, the critical step of silanization with sodium silicate is poorly reproducible, which requires an extended time duration, typically from a few days to weeks, before a sufficient layer silica shell can be formed to stabilize the nanoparticles in the alcohol solution [10]. Using Stober process as the last step, Liz-Marzán coated a thicker homogenous silica layer (thickness > 5 nm) in ethanol-water mixture using silane precursor TEOS and the silanol groups provided by sodium silicate as anchor points.

Zhou et al. in 2005 [11] synthesized, based on a simple chemical precipitation, nano-sized CdSe quantum dots at normal temperature in slightly alkaline conditions. Also, silica encap-sulation onto these QDs via a slow polymerization of SiO_2 using sodium silicate is done by adding ethanol. Cadmium selenide (CdSe) quantum dots were thinly encapsulated with a 1–2 nm thin silica in an aqueous sodium silicate at pH 10.5 over 5 days of vigorous stirring (**Figure 2**). However, despite the absence of aggregates proving improvement to disper-sity, the coated particles were hardly monodispersed and without a distinctive core-shell
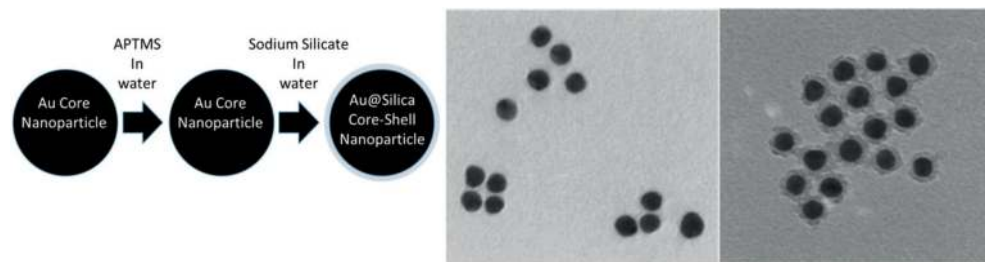
Figure 1. (Left) Schematic of aqueous synthesis procedure used by Liz-Marzán to coat thin silica shell on Au nanoparticles. (Right) TEM images of 15 nm-sized gold nanoparticles coated with 2 nm silica shells after addition of sodium silicate [6].
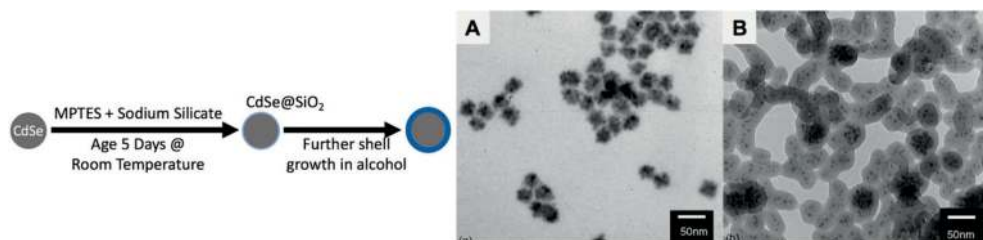
Figure 2. (Left) Schematic of aqueous synthesis procedure used by Zhou et al. to coat thin silica shell on CdSe nanoparticles using sodium silicate. (Right) TEM of CdSe NPs before (A) and after (B) encapsulation [11].
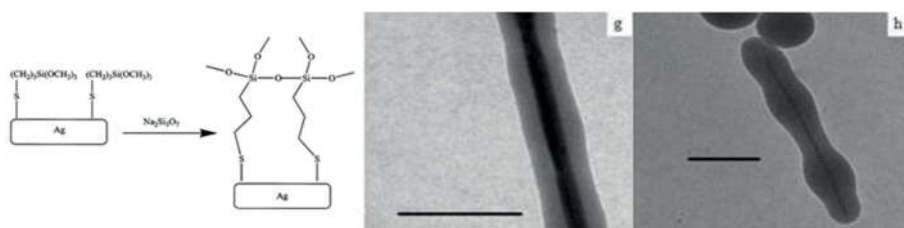
Figure 3. (Left) Schematic of 3-mercaptopropyltrimethoxysilane is binded via the sulfur to the nanowire surface with Ag, leaving three free –OCH$_2$ methoxy groups facing the water medium. Addition of sodium silicate produces silica, SiO$_2$. (Right) TEM images of Ag nanowires and silica-encapsulted Ag nanowires. Scale bar is 500 nm (g) and 100 nm (h). For thick layers of silica shells, the coating becomes inconsistent (h) [12].

structure. The authors attributed the success of silica-coating to the mercapto-groups present in the MPTMS, which are used to bridge the low affinity between CdSe core and silica shell. This principle would be repeated by Wolcott et al. [9] in the following year in their reported attempt to coat cadmium telluride (CdTe) quantum dots as they primed the CdTe nanoparticles with MPTMS prior to gradual silica growth under stirring over 72 h in aqueous sodium silicate solution.

