



Review paper

Recent progress on synthesis of ceramics core/shell nanostructures

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Abstract

Thin surface layers on fine particles were found to substantially change their functionalities and properties, such as chemical reactivity, thermal stability, catalytic activity, dispersibility, or optical, magnetic and electronic properties. Because of that, the core/shell nanostructures have opened up research opportunities in almost all areas of science and engineering, including medicine, catalysis, biotechnology, chemistry, optics, electronics, energy storage, etc. Immense efforts have been implied to produce and investigate different core/shell systems, and thereby, various synthesis techniques have been developed. In this review, we report a detailed overview of different synthesis techniques used for preparation of various ceramics core/shell nanostructures with tunable size and tailored structure.

Keywords: ceramics, nanostructures, core/shell particles, synthesis, review

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I. Nanotechnology: Core/shell nanostructures

With the development of nanotechnology and nanostructured materials, one of the primary research goals became to reach advanced properties and multifunc-

tionality, in order to achieve better performances and novel applications. Naturally, this has led to the discoveries of novel materials, but also brought the research attention to many other potential methods for combining two or more properties in one material.

Thin surface layers on fine particles were found to substantially change their functionalities and properties,

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such as chemical reactivity, thermal stability, catalytic activity, dispersibility, or optical, magnetic and electronic properties. These heterostructures were first realized in the late 1980s, with semiconductor nanoparticles [1–3], where they contributed to carrier confinement or separation, depending on the band gap alignment of the two semiconductor materials with different energy gaps. Since that the terminology “core/shell” was well accepted by researchers [4,5] and their use was extended to different areas of science and technology.

Up to now, concept of core/shell nanostructures has received a lot of research attention, bringing variety of solutions and systems with advanced properties. Even though the motive for the investigation of various core/shell nanosystems is different, this research field can be roughly classified into three perspectives.

Most of the core/shell nanostructures are developed with the idea *to combine two materials - and thus two properties within one structure*. In this way, the nanostructure itself is characterized with the properties of both core and shell, offering variety of new possibilities and uncountable combinations. For example, iron oxide nanoparticles covered with silica layer show magnetic properties arising from the core and luminescent optical properties arising from the shell [6]. In addition, magnetic core particles are often covered with a shell that is providing biocompatibility and chemical stability, in order to be used for biomedical applications [7,8]. Core/shell nanostructures, which are composed of one component that can attach antibodies and enzymes and the other that absorb light, can be used in therapeutic application for targeted drug delivery [9–11]. Often, shell is used to alter the surface charge and reactivity, or to provide good thermal stability of particles. Ultrafine metallic particles coated with shell materials that provide good colloid stability, and in the same time can be chemically inert and optically transparent, are often used as paints, magnetic fluids, paper coatings, etc. [12]. In the fields of structural materials, core/shell particles have been used as reinforcements and tougheners in composites due to complicated interactions between the particle surface and the matrix and the need for good bond between the reinforcement and the matrix [13,14].

In some cases, the benefit of core/shell nanostructure is arising from their *specific design and geometry*. The specific design of core/shell structure is used for lowering the costs, with the idea to use the inexpensive material as a carrier for a thin shell of active material [15]. A typical example are the core/shell pigments containing a core of cheap oxides covered with a layer of phosphates, which are produced as a more economically feasible solution for anticorrosive pigments than the traditional ones [16]. Often, different shell thickness is used to tune the selected property of particles. Thus, by changing the thickness of gold shell on sili-

ca particles, one can tune the absorption band from visible to infrared region and move the surface plasmon resonance band position to the desirable wavelength range [17]. Similar idea was utilized for the preparation of core/shell nanoparticles which exhibited the quantum confinement effect or novel electronic, magnetic and optical properties. For example, multifunctional core/shell nanoparticles consisting of gold cores covered with two shells - dense silica and CdSe quantum dots (CdSe-QD) - allow for versatile control of CdSe-QD and Au-metal interactions through the control of the size of Au nanoparticles and the thickness of the dielectric silica layer [18]. The factor of geometry is also broadly used in catalysis, where catalysts are covered with mesoporous shells and catalytic reaction rates can be tuned by adjusting the crystallinity and porosity of the outer shell.

In another group of core/shell systems we can classify those in which the particular combination and specific coupling of core and shell material *results in an entirely new property*, that none of the materials individually possesses. Nanostructures with ferromagnetic core and ferroelectric shell, for example, are extensively investigated over the last few years, since it was discovered that they are the ideal building block material for composite ceramics in which a new property: magnetoelectric effect, arises from strain mediated interaction between core and shell phases. In some other cases, the specific core/shell system is characterized with a property intermediate between those of both materials individually, like in the case of core/shell semiconducting nanocrystals, or bimagnetic core/shell systems, where intimate contact between core and shell produces an effective exchange coupling and offers the possibility to tune the magnetic properties for electromagnetic and permanent magnetic applications [19]. Recently, several types of core/shell structured electrode materials for lithium ion batteries are found to increase the diffusion coefficient of lithium ions and improve the reversibility of lithium intercalation and deintercalation [20].

Until today, core/shell structures have opened up research opportunities in almost all areas of science and engineering, including medicine, catalysis, biotechnology, chemistry, optics, electronics, energy storage, etc. Consequently, a large number of methods for synthesis core/shell particles have been developed and improved. Moreover, with the progress of nanotechnology, very advanced core/shell architectures with multishell layers and a quite complex structure, such are some architectures used in drug delivery and cancer therapy [21], have been developed and investigated.

In this review paper, we report a detailed overview of different synthesis techniques used for preparation of various ceramics core-shell nanostructures with tunable size and tailored structure.

II. Type of core/shell nanostructures

Core/shell particles are typically spherical in shape, but there are many more possible types of core/shell nanostructures based on the different core shapes, such as: nanotubes, nanowires, nanorods, nanorings and nanostars (see review articles 22–27). As can be seen in Fig. 1 various spherical core/shell nanostructures can be distinguished. Thus, core/shell particles can have dense, porous or eccentric cores and when the core material is completely removed from the structure either by calcination or dissolving with suitable solvent hollow nanostructures can be formed (Fig. 1a). Similarly, there are different types of shells: continuous and dense shells, continuous and porous/particulate shells or discontinuous/particulate shell (Fig. 1b). In addition, more complex nanostructures have been prepared and include: core/bilayered-shell, core/composite-shell or core/multilayered-shell nanoparticles (Fig. 1c).

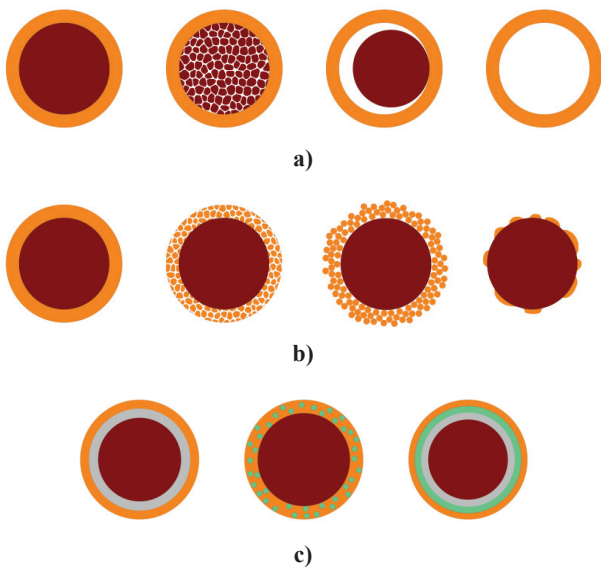


Figure 1. Schematic illustration of core/shell particles with different type of: a) cores, b) shells and c) core/shell particles with complex nanostructures

III. Synthesis of core/shell nanostructures

Various synthesis techniques have been developed for the synthesis of core/shell particles with controlled composition, type, morphology, shell thickness, core size and size distribution. Generally, they can be divided into: *gas phase processes* and *liquid phase techniques*.

3.1 Gas-phase processes

Synthesis of core/shell nanostructures in gas phase processes is mostly based on reaction/decomposition of flowing gases or volatile precursors, but some other methods, such as surface oxidation and flame synthesis, have also been developed. In all these techniques basic knowledge in gas-dynamics and gas-kinetics has been

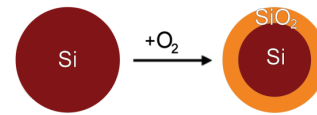


Figure 2. Schematic illustration of surface oxidation of silicon nanoparticle

utilized to obtain core/shell particles with a controllable composition and morphology, good adhesion of the shell, complete coverage of the core surface and desirable shell thickness.

3.1.1 Surface oxidation

Core/shell nanostructures can be simply synthesized by surface oxidation of core particles (Fig. 2). Thus, if silicon nanoparticles (or non-oxides, such as SiC, Si₃N₄ etc.) are exposed to oxygen, under the specific conditions, the exothermic surface reaction will cause the formation of a thin SiO₂ shell with the thickness dependent on the selected processing conditions (size of silicon particles, temperature, oxygen partial pressure, reaction time etc.).

