

A comprehensive study of synthesis and applications of core/shell nanoparticles

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Abstract

When we consider matter at nanoscale, one of the most important aspects to be considered is that due to the small size of the particles, these have increased surface area to volume ratio. The large value of this ratio increases the dominance of the surface atoms of the nanoparticles in relation to those in its interior. A special category of materials at nanoscale level has gained popularity in the recent times due to their interesting properties and applications. When classified on the basis of structure, the types of core/shell particles can have a large variety. Each of this structural classification has its own importance, method of synthesis and application. The core/shell nanoparticles have some distinct features that is responsible for their importance. The properties of Core/shell nanoparticles are highly modified from that of their simple pure nanomaterials, thus they usually called highly functional materials. The introduction of a different crust layer over the core particle has many reasons, such as it helps in implementing surface modification, increases functionality, stability and dispersibility, control on the release of the core, lowering the consumption of precious materials, and so on. These nanostructures can have a number of combinations in close interaction, depending upon the selection of material used, which highly influences the end application. This paper has an overview of the present methods involved in synthesis and tunable factors responsible for their end applications. The development of metal/metal oxide core-shell nanoparticles has become popular nowadays due to their widespread use in catalysis and other environmental remedial applications.

Keywords: nanoscale, surface modifications, functionality, tunable, environmental remedial applications.

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1. Introduction

Core/shell nanoparticles are the materials having varying properties. It consists of a core whose surface is modified with the deposition an exterior layered material which decreases its reactivity and increases the dispersibility and substantiality of the modified particle. The core/shell nanoparticles can be of varying shapes and sizes. These properties also affect their functionalities and their applications. These modified nanostructures can be grouped on the basis of combination of organic and inorganic materials used in these synthesis. In organic core and organic shell nanoparticles the core as well as the shell are organic materials or polymers. It has huge application in the drug delivery systems, in the catalysis and so on. These have modified properties such

as rigidity, toughness and are generally referred to as smart materials. In the case of organic core and inorganic shell, these nanostructures consist of polymers or different copolymers as cores and shells are inorganic materials such as silica, metals or metal oxides. The inorganic shells provide rigidity whereas the organic core is spongy in nature, so it introduces flexibility in the material. Therefore, this increases the strength of the particle and the resistance to oxidation. While the inorganic core and inorganic shells have excellent performance with enhanced magnetic properties, energy absorption. Inorganic core and organic shell nanoparticles find applications in the field of paints, pigments, cosmetics etc. A variety of shapes of core/shell nanoparticles are also possible such as spherical, hexagonal, multiple small cores coated by single shell, yolk shell or movable core within hollow shell material. Generally, two schemes are used to vary the shapes of the structures synthesized. The first methodology involves an even layering of the shell material over a hard or soft core of different shapes resulting in the preparation of the desired shaped particles. The other method involves the use of a suitable capping agent or some of the reagent to control the required dimension and growth. The coating efficiency is generally found to be depending upon the shape of the core. It is generally seen that uniform coating phenomenon is reduced if the core has a distorted shape from spherical.

The non-spherical nanostructures have larger surface area relative to spherical ones due to the introduction of sides and corners, thus they perform better as catalysts. A number of research works have been published highlighting some special properties and their applications based on their end use. It is assumed that the core shell nanoparticles will replace almost all the existing current technologies and will play a crucial role in the enhancement of future research.

This paper targets to emphasize on the present status in the synthesis and application aspects of core/shell nanoparticles. The parameters which influence the properties and end uses of these nanostructures have also been used. This study demonstrates the development of modified nanostructures with desired properties by varying the synthesis parameters. These have great potential, different research groups over the globe are making efforts to simplify the synthesis and find innovative and reliable means to produce core/shell nanostructures of different sizes and shapes.