Hunyadi et al. in 2006 [12] synthesized silver nanowires coated with a silica shell. Simona uses an indirect coating method that involved the use of a bifunctional linker, (HS(CH$_2$)3Si(OCH$_3$)3, 3-mercaptopropyltrimethoxysilane), so that the thiol SH groups bind Ag to the core surface [12]. Simona's approach is essentially seedless, surfactantless approach. Different volumes of sodium silicate Na$_2$O(SiO$_2$)$_3$ were added in alkaline pH and left overnight to allow formation of well-controlled layers of silica. The silica thickness was precisely controlled from ~10 to ~150 nm. The uniform silica coating over the whole surface of the nanowire is subjected to initial sodium silicate concentrations. Simona also found that MPTMS is critical to make a uniform layer of silver. When the MPTMS dosage exceeded 8.08 mM, the silica shell became undulating and inhomogenous (**Figure 3**). The reference experiment to synthesize SiO$_2$ on silver nanowires without the silane primer proved that the maximum shell thickness achieved was 5–10 nm only, regardless of the starting dosage of the silicate precursor. This outcome proves that silane performs a critical "surface-primer" function at interface of core-shell materials in the encapsulation process as a molecular binder.

Kobayashi et al. in 2007 [13] carried out silica encapsulation of nano-sized copper prepared from water-based solutions of copper salts. The silica shells chemically stabilized Cu colloids. Hydrazine and citric acid were used to reduce Cu salts and CTAB surfactants to stabilize 50 nm Cu metallic core particles. Then, silane-coupling agent, ATPMS, is added for surface functionalisation, and then Cu nanoparticles were coated with sodium silicate. Cu@SiO$_2$ core-shell nanoparticles are synthesized with ~10 nm silica layer. The mixed solution was left for 15 min for APTMS to attach on the surface of the core particles. Then, sodium silicate was added to the colloid, followed by tuning to pH 10 using CTAB resin for cation exchange. The synthesis time for the silica shell was 24 h. The key problem for using Cu-based particles is their fast oxidation in air environment. This arises from their instability toward oxygen to form CuO. To improve stability and reduce oxidation of copper nanoparticles, surfactant capping surrounding the copper particles inhibits oxygen molecules found inside the water-based medium from reacting with the copper. Previously, Kobayashi performed chemical stabilization by silica protection of cobalt nanoparticles prepared through reducing of Co salts in water-based medium. The silica shell forms a homogenous protection layer habiting O$_2$ molecules from reacting with the metallic cobalt nanoparticles. The nanoparticles were stable and chemically unchanged under high temperature in O$_2$ environment. This method has benefits such as (i) extraordinary colloidal stable dispersions in water, (ii) facile surface functionalisation to synthesize colloids for non-aqueous mediums and (iii) facile control of particle-to-particle interactions.

Hu et al. in 2009 [14] synthesized Fe$_3$O$_4$@SiO$_2$ magnetic composite nanospheres for fast and recyclable removal of lead and mercury from water (**Figure 4**). The Fe$_3$O$_4$@SiO$_2$ nanospheres were synthesized with the dissolution of sodium silicate in deionized water, into which Fe$_3$O$_4$ was added. HCL was added as a catalyst to adjust pH to 6.0 and the mixture stirred for 3 h at 80°C. A thin layer of silica coating visibly encapsulates the iron oxide spheres; the deposition of silica was also confirmed through XRD.

Wang et al. in 2010 [15] demonstrated a slightly different route starting with a suspension of Fe$_3$O$_4$ in deionized water at 80°C under a nitrogen flow, the pH was adjusted to 6.0 with
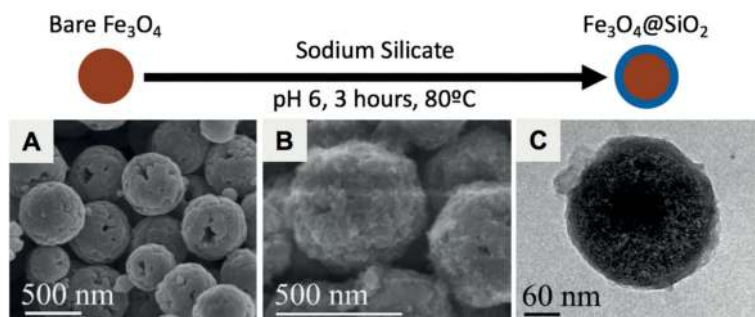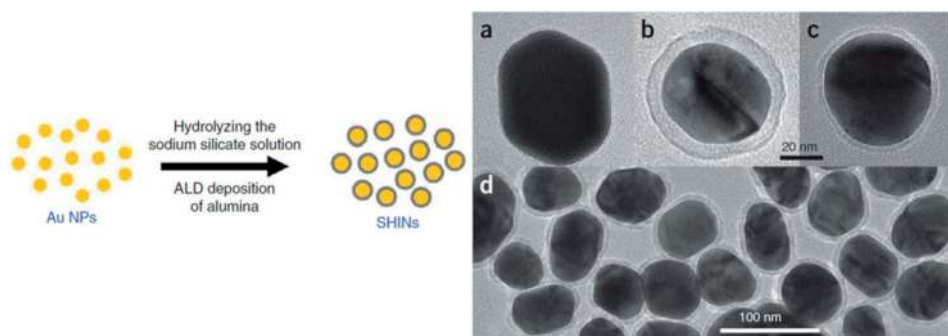

Figure 4. (Top row) Schematic of aqueous synthesis procedure used by Hu et al. to coat thin silica shell on Fe$_3$O$_4$ nanoparticles using sodium silicate. (Bottom row) SEM images of bare Fe$_3$O$_4$ microspheres (A, B) and (C) TEM images of Fe$_3$O$_4$@SiO$_2$ composite microparticles [14].

hydrochloric acid. Sodium silicate precursor was then added dropwise under strong stirring. The coating process was carried out for 5 h and the $Fe_3O_4@SiO_2$ nano particles collected via magnetic separation (**Figure 5**). In both Hu's and Wang's experiments, the silica shell was thin (<2 nm) and only just barely discernible under high-magnification TEM.