3.1.2 Flame synthesis

Core/shell nanostructures can also be prepared in low-pressure flame reactor. The method was developed by Jana *et al.* [28] and is based on addition of precursors/Ar mixture in low-pressure premixed H₂/O₂/Ar flames and subsequent formation of corresponding oxide core/shell nanoparticles. The appropriate selection of precursors is the most important for successful fabrication of core/shell particles and the reaction rate coefficient of the shell precursor must be larger compared to the precursor of the core. Thus, γ -Fe₂O₃ particles, with a diameter of a few nanometers, having a thin SiO₂ shell were synthesized from organometallic precursors iron-pentacarbonyl (Fe(CO)₅) and tetramethylsilane (Si(CH₃)₄). An axially movable, cooled sintered bronze plate burner was located on one end of a low-pressure reaction chamber. The precursors/Ar mixture was introduced in the burner and decomposed in H₂/O₂/Ar flames. In the reaction zone at the pressure of ~ 40 mbar precursors react with oxygen and the γ -Fe₂O₃/SiO₂ nanoparticles were formed. The obtained core/shell particles can be separated from the gas stream by different methods, such as thermophoresis, filtration, molecular beam probing, etc.

3.1.3 Synthesis based on reaction/decomposition of flowing gases

Different type of core/shell particles have been prepared by reaction/decomposition of flowing gases or volatile metalorganic precursors in a reactor consisting of two reaction zones or two sequential reactors. Thus, Powell *et al.* [29] fabricated TiO₂-core/SiO₂-shell particles via gas phase in a tubular, hot-wall, flow reactor. Titania particles were produced in the first part of the reactor, via the vapour phase reaction of TiCl₄

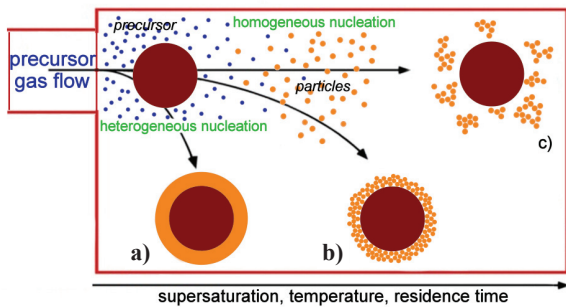


Figure 3. Different mechanisms of shell formation:
 a) chemical vapor deposition b) assembly of preformed nanoparticles and c) formation of separate silica aggregates

and oxygen. The gaseous reactant SiCl_4 was injected into the reactor at a point after the region in which titania particles were formed. There the SiCl_4 vapour reacted with oxygen in the presence of the titania particles to form silica shell. Silica shell can be formed by several mechanisms (Fig. 3) [29,30]. If temperature and supersaturation are high enough, SiCl_4 can react with oxygen and form silica nanoparticles by homogeneous nucleation. The formed nanoparticles can reach the titania particle surface, attach themselves to it and form a shell. Alternatively, the silica can grow to form separate silica particles (Fig. 3). However, at lower temperature and supersaturation, SiCl_4 can react with oxygen on the titania particle surfaces, nucleate heterogeneously and form a shell by chemical vapour deposition (Fig. 3).

Vollath and Szabo [31,32] reported on the synthesis of different core/shell nanostructures based on Al_2O_3 and ZrO_2 by two sequential microwave plasma reactors. Chloride precursor of the core phase was decomposed and oxidized in the first reactor, and the formed oxide-core particles were transported with gas flow in the second reactor. The second chloride reactant was injected into the second reactor and after the surface reaction the corresponding oxide shell was deposited on the core particles. When the alumina cores are small, or alternatively when the alumina shells are thin, amorphous alumina and crystalline zirconia structures were obtained. Otherwise, core/shell particles consisting of a crystalline zirconia core and a γ -alumina shell were formed. In addition, maghemite ($\gamma\text{-Fe}_2\text{O}_3$) particles coated with cubic zirconia were also successfully fabricated using two sequential microwave plasma reactors [32].

Srdić *et al.* [33] synthesized nanocrystalline zirconia surface doped with 3 and 30 mol% alumina (with the size of ~ 5 nm) by chemical vapour synthesis using two sequential hot-wall reactors (i.e. two serial reaction zones consisting of two alumina tubes heated separately by two resistance furnaces, Fig. 4). In the first reactor, zirconia precursor molecules are decomposed and react with oxygen forming zirconium oxide nanoparticles.

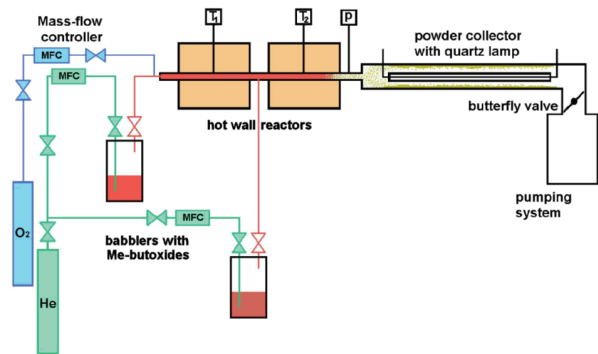


Figure 4. Schematic illustration of the CVS system used for the synthesis of core/shell nanoparticles

The ZrO_2 particles were used as seeds (substrates with a very large surface-to-volume ratio) for heterogeneous growth of alumina in the chemical vapour deposition mode in the second reactor. The obtained powders had the characteristic core/shell structure with ZrO_2 core and a very thin, amorphous shell consisting of zirconia highly doped with alumina [33]. The same method, but with some modifications, was used for the preparation of polymer-coated alumina nanopowders [34].

3.1.4 Spray pyrolysis

Different core/shell nanostructures can also be fabricated by a spray pyrolysis process. The process is similar to those mentioned above, however, instead of flowing gases there are flowing aerosols (mixture of very fine precursor droplets with the carrier gas). Synthesis of core/shell particles by spray pyrolysis process is based on solvent evaporation from droplets, formation of particles by reaction or precipitation and their subsequent coating usually in a reactor consisting of two reaction zones or two sequential reactors.

Rössel and co-workers [35] used a two-step spray pyrolysis method for the preparation of TiO_2 -core/ BaCO_3 -shell structures. During the first step, an aqueous $\text{Ba}(\text{OH})_2$ solution containing TiO_2 particles was dispersed in small droplets and by spray drying (using argon as an inert gas) transformed in TiO_2 -core/ $\text{Ba}(\text{OH})_2$ -shell structure (Fig. 5). During the second step the $\text{Ba}(\text{OH})_2$ layer was carbonated to BaCO_3 by reaction with a $\text{CO}_2/\text{H}_2\text{O}$ stream.

Chung *et al.* [36] used a continuous multi-step spray pyrolysis process for the preparation of NiFe_2O_4 -core/ TiO_2 -shell particles. Aqueous solution of iron chloride and nickel acetate tetrahydrate was atomized by an ultrasonic nebulizer and moved by air into the first reactor. NiFe_2O_4 particles, precipitated within the droplet in the first reactor, were moved by the carrier gas into the second reactor heated to 700°C , where titanium isopropoxide, $\text{Ti}(\text{OC}_3\text{H}_7)_4$, was injected by a syringe pump. The injected $\text{Ti}(\text{OC}_3\text{H}_7)_4$ was evaporated by a pre-heated N_2 carrier gas. The thickness of the titania layer was controlled by the amount of injected $\text{Ti}(\text{OC}_3\text{H}_7)_4$. Due to the specific requirement (prevention of the photo-

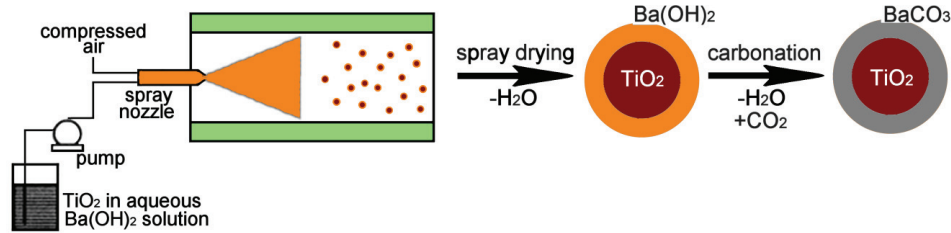


Figure 5. Scheme for the preparation of TiO_2 -core/ BaCO_3 -shell structures by spray pyrolysis

dissolution phenomenon) another layer had to be deposited between the NiFe_2O_4 core and the titania layer, as a passivation layer. It was shown that spray pyrolysis can be easily adjusted for the production of such bilayered core/shell nanostructures simply by adding a $\text{Si}(\text{OC}_2\text{H}_5)_4$ (tetraethoxysilane, TEOS) injection port between the two reactors [36]. Dehumidified N_2 gas was also used as a carrier gas for TEOS.