2. Synthesis

Various experimental parameters like temperature, time, concentration is varied to produce a wide range of core/shell nanoparticles. The core/shell nanoparticles synthesized for a particular application is to be designed by controlling and optimizing these parameters along with the selection of the appropriate material of the core/shell and the required shape. Full control over the process parameters along with the nucleation and growth of the shell is required to get the desirable characteristics in the synthesized particles. Some general methods are employed in the synthesis this class of nanoparticles, here these will be discussed in sections based upon the material of core/shell nanoparticles. On the basis of material properties of the core/shell nanoparticles, these are classified as: organic/organic core/shell nanoparticles, organic/inorganic core/shell nanoparticles, inorganic/inorganic core/shell nanoparticles.

The organic/organic core/shell nanoparticles are also called smart particles due to their extensive use in different fields. These have a polymer coating over a polymer core which results in increase in overall toughness of the particles, the glass transition temperature also changes. Generally, polymerization mechanisms (cross-linking, free-radical and copolymerization) are used in the synthesis of these particles. In some cases, inorganic materials mixed with the polymers are used for adhesion that improves the mechanical properties the particles obtained. As an instance, during the synthesis blending Sb_2O_3 in the core increases the toughness and mechanical strength of PVC in PMMA/PVC core/shell nanostructures. (Xie *et al.*, 2004). It has been observed that the properties of the inorganic materials are also affected besides the polymer (Lu *et al.*, 2006)

The organic/inorganic core/shell nanoparticles have a polymer at core coated with a metal oxide, metal chalcogenides or silica shell. They possess dual properties due to the presence of both an organic and an inorganic material. Since the core is organic, so it is prepared in a similar way as that of organic/organic core/shell nanostructures. Generally, the deposition of inorganic crust over the core is done using hydrolysis or sol-gel method followed by reduction, coprecipitation or calcination.

The inorganic/organic class of core/shell nanoparticles has a metallic or metal oxide core with a polymeric crust. The shell material is organic, which makes the core oxidation resistant and biocompatible. The core synthesis involves wet chemical reactions, reduction or hydrolysis, the shell deposition involves polycondensation and polymerization reactions. The nanoparticles prepared by wet chemical reactions are crystalline and have good magnetization, so these are widely used for synthesis of magnetic core nanostructures. It is difficult to control the size of the synthesized particles due to high tendency of aggregation. A single-layered polymer coat can prevent the agglomeration to some extent, and it can be easily removed as per requirement. The dispersibility of silica particles can also be enhanced using the polymer layer.

The inorganic/inorganic core/shell nanostructures are, generally, made up of metal, metal oxide or silica. The synthesis of this class involves processes like microwave treatment, precipitation and hydrothermal decomposition. The crystal lattice parameters and the chemical interaction between the interface of core/shell nanoparticles are taken in account for selecting the materials to be used. In cases of incompatibility of lattice between the constituents, an appropriate surfactant or ligand is used for the formation of the coat over core. The use of metal precursor salts increases the possibility of aggregation during the preparation of core. So, it is tried to be avoided by using any alternative process. If the use of metal salts as precursors is inevitable then a proper surfactant is selected which prevents the problem of agglomeration. The surfactant helps in modifying the interfacial energy between the incompatible constituents.

For an instance, the synthesis of ZnO shell over noble metals is very challenging as ZnO is hexagonal and it grows differently along the c axis. Thus, this synthesis was very problematic on account of the lattice mismatch; besides this no surfactant or ligand could help. (Wang, *et al*, 2010) This was recently solved to some extent with the synthesis of Ag/ZnO core/shell nanoparticles. These were synthesized for the first time by laser ablation technique, using a 248 nm KrF excimer pulsed laser ablation in a solution. (Zhao *et al*, 2015) Other attempts of coating ZnO were also made, a comprehensive growth mechanism stating a general scheme was developed. (Sun *et al*, 2013) Polyvinylpyrrolidone (PVP) and 4-mercaptobenzoic acid were crucial in the synthesis of Au/ZnO core/shell nanoparticles. The amphiphilic nature of PVP helps in the deposition of ZnO coating on metallic core which have hydrophobic ligands.