Li et al. in 2013 [16] proposed a shell-isolated nanoparticle-enhanced Raman spectroscopy (SHINERS) technique using core-shell structured gold@silica nanoparticles in aqueous solution with sodium silicate. The authors synthesized shell-isolated nanoparticles (SHINs) of sphere (55 and 120 nm diameter) finding that a 90°C reaction temperature accelerates the formation of silica shell on the gold nanoparticles. Gold nanoparticles were surface-primed using APTMS and coated with a 4 and 1 nm layer of silica using sodium silicate. Additionally,
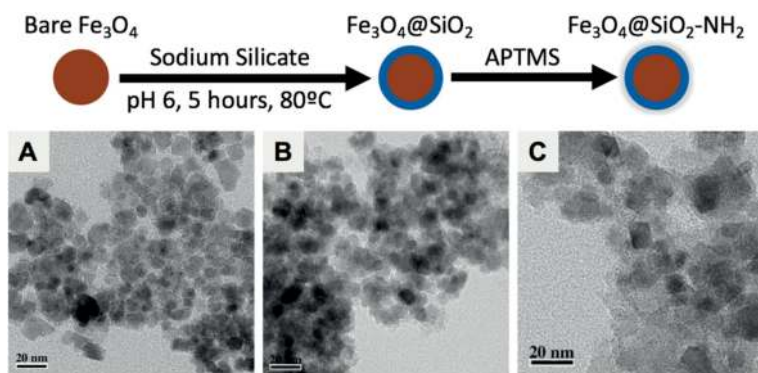
Figure 5. (Top row) Schematic of aqueous synthesis procedure used by Wang et al. to coat thin silica shell on Fe_3O_4 nanoparticles using sodium silicate. (Bottom row) TEM image showing (A) Fe_3O_4, (B) $Fe_3O_4@SiO_2$ particles and (C) $Fe_3O_4@SiO_2$–NH_2 [15].

Figure 6. (Left) Schematic of aqueous synthesis procedure used by Li et al. to coat thin silica shell on Au nanoparticles using sodium silicate. (Right) TEM photos of gold@SiO_2 nanoparticles. (a–d) Various pH levels are used to grow silica shells and using APTMS as surface primer. High pH of 11 and low pH of 8 conditions with 1 h. heating using sodium silicate solution were used to prepare the SHINs (a and b). (c and d) gold@SiO_2 NPs were synthesized of ~10.2 for 0.5 and 1 h, respectively, at pH 10 [16].

the authors noted that excessively high pH conditions (>11) resulted in a thin silica layer with pinholes and low conditions (pH < 8) resulted in thicker silica shells. The shell will be dissolved by sodium hydroxide interfering with the silica growth if the pH is too high, e.g. pH greater than 11. This results in holes of nano to micron sizes within the thin silica shells. The silica shell grows too fast and thickens quickly for a low pH of 8 for the sodium silicate medium (**Figure 6**). Therefore, plasmonic field enhancement from the metal surface cannot extend beyond the shell, and no signal is acquired.

Shin et al. 2015 [17] demonstrated that a single layer of self-assembled core metal particles with silica shells can produce 1~2 nm empty nano-gaps by assembling silica-gold nanoparticles (Au@SiO$_2$) and chemical etching on different substrates. Colloidal silica shell gold-core nanoparticles were prepared by adding 5% v/v (3-aminopropyl)trimethoxysilane to gold nanoparticle seed solution. The gold colloid reacted with aqueous APTMS solution under vigorous stirring for 30 min at room temperature. After mixing, sodium silicate aqueous solution was added. A 5 nm silica layer is grown by placing in 90°C hot bath for 1 h under fast stirring and allowing the solution to cool to normal temperature. By reacting for 0.5 h in hot bath, the silica layer is grown to thickness of 2.5 nm only.

3. MPTMS-assisted silica coating

Silanization methods have also been developed for surface stabilization of core nanoparticles using sodium silicate, attaching artificial resin polymers (e.g., polyvinylpyrrolidone) or substituting the depleted sodium citrate on the surface of core nanoparticle adding extra fresh sodium citrate to metal cores. After surface stabilization steps, traditional Stober method is used for thick silica coating of the core. This requires conventional silane precursors (TMOS, TEOS) to be dissolved in ethanol-water mixture, which facilitates its hydrolysis and condensation. As these hydrophobic precursors are insoluble in aqueous medium and cannot undergo hydrolysis, large amount of alchohol is used to dissolve hydrophobic silanes prior to silica condensation process. Besides using such hydrophobic silane precursors, there arises strong interest to discover water-soluble silane precursors for silica encapsulation in aqueous-based medium, which allows silica-coating process to be much simpler, cost-efficient and environmentally friendly for various applications [18].