Spray pyrolysis was used by Stopic *et al.* [37] for the synthesis of spherical TiO_2 - RuO_2 core/shell particles. Aerosol, obtained by ultrasonical treatment of Ti-based precursor, was entered into the first reactor zone and after solvent evaporation and precipitation within the droplets TiO_2 particles were formed. Titania particles, formed in the first reactor zone, were moved by the carrier gas into the second reactor. Then, RuCl_3 solution was ultrasonicated and, in second pyrolysis zone, mixed with the aerosol containing the formed TiO_2 particles. Nearly perfect core/shell particles were formed.

3.2 Liquid-phase techniques

In addition to the core/shell nanostructures produced from the gas phase, they have been synthesized by various liquid phase methods as well. Generally, they can be divided in four main groups:

- chemical deposition on core-particles,
- chemical deposition on functionalized core-particles,
- assembly of preformed nanoparticles by electrostatic interactions,
- assembly of preformed nanoparticles onto functionalized core-particles,

3.2.1 Chemical deposition on core-particles

Chemical deposition (also called deposition-precipitation) method is an attractive route for direct formation of an amorphous or crystalline layer on core-particles from corresponding salt. In this case, surface of the core-particles is used for heterogeneous nucleation

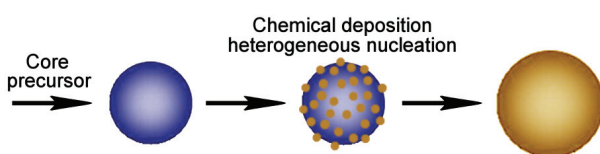


Figure 6. Schematic illustration of the shell formation by chemical deposition method

of solid shell phase (Fig. 6). Similar to the gas phase synthesis, whether a precursor will react and form particles in the surrounding liquid phase by homogeneous nucleation (which will then be attracted to the core-particles, see chapter 3.2.3) or directly react on the core-particle surfaces by chemical deposition depends on the processing conditions.

Considerable research work has been directed to the synthesis and application of ferrite nanoparticles with silica shell, which will be in this review used as a model system to elucidate the mechanisms of shell formation by chemical deposition method and describe the influence of processing parameters on shell thickness and uniformity. However, some other interesting core/shell systems will also be mentioned.

Mechanisms of shell formation

Many researchers used chemical deposition for the synthesis of spherical ferrite-core/silica-shell nanocomposite particles with very narrow size distribution and tunable shell thickness. The method is based on the well-known Stöber process [38], in which silica shell is formed around a core-particle via the hydrolysis and condensation of a silica precursor.

The ferrite core-nanoparticles with narrow size distribution and different compositions can be prepared by various methods, such as precipitation from solutions, microemulsion, aerosol-vapor methods, spray pyrolysis, laser pyrolysis, hydrothermal methods, high-temperature decomposition of organic precursors etc. However, the main problem regarding to the synthesis of core/shell particles is hard agglomeration of the ferrite nanoparticles due to their large surface to volume ratio and high surface energies [39]. This can be solved with stabilization and surface modification of the as-synthesized ferrite nanoparticles usually by citric acid. Citric acid creates a negative particle charge in the whole pH range, shifts the zeta potential towards more negative values and allows increasing organosilane affinity for the particle surface [39–41]. In the next step, the ferrite nanoparticles surface, coupled with $-\text{OH}$, or $-\text{C}-\text{OH}$ groups, are used for the chemical deposition of silica layer. The mechanism of the silica shell formation on the surface of the ferrite nanoparticles is depicted in Fig. 7 [42]. If TEOS is used as a precursor for shell formation, at first, sili-

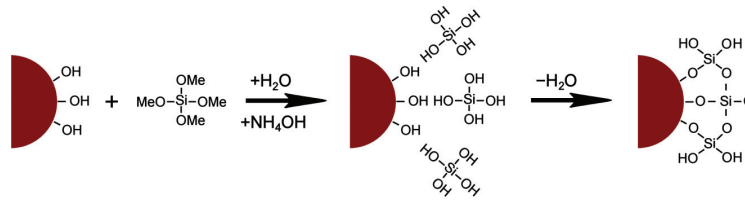


Figure 7. Mechanism of silica shell formation

cate groups will attach to the $-OH$ groups on the surface of the ferrite particles. After this first silica layer is formed, additional layers can be obtained by direct hydrolysis and condensation of TEOS on the surface of the existing silica layer.

Shell thickness and uniformity control

The control of the shell thickness has always been an important task during the synthesis of the core/shell nanostructures by the chemical deposition method. Thus, influence of processing parameters on the shell thickness and uniformity is well demonstrated by Maurice and co-workers [40], who prepared maghemite-core/silica-shell nanoparticles from citrate-modified $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles and TEOS. The silica shell was formed by the hetero-condensation of TEOS in a mixture of ethanol and water in presence of a small amount of ammonia as a catalyst [40,43]. It was shown that the shell thickness can be well-controlled by changing the concentration of ammonia and/or TEOS. Thus, for a given TEOS and ferrite-nanoparticles concentration, a low concentration of ammonia led to the formation of a non-uniform shell around the particles, but a larger amount of ammonia led to the formation of maghemite free silica particles as a result of rapid hydrolysis of TEOS (Fig. 8a). On the other side, for an optimized ammonia concentration and a given ferrite-nanoparticles concentration, there is a minimal concentration of TEOS necessary to ensure a complete covering of particles, and above it the thickness of the shell can be tuned with the TEOS concentration (Fig. 8b) [40].

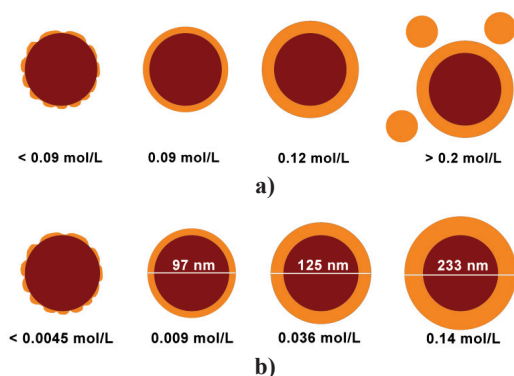


Figure 8. Illustration how ammonia (a) and TEOS (b) concentration have influence on silica shell thickness

Similarly like in ferrite/silica systems, the controlled deposition of silica on $(\text{Ba,Sr})\text{TiO}_3$ particles, having surface modified by citric acid, was based on a seeded growth process and the hydrolysis/condensation of TEOS catalyzed by ammonia in highly diluted ethanol solution [44,45]. Such procedure can lead to the deposition of uniform and homogeneous silica shell, avoiding the formation of silica nuclei. In addition, the selected method allowed the control of the silica shell from 2 to 80 nm (with an accuracy of 1–2 nm) only by changing the amount of TEOS used in the reaction (Fig. 9).

However, the chemical deposition processes are sometimes related to the formation of thin, even monolayer, shell structures and thicker shell can be obtained only by modified methods. One of the elegant ways is to use the multistep deposition process also called layer-by-layer deposition, which was applied for the fabrication of BaTiO_3 -core/ Al_2O_3 -shell and ZrO_2 -core/ Al_2O_3 -shell particles [46,47]. The core (BaTiO_3 or ZrO_2) nanoparticles, dried to remove any surface-bound water, were dispersed in dry toluene

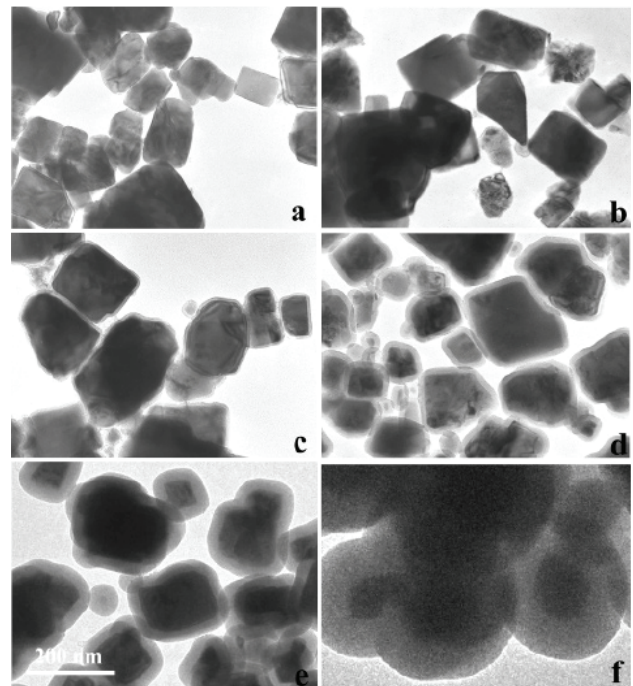


Figure 9. TEM images of $(\text{Ba,Sr})\text{TiO}_3$ nanoparticles with different thickness of silica shell: a) 0, b) 2, c) 7, d) 13, e) 25 and f) 80 nm (bar = 200 nm) [45]. Reprinted with permission from S. Mornet et al., *Chem. Mater.*, 17 (2005) 4530–6. Copyright 2005 American Chemical Society.

and mixed with methylalumoxane (MAO). Methylalumoxane was anchored to the surface of the nanoparticles by covalent Al–O bonds formed in the mutual reaction. After washing off excess MAO and exposure to air, the MAO on the nanoparticles surface rapidly oxidizes/hydrolyzes to form a shell of Al_2O_3 . This step is applied multiple times to incrementally increase the Al_2O_3 shell thickness [47].