The synthesis of modified shapes like hollow shell or yolk/shell nanostructures are synthesized for special applications. A simple synthesis method to get hollow Pd/CeO₂ core/shell nanoparticles consisting of Pd cores with CeO₂ hollow shells is discussed in (Zhang *et al*, 2015). A one-pot hydrothermal reaction was used to prepare a metal/ Al₂O₃yolk/ shell nanoparticles (Zhang *et al*, 2015). A metallic core was coated by carbon that was then used for nucleation for a layer of Al₂O₃. When the hydrothermal reaction was extended, the carbon shell diameter increased by 100 nm. The shell thickness could be controlled by varying the salt concentration. It has been demonstrated that changing the magnetite shell thickness, the magnetic properties can be altered to obtain multi-functionality and new improvised properties (Ivanov *et al*, 2016).

Properties such as blocking temperature, magnetization are dependent on the particle size while the catalytic activity, selectivity, melting point, optical properties varies with the shape of the particle. The efficiency of the desired shape coating also depends upon the shape of the core materials involved in the synthesis and its symmetrical nature. The size of the shell can be controlled by optimizing the concentration and reaction time for the synthesis. The shape can also be monitored by controlling the thermodynamic and kinetic parameters. The shape, phase of the medium and size influences the characteristics of magnetic core/shell nanoparticles. Magnetic nanoparticles have a wide range of applications and mainly Iron (III) Oxide is mostly used as it has magnetic properties and chemical stability.

The kind of salt precursor or the capping reagent used and its concentration determines the shape of the synthesized core/shell nanoparticles. Later, it can be further characterized using different techniques. Thus, it has application in the process of the shape-controlled synthesis of mainly magnetic core/shell nanoparticles. Certain core/shell nanoparticles of a definite shape can be synthesized using an appropriate salt, solvent and surfactant/capping reagent. With change in capping reagent concentration, the shape of the magnetic core/shell nanoparticles varies at lower concentration as in (Fatima *et al*, 2018).

Variation in shape changes the surface exposed and also alters the crystalline arrangements thus it allows varied applications. Moreover, the rate of formation of nanoparticles can be increased to a greater extent by adopting the shape variation techniques. The optimization of parameters to obtain Fe₃O₄ of cubical and tetrahedron shapes has been discussed in (Fatima *et al*, 2018).. It was cubic when 0.5M KOH (capping agent) was used and on increasing the concentration to 1M octahedron shape was observed. This happened as increase in the hydroxyl concentration to 1M fastens the rate of formation of octahedron shape rather than cubic at the lower concentration. The octahedron shape was formed after achieving the cubical shape by growth at the cubical corners as in (Fatima *et al*, 2018). When the concentration of KOH was further increased, it led to unsymmetrical growth and distortion from octahedron shape. It has been found that crystal growth occurred in different planes and therefore different shapes were observed as in (Fatima *et al*, 2018). The anisotropy of the core/shell nanoparticles, which relates the regularity of arrangement in the particles, varies inversely with it. Considering the iron core, the magnetization values varies directly with the symmetry.

Table 1. Tuning parameters for controlling the morphology of core/shell nanoparticles

PROPERTY	TUNING PARAMETERS
Size	Reaction period
Shape	Type and concentration of appropriate salt precursor, solvent media and surfactant or capping reagent.
Nature (Amorphous)	Salt precursor concentration
Crust thickness	Salt precursor concentration Reaction period

It was found that in the synthesis of octahedral Au core, incomplete coating was observed whereas spherical shapes were completely coated as in (Chaudhuri *et al*, 2012). Thus, the efficiency of formation of uniform shell decreases if the shape of the core is distorted from the sphere.

Magnetic iron core particles were synthesized and discussed in (Balakrishnan *et al*, 2009). The particles were synthesized by chemical reduction of FeCl₂ in an aqueous medium with sodium borohydride. These were surfaced with amine-terminated poly(ethylene glycol). It was observed that the particles became more amorphous with the increase in reactant concentration.

Taking the case of the catalytic activity in the metallic nanoparticles, It was found as in (Narayanan *et al*, 2014)

that it was more in the non-spherical shapes as compared with the spherical ones because of increase in the number of exposed surfaces and increase in the surface area. The losses in the yield mainly occur during the separation process.