Recently, several research groups have reported the use of 3-mercaptopropyl-trimethoxysilane (MPTMS) as a water-soluble silane precursor to synthesize thick silica shells in fully aqueous medium. Previously, Niu [19], Nakamura [20], Lee [21], Shah [22] and Shang [23] successfully silica-coated metal nanoparticles, quantum dots and iron-oxide nanoparticles using water-based MPTMS in aqueous solution under mild conditions. Using MPTMS as a water-soluble silane precursor, direct alcohol-free silica coating in water-based medium becomes possible. This straightforward, one-pot method uses MPTMS as (i) surface primer, which renders particle-surface vitrophilic, (ii) a silane-precursor, which provides a thick silica shell layer >10 nm for particle stabilzation, (iii) surface modifier, which provides Thiol SH groups and (iv) a negative surface charge for dispersibility. Furthermore, speed, thickness and uniformity

can be easily controlled through the concentration of precursor, reaction times and reaction temperatures, making aqueous routes far less complex than classic Stober method.

Niu et al. in 2010 [19] reported a facile route to fabricate homogenous, monodisperse, accurately size-tunable, SH-functionalized and magnetic silica-shell nanocomposite nanospheres (SHSSCNs) with sizes less than 100 nm. These nanocomposite nanospheres are synthesized based on the self-assembly of magnetic nanoparticles and a surface-priming copolymer polystyrene-block-poly(acrylic acid) (PS-b-PAA) in aqueous medium, followed by an easy silanization reaction with a silane precursor MPTMS to grow a silica shell on the interface of magnetite micelles at ambient temperature. (Step 1) Hydrophobic magnetite (Fe_3O_4) nanocores with a dimension of 5 nm were added to form magnetite-based micelles through their self-assembly in water with an amphiphilic block copolymer, PS-b-PAA. After filtration with deionized water, (Step 2) MPTMS was used to grow a hybrid silica layer by hydrolyzing and condensing the silane onto surface of the magnetic micelles under alkaline conditions. At the same time, SH groups were functionalised onto the surface of the nanocomposite particle in situ by using MPTMS silane as precursor, which is obviously distinct from traditional silica-encapsulation techniques reported to date. This is possible due to the fact that the core particles are encapsulated by a layer of polymeric shell, which allows the MPTMS silane to attach easily and directly onto the polymer shell's abundant surface hydroxyl groups. During the silica-encapsulation procedure, MPTMS performs as the silane precursor, thiol-functional linker and surface-capping stabilizers for the magnetite micelles and also for SH-modification of the nanoparticles in the silanization step.

Nakamura et al. in 2011 [20] used MPTMS for surface modification of quantum dots and synthesis of the silica shell to grow a layer of organosilica dense shell. MPTMS, quantum dot QD605 and NH_4OH were added and then heated for 3 h to grow the silica layer at 100°C. Extra steps like filtration or exchanging the reacting medium or adding alcohol were required. The growth of the silica shell was easily done in 3 h (**Figure 7**). The procedure is fast and easy, and the thiol groups inherent in silica shell enable easy surface bioconjugations to produce functionalised multiluminescent bioimaging markers. MPTMS and ammonia NH_4OH were mixed and then incubated to grow the silica layer. Fluorescent markers such as QD 605 and
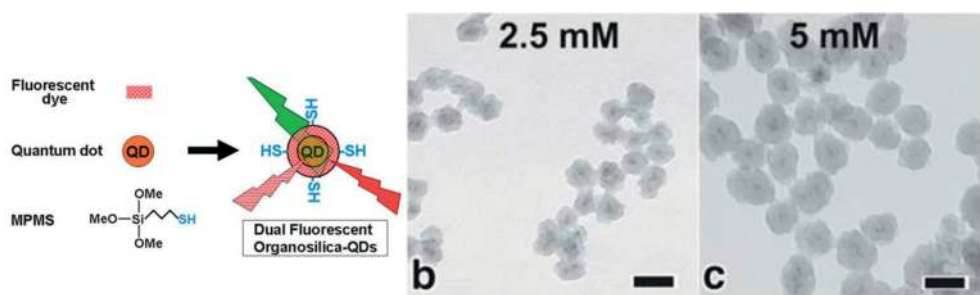

Figure 7. (Left) (a) Synthesis of dual fluorescent thiol-OS-QDs by Nakamura et al. to coat thin silica shell on Au nanorods using sodium silicate. Synthesis scheme for a single-step fabrication of double fluorescent thiol-OS-QDs. (Right) TEM images of thiol-OS-QDs with different silica shell thickness regulated by MPTMS dosage (b and c) [20].

rhodamine B were added. After reaction, the solution was centrifuged to discard unreacted contents. The aqueous silica encapsulation using Nakamura's ultra-fast technique took only 3 h, as opposed to using conventional reverse emulsion technique, which requires 1 day or using water-based sodium silicate, which requires 3 days. In addition, the presence of intrinsic thiol SH groups allows conjugation with thiol-reactive dyes or biomolecules, without the need for additional surface functionalization steps.

Lee et al. in 2011 [21] reported that for in vivo applications, such as biological imaging and medicine, nanoparticles must be safe in cell toxicity. Gold nanorods are often surface-capped and stabilized with CTAB cetyltrimethylammonium bromide, which will disrupt cell biology and cell growth as a cytotoxic surfactant. Silica coating and surface encapsulation of single nanoparticles can provide a safer substitute to surface CTAB for both decreasing cytotoxicity and improving colloidal stability. Lee synthesized silica-coated gold nanorods in aqueous medium. In his synthesis technique, Au nanorods were mixed to a solution of (3-aminopropyldimethylethoxysilane) and MPTMS for 12 h under stirring after which NH_4OH was added to form silica shell thickness < 2 nm. The authors found that the amount of amino-silane affected the growth of silica layer surrounding gold-NRs (**Figure 8**).