Shell formation on hydrophobic core-particles

All methods for the preparation of core/shell particles based on the Stöber process are easily adjusted for hydrophilic core-particles. However, due to the reactions in aqueous/alcohol solutions, problems arise with the use of hydrophobic core particles. One possible solution is the functionalization of the surface of the hydrophobic particles (see chapter 3.2.2). Alternatively, reverse microemulsion techniques, in which the micelles are used to confine the seed particles and control the deposition of silica within the micelle [24,48–50]. The reverse microemulsion technique was used, for example, for the synthesis of silica coating of CoFe_2O_4 nanoparticles [49,51,52].

Microemulsion was obtained by mixing ferrofluid (dispersion of spherical CoFe_2O_4 nanoparticles, prepared through thermal decomposition of metal acetylacetonates, in hexane or cyclohexane), TEOS and ammonia in a micellar solution. The core/shell nanoparticles with narrow particle size distribution were formed during the base-catalyzed hydrolysis of TEOS within micelles and destabilized from the microemulsion by using methanol.

3.2.2 Chemical deposition on functionalized core-particles

The direct chemical deposition of homogeneous shell is usually very difficult or even not possible due to various reasons such as the hydrophobic nature of the core surface, inadequate surface charge of the core-

particles, incompatibility of the core surface groups with attaching shell precursor, etc. Thus, in order to grow homogeneous shells, the core-particles are usually functionalized with an appropriate agent (Fig. 10).

Mechanisms of shell formation

Functional groups at the surface of the unmodified silica nanoparticles are predominantly silanol (Si–OH) or ethoxy (Si–OC₂H₅) groups [53]. This is the reason why the corresponding synthesis methods for core/shell particles are easily adjustable to hydrophilic core-particles, but due to the reactions in aqueous/alcohol solutions hydrophobic particles must undergo a ligand exchange before the deposition. Various types of functional silanes were used, all of which have trimethoxysilyl, triethoxysilyl, or silanol groups at one end and an amino, thiol, phosphonate or other group at the other end (Table 1) [22,24,54–58]. In addition, some other functionalization agents have been utilized, such as poly(diallyldimethylammonium chloride) (PDDA), cetyltrimethylammonium bromide (CTAB) polyethyleneglycol (PEG), glutaraldehyde etc. [59–61].

Three different strategies for the functionalization of core-particles in methods based on the Stöber process could be recognized [57]. Firstly (Fig. 11a), surface hydroxyl groups of the core-particle can react with –OMe group (–OCH₃ or –OC₂H₅) of the used silane coupling agents [R–(CH₃)_nSi(OMe)₃] through the exchange of –OH with –R groups and, thus, form the desirable surface modification. The second possibility (Fig. 11b) is to chemisorb the appropriate functional silane (with the –S– bridge) onto the non-oxide nanoparticle surface, and then create a surface covered with another ligand, –R, by the formation of siloxane bonds via the hydrolysis of –OMe groups and condensation with other silica species in solution. The third strategy is based on the attachment of an appropriate

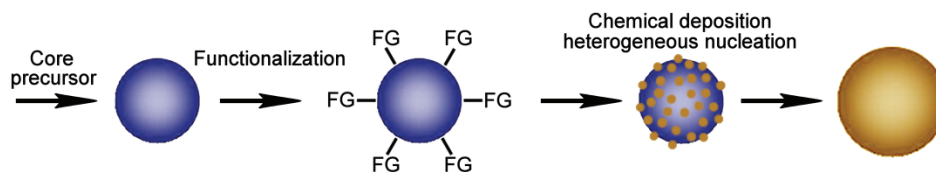


Figure 10. Schematic illustration of chemical deposition on functionalized core-particles

Table 1. Functional silanes

Functional silanes	Silane-group	R-group
3-aminopropyltrimethoxysilane (APTMS)	trimethoxysilyl group	amine group
3-aminopropyltriethoxysilane (APTES)	triethoxysilyl group	amine group
3-mercaptopropyl(trimethoxy)silane (MPTMS)	trimethoxysilyl group	thiol group
vinyltriethoxysilane (VTEOS)	triethoxysilyl group	vinyl-group
2-(Diphenylphosphino)ethyltriethoxysilane	triethoxysilyl group	diphenylphosphine group
propyltrimethoxysilane (PTMS)	trimethoxysilyl group	methyl

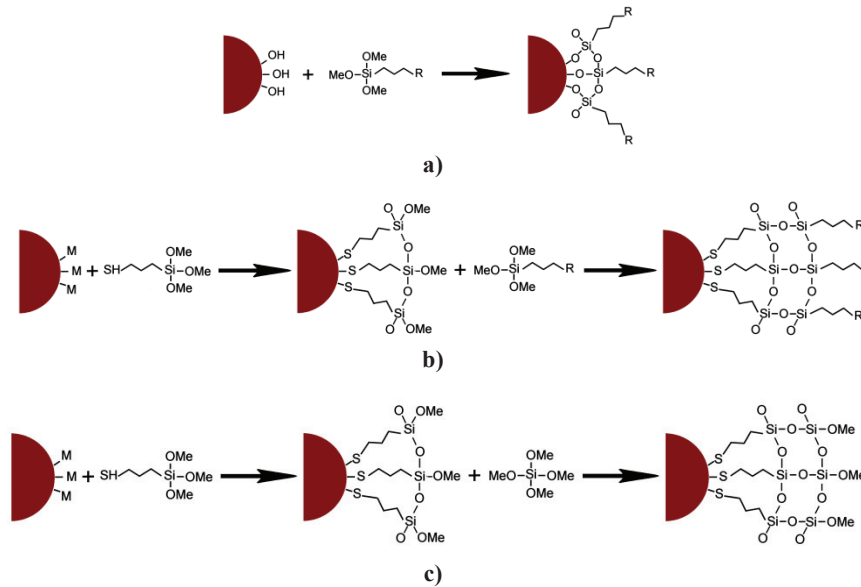


Figure 11. Different strategies for the functionalization of core-particles

functional silane on particle surface, which would initiate subsequent silica shell formation (Fig. 11c).

The selection of the appropriate functionalization agent is very important, thus, a few characteristic examples are given below.

Functionalization with CTAB

As it was already mentioned, the problem with hard agglomeration of ferrite nanoparticles during the synthesis of core/shell nanostructures can be solved by their surface modification with citric acid. However, sometimes it is more convenient to use oleic acid instead of

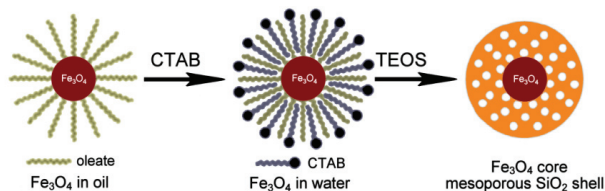


Figure 12. Schematic illustration of shell formation on the CTAB-functionalized core-particle

citric acid, but the ferrite nanoparticles, modified with oleic acid, can be dispersed in water only with additional functionalization, for example, with cetyltrimethylammonium bromide, CTAB. The hydrophobic side-chain of CTAB associates with the alkyl tail of the oleic acid through hydrophobic van der Waals interactions, whereas the hydrophilic group of CTAB enables them to be dispersible in water [60,61]. The hydrophilic groups of CTAB are very helpful in subsequent shell formation and also can be used as an organic template for the growth of mesoporous silica shell (Fig. 12) [61,62].

Functionalization with APTMS or APTES

Functionalization with 3-aminopropyltrimethoxysilane (APTMS) or 3-aminopropyltriethoxysilane

(APTES) has also been frequently used for preparation of core/shell structures [63–66]. It creates surface $-\text{NH}_2$ groups, that can directly react with corresponding shell-forming chemicals, or can be further modified (such as by subsequent conversion into ammonium ions by stirring the silica spheres in a dilute hydrochloric acid solution).