3. Applications

Due the diversity in the size and shape of core and crust, type of materials used in synthesis, the core/shell nanoparticles are used extensively and have a broad stretch of applications. Classes of inorganic/inorganic core/shell nanoparticles are used on a larger scale for the photocatalytic purposes and are involved in the enhancement of the semiconductor efficacy, catalysis, optical properties etc. It can be further classified on the grounds of nature of the surface material containing mainly silica or any other inorganic material. Silica as a crust is involved in redox reactions, in reduction of the bulk conductivity, increasing stability etc. as in (Chaudhuri *et al*, 2012) thereby showing varied applications because of its inertness. The CdS/ZnS core/shell nanostructures have higher photocatalytic activity than pure CdS and ZnS as in (Reddy *et al*, 2017) for the degradation of methyl orange.

The core/shell nanoparticles with inorganic/inorganic composition, are also used in the enhancement of the electrochemical properties and sensor-based applications. Sensors made up of Ag/WO₃ nanostructures have enhanced performance and showed shorter recovery time when compared with Ag-WO₃ mixture, pure WO₃ and Ag, as in (Xu *et al*, 2014) thereby showing synergistic improvement in the sensor working phenomenon by altering the nature of the material due to increase in the sensitivity to pollution, thermally stable. It also shows adsorption properties and is widely used for removing harmful chemicals, pigments, colours and dyes. (Meng *et al*, 2016) used a combination of SiO₂/Co(OH)₂ core/shell nanoparticles for the adsorption of Rhodamine B (xanthene dye) that showed increase in the adsorption capacity of the dye pollutant from 0.14 mg/mg to 0.41 mg/mg with decrease in the dose of these particles from 7 mg to 1 mg.

Inorganic core with organic shell nanoparticles are used in the pigments, drug delivery and absorption phenomenon; the increased oxidation stability of the core, electromagnetic shielding shows enhanced biocompatibility. It has also been used for water treatment as in (Sari *et al*, 2017). Fe₃O₄/glucose core/shell nanoparticles and was capable of absorbing 93.78% of lead ions and thus promoted the removal of heavy metal ions from the wastewater as in (Sari *et al*, 2017).

If the nanostructures have organic core, these can be widely used for broad spectrum of applications. Core is organic and therefore a flexible nature of the particle is observed. It can handle certain amount of pressure and thereby used in the synthesis of a variety of construction and building materials, thermal and colloidal stability and provides oxidation resistance.

Organic/organic core/shell nanoparticles alter the rigidity and has wider applications in the pharmaceutical industry, biosensing, biomaterials etc. These can also be used as nano-reactors in the upcoming time. By change in the volume transition phenomenon within the thermosensitive shell the catalytic activity of the nanoparticles can also be regulated to a greater extent as in (Ballauff *et al*, 2007). It was found that volume transition within a thermosensitive network can be used as an on-off switch controller and with a tunable catalytic activity of nanoparticles of any order of magnitude more than one can occur.

4. Discussion and Future Prospects and conclusion

The stability and structural integrity of core/shell nanoparticles is intact even in aqueous media. These structures can be successfully applied for various applications including catalysis, biomedical and photocatalytic usage. The metal core and metaloxide shell nanoparticles have extraordinary scope of use in environmental remediation and bacterial disinfectants. The pharmaceutical industries have also been largely benefitted by use of core/shell nanoparticles. Further detailed study of these nanoparticles will also improve the present scenario in the field of wastewater treatment on a broader scale. Accounting to the excellent electronic and physiochemical properties, nanoscale structures of metals like Au, Pd, Ag and Pt are being explored extensively. Metal oxide shells possess good photocatalytic, magnetic, photon harvesting and electronic capability that makes them appropriate to be considered for developing excellent transistors, sensors, bioimaging and photovoltaic devices. The metal/semiconductor core/shell nanoparticles have a great potential in wastewater treatment as photocatalysts. The metal cores of noble metals like gold and silver with metal oxide shell have potential to be used in air purification. Moreover, these assemblies are very cost efficient. As nanotechnology is one of the burgeoning topics, this special category of nanostructures will play a significant role in the future, innovation and further strategies should be adopted to make it more energy efficient, reliable and economical.

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