Shah et al. in 2014 [22] reported a novel direct silica coating in water-based silica-coating routes, which is alcohol-free one-step method using "pre-hydrolysed" MPTMS making silica coating far less complex than classic Stober method. This technique presents a facile, scalable, environmentally friendly process for thick coating of metal particles with a thick (5–30 nm) silica shell. The success of the process is using "pre-hydrolysed" MPTMS as silane precursor. Silica coating could be directly attributed to the strong and direct metal-thiol bond. Briefly, metal nanoparticles were washed and re-dispersed in deionized water before being combined into a pre-hydrolysed MPTMS in DI water. Ammonia was added as catalyst. While growth was easily scalable, the growth rate of the silica shell is controllable to 25, 11.7 and 10 nm/h. during condensation. The process slows down owing to eventual consumption of hydrolysed MPTMS. Different metal NPs (i.e., gold, silver, platinum) are successfully encapsulated with a silica layer under a completely alcohol-free environment, whose shell thickness can be easily and precisely synthesized by changing the growth duration (**Figure 9**). This novel water-based procedure is used for the fabrication of SERS-enhanced silver@SiO_2 nanoparticles without the
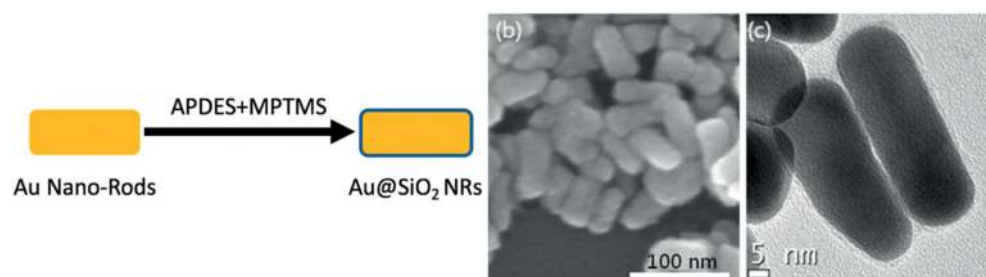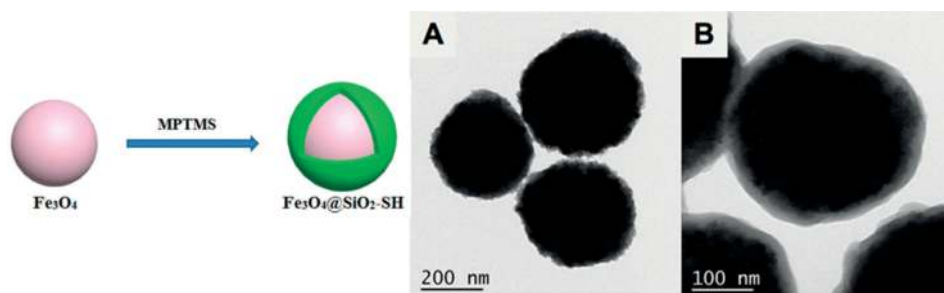

Figure 8. (Left) (a) Schematic of aqueous synthesis procedure used by Lee et al. to coat thin silica shell on Au nanorods using sodium silicate. (Right) Images of AuNRs sized 50 nm, (b) SEM image of core-shell Au nanorods and (c) TEM image of silica shell (<2 nm) AuNRs [21].

fluorescence background, which is used for bioimaging as SERS markers. The facile silica-encapsulation procedure developed here presents a highly potential encapsulating method and protection for the metallic core nanoparticles. The resulting highly negatively charged and SERS-enhanced metal@SiO$_2$ nanoparticles with thiol-functionalised surfaces hold great potential for biomedical applications. Such as fluorescence-free SERS-enhanced nanoparticles are useful for ultrasensitive bioimaging and biodetection applications.

Shang et al. in 2016 [23] synthesized iron oxide Fe$_3$O$_4$ nanoparticles coated with 10–20 nm thick silica shells using the same method reported by Shah et al. [22] after reacting for 2 h at room temperature with constant stirring (**Figure 10**). Hydrolysed MPTMS is formed by adding MPTM into deionized water and stirred [22]. Thereafter, Fe$_3$O$_4$ spheres were added into pre-hydrolysed MPTMS solution followed by adding ammonium hydroxide. Fe$_3$O$_4$@SiO$_2$-SH spheres (0.1 g) were dispersed in H$_2$O$_2$, in order to oxidize SH groups to SO$_3$H groups to form Fe$_3$O$_4$@SiO$_2$-SO$_3$H sulfonic acid-functionalised spheres. When Fe$_3$O$_4$@SiO$_2$ spheres and PdCl$_2$ solution were added, Pd^{2+} ions could be surface immobilized onto the surface of silica shell via coordination interaction between SO$_3$H groups and Pd^{2+} ions. Pd^{2+} ions immobilized on the
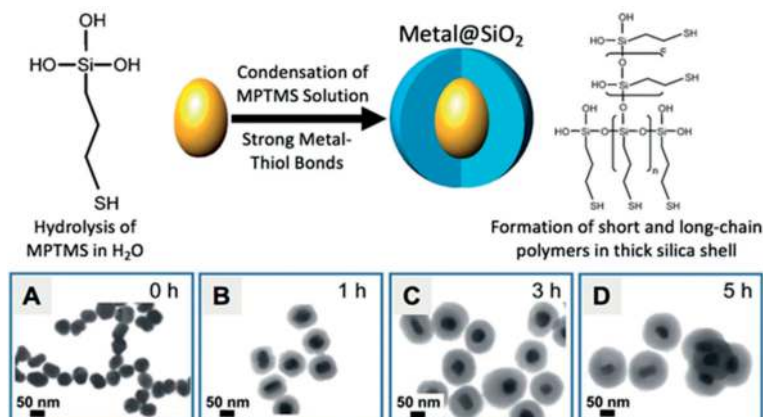
Figure 9. (Top row) Schematic of aqueous synthesis procedure used by Shah et al. to coat thin silica shell on Ag nanospheres using MPTMS. (Bottom row) Ag@SiO$_2$ (A) and Ag@SiO$_2$ after coating for (B) 1 h, (C) 3 h and (D) 5 h [22].