A good example is the fabrication of silica-core/gold-shell particles from $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$. The direct chemical deposition of metallic gold from anionic complexes is only favored under highly acidic conditions (at $\text{pH} < 2$, below the isoelectric point of silica) where the silica surface is positively charged. However, under these conditions HAuCl_4 is not significantly dissociated and the hydrolysis of HAuCl_4 increases only above $\text{pH} > 2$ (with formation of anionic gold species, e.g., $[\text{AuCl}_x(\text{OH})_{4-x}]^-$). Therefore, functional-

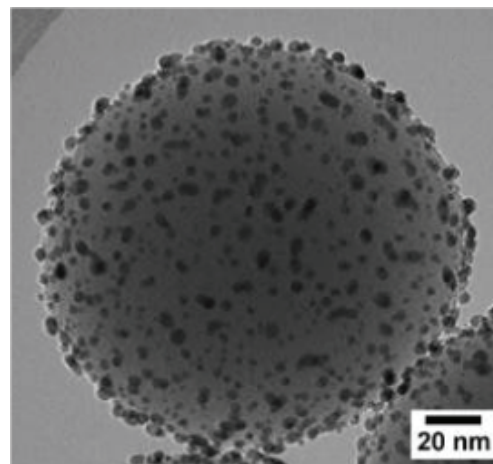


Figure 13. TEM image of the gold shell formed at functionalized silica-core particle [66]. Reprinted with permission from N. Phonthammachai et al., *Langmuir*, 24 (2008) 5109–12. Copyright 2008 American Chemical Society.

ization of core-particles and creation of their positively charged surface is necessary [65–67]. One strategy employed functionalization of the silanol groups on the silica cores with APTES which creates the surface $-\text{NH}_2$ groups. The surface modified silica particles were used as seeds for the formation of a particulate gold shell with the structure strongly dependent on pH, temperature and deposition time [66]. It can also be possible to further modify the APTES-functionalized silica surface by subsequent conversion of the amine groups into ammonium ions by stirring the silica spheres in a dilute hydrochloric acid solution. These positively charged ammonium groups on silica surfaces can strongly absorb gold anions ($[\text{AuCl}_x(\text{OH})_{4-x}]^-$) and form gold shell with controllable characteristics (Fig. 13). Further growth of uniform gold shell with desirable thickness can be obtained in the next step, by chemical deposition from aqueous solution of HAuCl_4 and K_2CO_3 in presence of reducing agent and precise control of pH and concentration [66].

Functionalization with MPTME

Many researchers [57,68–72] have recognized that the use of 3-mercaptopropyl(trimethoxy)silane (MPTME) is very effective in the preparation of core/shell nanostructures especially with metallic cores. Furthermore, Liu *et al.* [18] have shown that MPTME was better suited for the surface activation of gold nanoparticles than APTMS or APTES because of the stronger binding of the thiol groups to the gold surfaces. Fu *et al.* [71,72] used MPTMS-functionalization for nickel or cobalt nanoparticles (Fig. 14). They dispersed metallic nanoparticles in anhydrous toluene solution containing MPTMS and obtained complete complexation of the $-\text{SH}$ groups of MPTMS with the surface of nanoparticles after aging at room temperature. The modified core-nanoparticles were then coated with uniform layers of silica by the controlled hy-

drolisis and condensation of TEOS [71,72]. Jana *et al.* [57] also utilized MPTME for the functionalization of Au, Ag, and ZnS-CdSe nanoparticles. The thiol group of this functional agent was chemisorbed onto the non-oxide nanoparticle surface, and the trimethoxysilane groups initiated the silica layer formation on the particle surface

3.2.3 Assembly of preformed nanoparticles by electrostatic interactions

Core/shell structures can be prepared by assembling the previously formed nanoparticles on the oppositely charged surface of the core-particles (Fig. 15). Usually the assembly process has been performed by homogeneous nucleation of the nanoparticles from the liquid phase in which the core-particles are homogeneously dispersed. The assembling process is strongly pH-sensitive, as the pH has to be adjusted at the value where, for example, negatively charged core-particles will attract positively charged shell-nanoparticles (or vice versa). In addition, uniform core/shell structure can be obtained only if agglomeration of the nanoparticles during the deposition process is prevented.

Adjustment of opposite surface charges

A typical example of the assembling of the oppositely charged core and shell particles is the fabrication of perovskite based core/shell structures developed by Buscaglia *et al.* [73]. They assembled the previously formed SrTiO_3 or BaZrO_3 nanoparticles on the oppositely charged surface of the of BaTiO_3 spherical particles. SrTiO_3 and BaZrO_3 nanoparticles were prepared from aqueous chloride solution of $\text{TiCl}_4 + \text{SrCl}_2 \times 6\text{H}_2\text{O}$ and $\text{ZrCl}_4 + \text{BaCl}_2 \times 2\text{H}_2\text{O}$, respectively. The prepared chloride solution was then quickly added to a suspension of BaTiO_3 particles in an aqueous NaOH solution. Synthesis was carried out in a closed teflon vessel due to the better control of the coating process and avoiding product contamination with adsorption of CO_2 from air. Under opti-

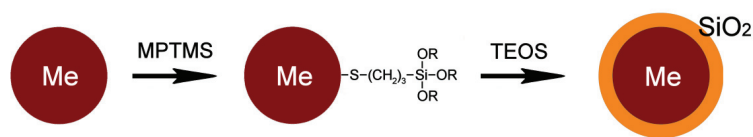


Figure 14. Schematic illustration of shell formation on the MPTMS-functionalized core-particle

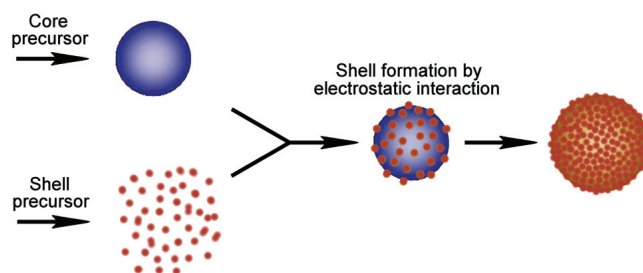


Figure 15. Schematic illustration of the assembling of the oppositely charged core and shell particles

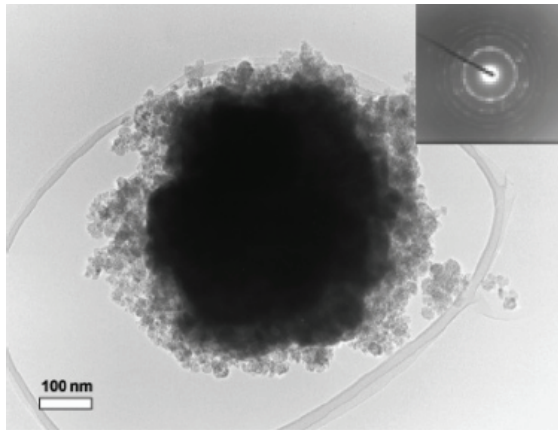


Figure 16. TEM image of BaTiO₃-core/SrTiO₃-shell particles [73]. Reprinted with permission from M.T. Buscaglia et al., *Chem. Mater.*, 18 (2006) 4002–10. Copyright 2006 American Chemical Society.

mal processing conditions, SrTiO₃ or BaZrO₃ nanoparticles were homogeneously nucleated in surrounding liquid phase and attached on the surface of BaTiO₃ spherical particles to form uniform particulate shell (Fig. 16).

Even though this assembling method has been widely used for fabrication of different core/shell particles, its drawback is that it is strongly pH-sensitive and the nanoparticles can be easily desorbed from the core-surface if pH is even slightly changed. Claesson *et al.* [74], for example, demonstrated that the maximum attraction for maghemite to the silica surface is expected to be at pH = 3.0–4.0, and for cobalt-ferrite, the maximum attraction was found in the range of pH = 4.0–4.3. Thus, even a small change in pH has a considerable influence on the structure of the synthesized core/shell particles. Similar conclusions, for the SiO₂-core/Fe₃O₄-shell structures, were brought out by Nikolic *et al.* [75], who investigated the assembling process of ferrite nanoparticles on monodispersed silica particles prepared by the Stöber process. Figure 17 confirms that the silica and ferrite particles have oppositely charged surfaces in the pH range between ~3.0 and 6.2. Thus, if the pH is higher than 6.2 there is no electrostatic interaction between silica and ferrite particles and therefore the shell cannot be formed. On the other hand, even at pH < 4 there are appropriate conditions for shell formation between silica and ferrite particles, but at these pH values the ferrite particles cannot be formed.