Figure 10. (Left) Schematic of aqueous synthesis procedure used by Shang et al. to coat thin silica shell on Ag nanospheres using MPTMS. (Right) (A, B) TEM micrographs of resulting Fe$_3$O$_4$@SiO$_2$-SH spheres [23].

surface of Fe_3O_4@SiO_2 particles oxidized the pyrrole monomer to give PPy-Pd layer surrounding Fe_3O_4@SiO_2-SO_3H spheres. The nanocomposite Fe_3O_4@SiO_2-SO_3H@PPy-Pd nanoparticles reduced 4-nitrophenol and undergo Suzuki coupling reactions as a nanocatalyst.

4. MPTES-assisted silica coating

Cui et al. in 2011 [24] proposed that highly stable Au@SiO_2 nanoparticles with functional groups were easily fabricated by pre-hydrolysis of MPTES in a water together with gold nanoparticles. In the preparation of organosilica shell, heterofunctional poly(ethyleneglycol) (SH-PEG-COOH) solution was added into solution containing Au nanoparticles and then MPTES is added. The solubility of MPTES in the aqueous solution is very low and tends to form an emulsion. NH_4OH was then added to adjust the solution pH to 8.5–9. The synthesis performed under static conditions for 48 h without stirring or shaking is the unique advantage of simplicity of the present method. The size of organosilica outer layer can be easily tuned by controlling the MPTES added. Steric hindrance caused by SH-PEG-COOH polymers, which are formed on gold surface, can inhibit gold particles aggregation, and therefore, polymer brushes perform a critical role in core-shell nanoparticles. Without any SH-PEG-COOH steric hindrance, gold particles will agglomerate and nucleate from the mixture even in MPTES solution. Au@SiO_2 particles appear to be rounded in shape and singular in nature. Every particle is sized about 55 nm and has a single gold core. The silica layer is about 15–75 nm in thickness (**Figure 11**). The silica thickness could be simply tuned by the concentration of MPTES. The surface charge of these Au@SiO_2 core-shell particles was measured to have 51.7 mV in zeta potential. Conventional Au@SiO_2 core-shell particles are measured to have 38 mV in zeta potential. These zeta measurements confirm the improved stability of the Au@SiO_2 nanoparticles upon organosilica shell coating.

Gao et al. in 2015 [25] synthesized multifunctional gold nanostars through the direct silica coating in aqueous solution using "pre-hydrolyzed" MPTES. Organosilica shells are synthesized by first hydrolyzing 3-mercaptopropyltriethoxysilane (MPTES) as silane precursor in water. Due to the large amount of SH groups provided by MPTES, the tedious step of surface modification is avoided, and the synthesis technique is easily controlled and simple. Gao reported this simple synthesis of highly functional anisotropic Au nanostars via directly coating silica on the surface
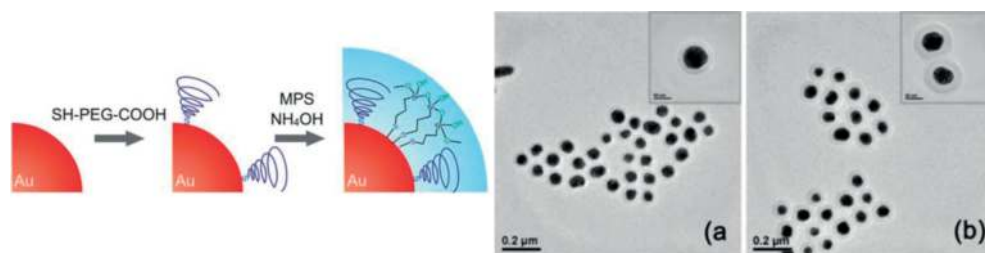
Figure 11. (Left) Proposed growth mechanism of Au@organosilica nanoparticles by Cui et al. using MPTES in water medium. (Right) TEM images of gold@silica core-shells with the 55 nm gold particles and varying silica thicknesses: (a = 15 and b = 20 nm) [24].
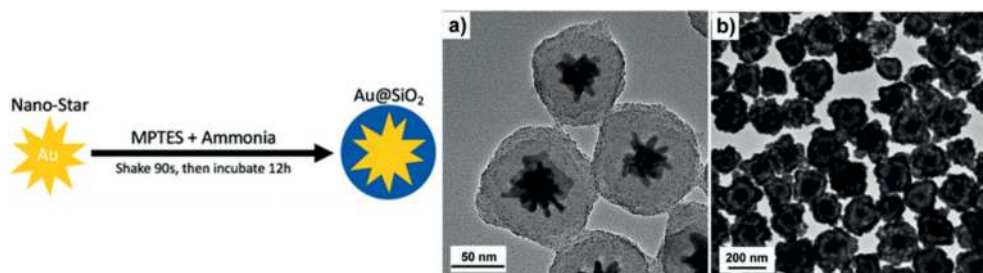
Figure 12. (Left) Illustration of the design of gold nanostars@SiO$_2$ coated using MPTES in water medium by Gao et al. (Right) TEM images of synthesized gold nanostars@SiO$_2$ (a) Scalebar 50 nm (b) Scalebar 200 nm [25].

of nano-sized star-shaped gold cores and subsequently immobilization of gadolinium chelates. Highly dispersed and uniformly sized Au-Gd nanostars@SiO$_2$ absorb strongly within the NIR spectrum and give out strong SERS waves which can strengthen magnetic resonance imaging. More silica coating was grown by adding MPTES and NH$_4$OH to the water-nanostars mixture and stirring for 1–2 min. The suspension was left for half a day to produce star-shaped Au@Silica. Obviously, 60 nm Au@SiO$_2$ nanostars and 20 nm silica shell, which are highly homogenous, are seen under TEM imaging (**Figure 12**). In addition, using this one-step procedure, in situ surface immobilization of SH groups onto Au@SiO$_2$ nanostars on the outer surface can be easily done for subsequent bioconjugation. This nanocomposite with distinct core-shell structure preserves the star shape and as a result gives efficient conversion from photo to thermal effect. The silica outer coating could prevent Raman markers from detachment loss. This ensures that Au nanostars@SiO$_2$ has greater Raman signals strength and sensing ability. A facile way via aqueous-coating silica directly on Au star-shaped cores to fabricate functional nanoparticles for applications in bioimaging and detection of cancer supports future research in silica-coated nanostructures for cancer therapy and diagnosis applications.

5. MTMS-assisted silica coating

Core-shell nano/microcapsule is a fast expanding area of research because of their wide applications, such as effective storage, controlled release and strong adsorption. Batch production of oil-loaded nano/microcapsules favors facile one-step fabrication methods.

Fei et al. in 2006 [26] synthesized monodisperse functionalised silica microcapsules using a one-pot procedure at room temperature. Silica encapsulation of oil microdroplet is reported. This is done without using any mediating agent or surfactant. Fei synthesized silica nano/microcapsules using self-silanization reaction at water-oil interface. N,N-diethyl-m-toluamide (DEET, Aldrich) was chosen as PCM to be silica-encapsulated. A water-oil solution of methyltrimethoxysilane (MTMS) and DEET was mixed into water and 3-aminopropyltrimethoxysilane (APTMS) and sonicated to get a white dispersion. When MTMS and APTMS are mixed, sol-gel reaction takes place and the solution reacts to give white-colored suspension. Adding MTMS or APTMS alone into water, there is no whitening or sol-gel reactions to be observed. Ottenbrite et al. [27] reported similar sol-gel effect. Monodisperse spheres are about 900 nm in diameter. The spheres had sizes

of 900 nm and shell layer of 70 nm thick (**Figure 13**). During the hydrolysis and sol-gel reactions between MTMS and APTMS, MTMS diffused from micro-droplet to the oil surface. Microparticle size and shell dimensions can be easily adjusted by tuning the precursors dosage and concentrations, subjected to oil loading and sphere hardness requirements. In summary, silica-coated nanospheres were synthesized in a facile way [26]. In this one-step sol-gel technique, no use of intermediate agents or surfactant were required.