Buscaglia *et al.* [76] developed the method based on the electrostatic interactions to fabricate BaCO₃-core/TiO₂-shell nanostructure and showed that it can be done only by fine-tuning the relevant processing parameters. The main idea was to disperse fine BaCO₃ particles in an aqueous TiCl₄ solution from which TiO₂ nanoparticles will be formed and assembled on the BaCO₃ surfaces. However, BaCO₃ is soluble in water at pH < 7 and only in highly acidic conditions hydrolysis of TiCl₄ can be suppressed, preventing precipitation of amorphous

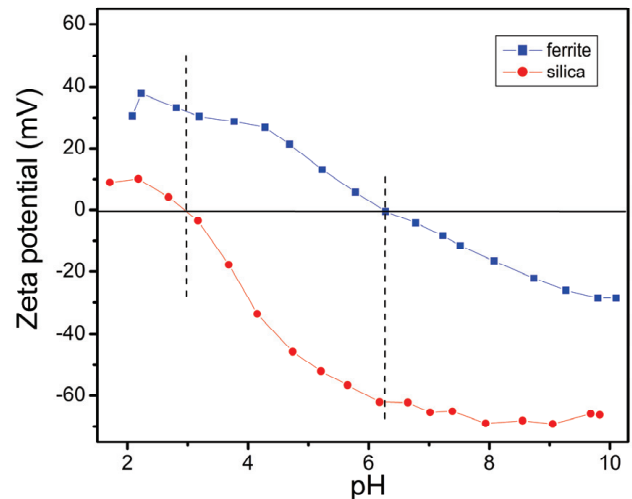


Figure 17. Aqueous electrophoresis curves silica and maghemite particles

or crystalline TiO₂ [77]. By further investigation, it was found that the stability of aqueous solution containing Ti⁴⁺ ions can be extended up to neutrality or even slightly basic conditions by using a mixture of H₂O₂ and NH₃ [78,79]. Because of that Buscaglia *et al.* [76] dispersed fine BaCO₃ particles in an aqueous TiCl₄ solution stabilized using the appropriate H₂O₂/NH₃ ratio at pH between 7 and 10, where the zeta potential of BaCO₃ is positive, while that of TiO₂ is negative. Therefore the amorphous titania nanoparticles, produced by the hydrolysis of Ti⁴⁺, were formed and spontaneously self-assembled at the surface of the BaCO₃ core-particles.

Prevention of nanoparticle agglomeration

As already mentioned, the uniform shell cannot be formed if the nanoparticles tend to agglomerate during the deposition process. Because of that, diluted dispersions of the nanoparticles, subjected to ultrasonication and intensive mechanical stirring are usually utilized. However, some other solutions have been suggested performed and two characteristic examples are given below.

Nikolic *et al.* [75] observed that, during the assembly of NiFe₂O₄ nanoparticles on the silica core-particles, a perfect nickel-ferrite shell cannot be formed on the entire surface of the silica particles even if the appropriate pH was used (where the opposite surface charges of silica and nickel particles were obtained). They concluded that the formation rate of nickel-ferrite particles, at the selected relatively high pH, becomes faster than the deposition rate on the silica core. Consequently, self-aggregation dominates the competing formation of the ferrite shell. Surface modification of the nickel-ferrite nanoparticles with citric acid prior to their deposition on the silica core prevented the self-aggregation process and resulted in the formation of a uniform shell (Fig. 18).

Lee *et al.* [80] tried to optimize the conditions for synthesis of SiO₂-core/TiO₂-shell particles. Silica core-particles, prepared by the Stöber method, were dis-

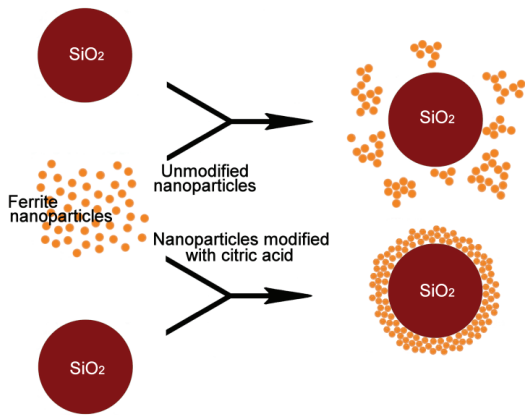


Figure 18. Schematic illustration how the surface modified of ferrite nanoparticles can have influence on core/shell structure

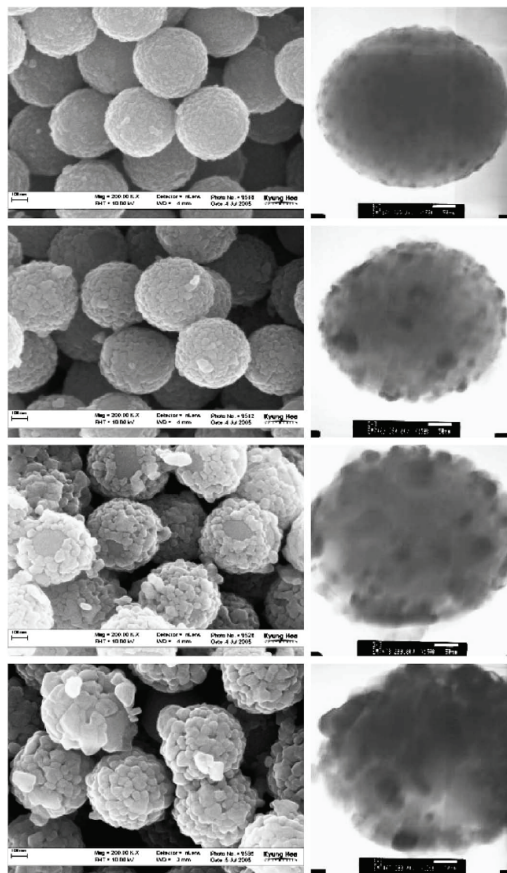


Figure 19. SEM and TEM micrographs of SiO₂-core/TiO₂-shell particles prepared by layer-by-layer process using: a) 1, b) 2, c) 3 and d) 5 step deposition [80]

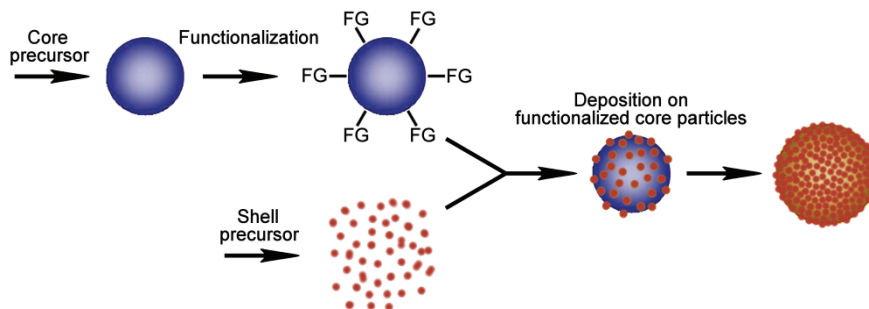


Figure 20. Schematic illustration of the assembling process onto functionalized core-particles

persed in ethanol and an appropriate amount of distilled water and hydroxypropyl cellulose was added. Titania shell was obtained by slowly adding $Ti(OC_4H_9)_4$, previously dissolved in ethanol, to the prepared silica sol. It was shown [80] that with the low concentration of $Ti(OC_4H_9)_4$ (0.06 mol/L) a very thin shell (~9 nm) can be obtained. The shell thickness can be increased by increasing the $Ti(OC_4H_9)_4$ concentration, but there is the upper concentration limit above which the growth of necks between the particles appears, promoting their agglomeration. Because of that, for preparation of a thicker shell, the agglomeration has to be suppressed or another synthesis method has to be employed. The solution was found in a multistep titania deposition process (i.e. layer-by-layer deposition). Figure 19 clearly shows that agglomeration of the titania nanoparticles was successfully avoided and an increase of the titania shell thickness with the increase of number of deposited layers was obtained.

3.2.4 Assembly of preformed nanoparticles onto functionalized core-particles

The direct assembly of nanoparticles on the core surface is often not possible due to a variety of reasons, including different nature of the core and shell particles, strong tendency of the nanoparticles to detach from the core surface, inadequate surface charge of the core and/or shell nanoparticles, incompatibility of the core surface groups with the surface of attaching nanoparticles, etc. The problem can be solved with functionalization of the core-particles (Fig. 20). Two different approaches can be recognized and both are described in this section: i) assembly by electrostatic interaction and ii) assembly by chemical coordination.

Assembly by electrostatic interactions

The functionalization of the core-particles can improve the assembling of the preformed nanoparticles if this changes the surface charge of the core-particle and, thus, increases the electrostatic attraction between the core and the shell.

A typical example is fabrication of silica-core/silica-shell nanostructures by the assembling of the primary silica nanoparticles synthesized by neutralization of highly basic sodium silicate solution, on the surface of monodispersed silica cores prepared from TEOS

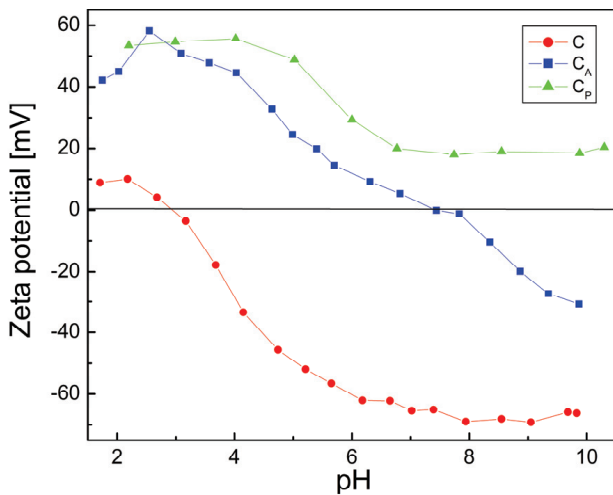


Figure 21. Aqueous electrophoresis curves obtained for non-functionalized, APTES-functionalized and PDDA- functionalized silica particles

[81,82]. In this case, both the core and shell particles had isoelectric point at pH between 2.5 and 3 and negative surface charge at higher pH values. Thus, there is no electrostatic interaction between them and uniform shell cannot be formed. The assembling was improved by functionalization with 3-aminopropyltriethoxysilane (APTES) or poly(diallyldimethylammonium chloride) (PDDA), as they extended the interval in which SiO_2 core particles are positively charged, at pH up to ~ 7.5 or even above 10, respectively (Fig. 21). The functionalization enabled preparation of mesoporous, relatively uniform and continuous silica shell on monodispersed silica core particles (Fig. 22).

Similar problem appeared during synthesis of silica-core/gold-shell nanostructures. It was shown by Oldenburg *et al.* [17,54] that core/shell structure cannot be formed if unmodified silica spheres are used as the core-particles. This was explained by the repulsion of the negatively charged gold nanoparticles from the negatively charged silanol groups of the unmodified silica particles. Because of that functionalization with APTMS was performed [17,54,83]. The functionalization with APTMS introduces an amine group to the silica surface. With an available lone electron pair, the amine group is able to bind to the gold nanoparticles [54]. Thus, when the functionalized silica particles were added to the previously prepared aqueous suspension, gold nanoparticles were easily attached to the silica surface.

The influence of pH on the assembly by electrostatic interactions is well demonstrated by Nikolic *et al.* [75], who synthesized core/shell structures by depositing NiFe_2O_4 nanoparticles onto functionalized spherical silica particles. They showed that acidic conditions ($\text{pH} < 6$) are not favorable for the formation of NiFe_2O_4 nanoparticles and their subsequent deposition on the surface of silica core-particles. However, both SiO_2 and NiFe_2O_4 particles are negatively charged for $\text{pH} > 6$.

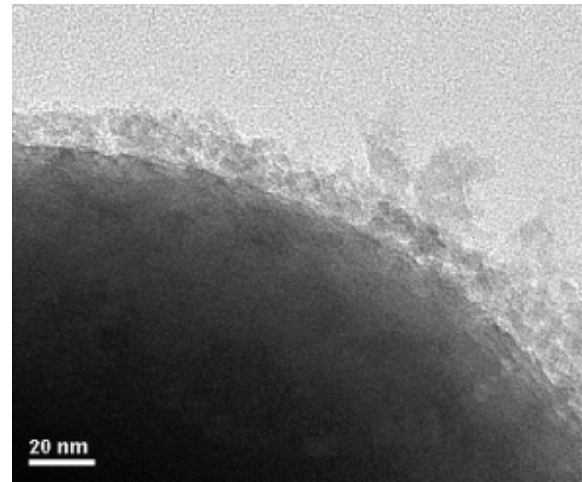


Figure 22. TEM image of mesoporous silica shell deposited on silica core [82]

Because of that functionalization of silica surfaces was performed with APTES and PDDA [75]. This enabled the assembly of core/shell nanostructures by electrostatic interactions as the APTES-functionalization insured an opposite surface charge of ferrite and silica particles in the pH range up to 7.5. Moreover, functionalization with PDDA extended this interval up to $\text{pH} = 10.5$.

The formation of silica-core/gold-shell particles was investigated by Shi *et al.* [67], who proposed the assembling mechanism of the gold nanoparticles onto the APTES-functionalized silica particles (Fig. 23). Organic functionalization of the silanol groups on the surface of silica particles with APTES resulted in the formation of amine groups on their surfaces. The amine groups ($-\text{NH}_2$) were subsequently converted into ammonium ions ($-\text{NH}_3^+$) by dispersing the silica particles in a dilute hydrochloric acid solution. These positively charged silica spheres were necessary to attract citrate ion-modified gold nanoparticles. Thus, the surface modified gold nanoparticles were adsorbed to the positively charged ammonium ion-functionalized silica nanospheres via electrostatic interactions [67].

Assembly by chemical coordination

The second approach to assembling core/shell nanostructures is related to the functionalization of the core-particles and the creation of desirable surface-groups that can chemically bond the shell nanoparticles from the surrounding liquid. Various functional agents, that contain hydrolyzable groups at one side and nonhydrolyzable groups at their other side, were used. The hydrolyzable group can react with the surface of the silica particle, whereas the nonhydrolyzable group (amino, thiol, phosphonate or other group) can bind to the surface of the nanoparticles and link them to the silica surface.

It is usually very difficult to determine the dominant mechanism responsible for the assembly of a nanoparticle to the surface of a core-particle. Most of them are

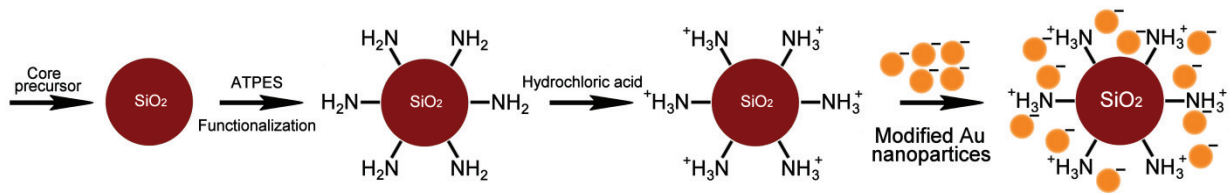


Figure 23. Schematic illustration of the assembling of modified gold nanoparticles on the APTES-functionalized silica particle

defined as an assembly by electrostatic interactions and only in a few examples chemical coordination was mentioned. Thus, for example, Westcott *et al.* [54] investigated the formation of the shell of gold nanoparticles on thiol-functionalized silica nanoparticles (treated with MPTMS) and mentioned that the interaction of the gold nanoparticles with the silica nanoparticles cannot be purely electrostatic. Philipse and Vrij [84] described the deposition process of the magnetic particles onto MPTMS-functionalized silica and proposed the interaction mechanism. They thought that the methoxy groups of MPTMS are first hydrolyzed in the presence of ammonia, thereby forming oligomers that bind to the silanol groups on the surface of the silica particles through a condensation reaction.

3.3 Synthesis of complex core/shell nanostructures

Recently, synthesis of complex core/shell nanostructures (multilayered core/shell particles, hollow particles, eccentric core/shell particles etc.) has begun to draw considerable attention. Due to the complex structure, these multifunctional nanoparticles have been usually synthesized by combinations of different gas- and/or liquid-phase methods mentioned above. Because of that, only some characteristic examples will be presented in this section.

Multilayered core/shell structures

Gas phase processes have been used for fabrication of bilayered core/shell nanostructures, usually by reaction/decomposition of flowing gases or volatile metal-organic precursors in a reactor consisting of three reaction zones or three sequential reactors. Thus, Fotou and Kodas [85] produced bilayered core/shell particles, consisting of Al_2O_3 and SiO_2 thin layers on TiO_2 , via gas phase in a hot-wall reactor with three reaction zones. The titania particles produced in the first reaction zone by reaction of TiCl_4 vapor with O_2 entered the second reaction zone where AlCl_3 was introduced. Alumina

layers were formed by the chemical vapor deposition. Then, titania particles with alumina shell entered the third reaction zone where SiCl_4 was introduced. It was confirmed that coating in this case took place by deposition of silica particles or aggregates on $\text{TiO}_2/\text{Al}_2\text{O}_3$ core/shell particles that were formed by the gas phase reaction of SiCl_4 with O_2 [85].

Multifunctional core/shell nanoparticles have also been prepared by combination various liquid phase techniques and four typical examples will be described here. The first example is a process for synthesis of gold/silica/CdSe nanoparticles developed by Liu *et al.* [18]. It included synthesis of gold nanoparticles, gold-particle surface functionalization with MPTMS, chemical deposition of a dense silica shell, modification of the silica surfaces with APTMS and final assembly of CdSe quantum dots (CdSe-QD) onto the gold/silica particle surfaces by strong interaction with $-\text{NH}_2$ ligands (Fig. 24). This nanostructure allows for versatile control of CdSe-QD and Au-metal interactions through control of the size of Au nanoparticle and the thickness of the dielectric silica layer.

Abramson *et al.* [86], for instance, reported the synthesis of bilayered $\gamma\text{-Fe}_2\text{O}_3/\text{SiO}_2/\text{TiO}_2$ nanoparticles using a two-step chemical deposition method. In the first step, ammonia, ethanol and TEOS were successively added to an aqueous dispersion of citrate-coated $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles. The obtained Fe_2O_3 -core/ SiO_2 -shell powder was washed and finally redispersed in absolute ethanol. In the second step, TiO_2 layer was deposited by successively adding $\text{Ti}(\text{O}i\text{Bu})_4$ dissolved in absolute ethanol to the prepared suspension of $\gamma\text{-Fe}_2\text{O}_3/\text{SiO}_2$ nanoparticles under N_2 atmosphere.