Jin et al. in 2010 [28] presented a one-step "sol-gel" method for the formation of silica-coated core-shell microcapsules of phase change materials (PCM) in aqueous medium without using surfactants or dispersants. The main issues associated with the use of polymeric shell materials for encapsulating core PCM materials are their low thermal conductivity and undesirable residues such as formaldehyde. Silica shell material has a much higher thermal conductivity and chemical stability than the polymeric materials. There have been many reports on the use of silica as the shell material of microcapsules or nanocapsules for controlled release and targeted drug delivery, and protecting active agents. Various methods have been proposed for making silica-shelled PCM microcapsules, including Pickering stabilization, water/oil/water emulsion templating using sodium silicate as the precursor, water/oil or oil/water emulsion templating using tetraethylorthosilicate (TEOS) as the precursor under acidic or basic conditions and hydrolysis-condensation reactions using tetraethylorthosilicate (TEOS) as the silica precursor with surfactants. Jin silica-coated nonadecane using methyltrimethoxysilane (MTMS) and 3-aminopropyl trimethoxysilane (APTMS) as silica precursors without any surfactants in an aqueous solution of distilled water. The synthesis was done under magnetic stirring to produce clear spherical, core-shell microparticles. A clear core-shell microstructure of few microns and a shell thickness about 500 nm (**Figure 14**). Positively charged amine groups of the APTMS suggest that MTMS in the oil phase diffuses to the oil-water interface where it reacts with the APTMS in the water phase to form a silica shell around the oil droplet. This effect was also observed by Ottenbrite [27] in their synthesis of organosilica nanoparticles, using aminopropyltriethoxysilane as the silica precursor. Jin found that increasing the volume of APTMS in water above 2% results in gelling, and no microcapsules were formed.
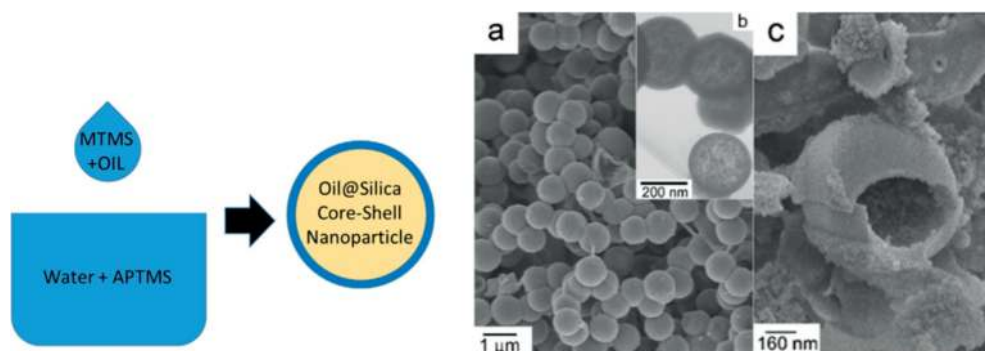
Figure 13. (Left) Illustration of the design of gold nanostars@SiO$_2$ coated using MPTES in water medium by Fei et al. SEM images of monodisperse organosilica nanocapsules of 900 nm diameter and 70 nm thick. (Right) SEM images of organosilica nanocapsules containing DEET about 300 nm diameter and 30 nm thickness (a) Scalebar 1 μm, (b) TEM image, and (c) Scalebar 160 nm [26].

Figure 14. (Left) Illustration of the design of silica-coated nonadecane using MTMS in water medium by Jin et al. (Right) SEM images of PCM microencapsulated spherical capsules: (a) an intact microcapsule and (b) a broken microcapsule of core-shell microstructure [28].

6. Conclusion

In this chapter, we summarize up-to-date the four major water-based silica-coating strategies for a variety of core nanomaterials. Currently, there are four successful water-based routes using different water-soluble silane precursors, namely sodium silicate, MPTMS, MPTES and MTMS. We reviewed these techniques in aqueous condition and their final core-shell morphologies. Their effective silica encapsulation leads to improved colloidal properties and creates new emerging materials based on silica-coated core-shell nanostructures. In particular, these simple large-scale aqueous synthesis techniques for silica-coated nanoparticles and their morphologies are important for paving new and practical applications. Four major water-based routes for silica-coating core-shell nanostructures are analyzed and their findings relating to sodium silicate, MPTMS, MPTES and MTMS are summarized below:

1. Sodium silicate as a precursor and its resultant shells are highly dependent on pH conditions and coating process requires a long period of time, lasting a few days.

2. Sodium silicate precursor is suitable for very thin silica-shell coatings (<2 nm), whose resultant silica-shell surface is often uneven, irregular and inhomogeneous.

3. Sodium silicate can be precipitated into silica-shell coatings under fully aqueous conditions (thin coat <6 nm), as well as under ethanol-water conditions (thick coating >10 nm).

4. Sodium silicate provide only –OH groups, which may demand extra functionalisation step to provide additional groups, such as –SH, –NH$_2$, –CHO, –COOH for conjugation.

5. MPTMS and MPTES precursors are effective in silica-coating metallic and semiconductor nanomaterials of different morphologies (nanospheres, nanorods, nanostars)

6. "Pre-hydrolysis" of MPTMS and MPTES is an essential step to successful silica coating.

7. MPTMS and MPTES precursors produce silica-coated core-shell nanomaterials that are highly monodispersed, spherical and uniform with smooth outer surfaces. Thickness can be easily controlled and thick dense shell can be coated within a few hours.

8. MPTMS and MPTES precursors provide intrinsic thiol –SH and silanol –OH functional groups, without any need for extra step of surface modifications.

9. MPTMS and MPTES are proven effective for metals and semiconductors-based core-materials.

10. MTMS is proven effective in silica encapsulation of oil-based nano/microstructures.

11. MTMS is used in tandem with APTMS as a catalyst under oil/water emulsion.

This chapter reviewed a series of potentially reliable and reproducible synthesis techniques for high-quality silica-encapsulated core-shell nanomaterials. We compared and provided insights into the development of four water-based techniques to fabricate novel silica-encapsulated nanocomposites with unique core-shell architecture. These synthesis routes take place under mild reaction conditions, at ambient temperature and pressure, which are potentially applicable for large-scale production. The facile synthesis of silica shell under aqueous environment allows greater repeatability, facile steps for silanization, as compared with alcohol-based conventional Stober methods. They possess great potential to upscale batch production and present a biocompatible system that can be utilized for biomedical applications. The universality of these techniques were experimentally proven and demonstrated using a wide variety of core materials including Ag, Au, Pt, Fe_2O_3, CdTe, Gd, PCM, DEET and many others. In future, we hope to update the scientific community with more up-to-date research studies on the development of similar useful techniques for a simple one-pot aqueous synthesis of silica-encapsulated core-shell nanomaterials.

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