A process combining the assembly of magnetic nanoparticles on the spherical silica cores with subsequent chemical deposition of the second silica layer was used for the preparation of complex multifunctional core/shell nanostructure for biomedical applica-



Figure 24. Schematic illustration of the synthesis of gold/silica/CdSe nanoparticles

tion [74]. In the first step the magnetic nanoparticles were deposited onto the surface of MPTMS-functionalized silica spheres. The thiol-functionalized silane irreversibly binds the ferrite particles to the silica surface. The second silica layer was prepared from TEOS by the Stöber method ensuring the biocompatibility of the obtained structure.

Shi *et al.* [67] prepared size tunable and structure tailored complex core/shell spheres containing silica cores with two shells. The first shell was made of gold nanoparticles on which the second silica shell with controlled structure was deposited. The citrate-modified, negatively charged gold nanoparticles were assembled by electrostatic interaction on the APTES-functionalized silica spheres subsequently modified with a dilute hydrochloric acid solution (to create positively charged silica with surface $-\text{NH}_3^+$ groups). In addition, they demonstrated that the second shell can be dense, corrugated or porous (Fig. 25). The dense shell can be obtained by controlled hydrolysis of TEOS in presence of ammonia. The formed silicate anions replace the negative citrate ions around the gold nanoparticles and enable the growth of the silica shell. The dense silica layer will not be formed if APTES-functionalization is not adequate, i.e. if the concentration of APTES is low. In this case, some non-functionalized silanol groups, left on the silica surface, will dissociate to form surface SiO^- groups and thus repel the silicate anions. A corrugated silica shell can be formed simply by etching the dense silica layer with KCN solution, whereas a porous silica shell can be formed if sodium silicate instead of TEOS is used (Fig. 25).

Hollow particles

Hollow structures can be obtained simply in two steps, by first synthesizing core/shell structures and then removing the core material via calcination or leaching. Various methods have been used to prepare hollow spheres, and polymers such as polystyrene are widely used as they can be easily removed. Thus, silica layers on polystyrene cores were deposited in processes based on chemical deposition from silica precursors

[25,87,88]. It was shown that TEOS is not suitable for coating polystyrene, which is hydrophilic and negatively charged. Organo-silica precursors, such as vinyltrimethoxysilane (VTMS), decrease the number of OH-groups and increase the number of hydrocarbon groups at the surface. Both phenomena reduce the hydrophilic character of the surface leading to higher interface tension and direct growth of the silica shell [88]. In the final step of core/shell particle synthesis polystyrene was usually removed by heating to 500–600 °C and mono-dispersed hollow spheres with thickness from tens to few hundreds of nanometers were formed.

Eccentric core/shell particles

Recently, eccentric core/shell structures, in which the core is partially or completely separated from the shell, attracted much attention because of their unique catalytic behavior and persistence against aggregation of the encapsulated particles under heating [89–92].

A simple approach, adopted by Demirors *et al.* [91], is applicable to core/shell structure which during further heat-treatment undergoes higher shrinkage of the core than the shell enclosing them. This method was used for preparation of eccentric TiO_2 -core/ SiO_2 -shell particles. In the first step, silica coating of porous titania particles was obtained by Stöber method. After calcination of the synthesized particles at 600–625 °C a unique eccentric core/shell structure was prepared, as a result of extensive shrinkage of the highly porous titania core with respect to the silica shell (Fig. 26).

Eccentric core/shell structures can also be prepared with the so-called template-assisted selective etching method, a multistep process developed recently [89,93–95]. In the first step, core/shell particles are prepared and then parts of cores or shells are selectively removed by dissolution with a solvent. A similar multistep approach is based on the synthesis of a core with two shells and subsequent removal of the middle shell by etching or controlled heat-treatment [91–93].

An interesting way for the preparation of eccentric core/shell structures with very fine cores (Fe_3O_4 or Au nanoparticles) and tunable functionalized mesoporous

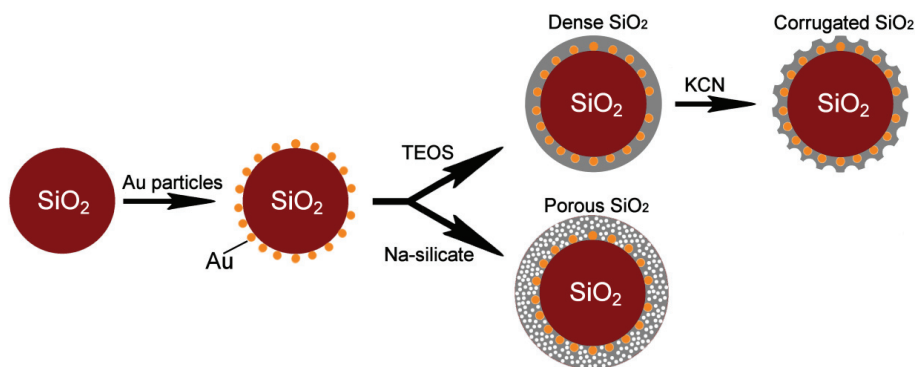


Figure 25. Schematic illustration of the synthesis of bilayered core/shell nanostructures with dense, corrugated or porous silica shell

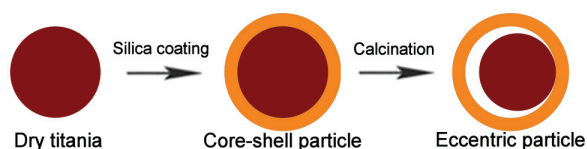


Figure 26. Schematic illustration of the synthesis of eccentric core/shell particle

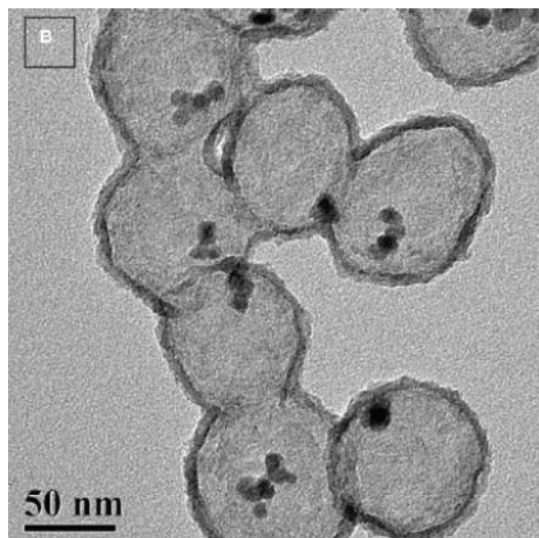


Figure 27. TEM image of eccentric $\text{Fe}_3\text{O}_4/\text{SiO}_2$ core/shell nanoparticles [92]. Reprinted with permission from Y. Yang et al., *Chem. Mater.*, 23 (2011) 3676–84. Copyright 2011 American Chemical Society.

silica shell, based on the one-step organo-silane-assisted etching method, was developed by Yang *et al.* [92]. First, the core/shell particles were formed by deposition of mesoporous silica shell on the functionalized Fe_3O_4 or Au nanoparticles, by incomplete hydrolysis and condensation of TEOS. Then, organo-silane precursor 1,2-bis-(trimethoxysilyl)ethane was added, which accelerated the hydrolysis of Si–O–Si bonds (i.e. dissolution of the inner mesoporous silica layer). However, at the same time, organo-silane was deposited on the surface of the core/shell particles, forming a protective layer that prevented the hydrolysis of the Si–O–Si bonds near the outer surface of the core/shell particles [92,96]. Thus, the formation of the outer mesoporous organo-silica shell and the selective dissolution of the inner mesoporous silica shell occur at the same time and the eccentric core/shell particles were finally formed (Fig. 27).

IV. Conclusions and outlook

With the development of nanotechnology and nanostructured materials, one of the primary research goals became to reach advanced properties and multifunctionality, in order to achieve better performances and novel applications. Naturally, this has led to the discoveries of novel materials and development of new strategies in synthesis and processing of desirable nanostructures. Thus, thin surface layers on fine particles were found to substantially change their func-

tionality and properties, such as chemical reactivity, thermal stability, catalytic activity, dispersibility, or optical, magnetic and electronic properties. These core/shell nanostructures were first realized in the late 1980s, and since then has been well accepted by researchers and their use was extended to almost all areas of science and engineering, including medicine, catalysis, biotechnology, chemistry, optics, electronics, energy storage, etc. In this paper a detailed overview of different synthesis techniques used for preparation of various ceramics core/shell nanostructures with tunable size and tailored structure is presented. An original and unique systematization of all those fabrication methods is given and many different approaches important for the shell uniformity and thickness control are described.

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