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Multilayer Thin Films on Fine Particles

Sajjad Habibzadeh, Ehsan Rahmani, Mohammad Reza Saeb, Mohammad Reza Ganjali and Jamal Chaouki

Abstract

The tunable construction of multilayer thin-film-based particulate has opened up new horizons in materials science and led to exciting new developments in many scientific areas during the past two decades. Indeed, to utilize the synergistic properties of thin film coatings and the core particles, the thin film immobilized on fine particles can be a promising approach. The interaction between the thin films and the core fine particles results in adjustable properties of the coated particles. Therefore, such coated systems have been considered as an important class of emerging powder technology for a wide range of applications. Namely, multilayer structural features can lead to designing a highly active and selective catalytic systems. In addition, multilayer-coated nano/micro particles (NMPs) can be employed in the development of many new properties, ease of functionalization, conjugation of biomolecules, etc. Such structure with multilayer coatings can also revolutionize the energy storage and conversion systems.

Keywords: fine (nano/micro) particles, powder technology, multilayer coatings, thin films

1. Introduction

Single-and/or multilayer deposition of films or coatings of particular interest, without altering their bulk properties can be employed to tune the surface properties of fine particles in different fields such as catalysis, energy production, microelectronics, optoelectronics, etc. [1–3]. In particular, multilayer deposition on particles offers a broad range of nanostructured thin films suitable for multiple applications, including photocatalysis [4], advanced energy storage systems [5], drug delivery [6, 7], etc.

Individual fine particles (nano/micro particles, NMPs) were previously studied due to their much superior properties as compared to the agglomerated ones. Later, it was found that composite or coated semiconductor particles could render more enhanced performance than their corresponding individual particles where they might even develop the particles with novel features. Lately, multilayer semiconductor nanoparticles have been synthesized towards improving properties of such semiconductor materials [8]. Furthermore, the demands of modern technology pushed the research activity more forward to synthesize more advanced materials. This demand accompanied by the development of characterization techniques has also greatly helped to establish the structures of multicomponent nano/micro

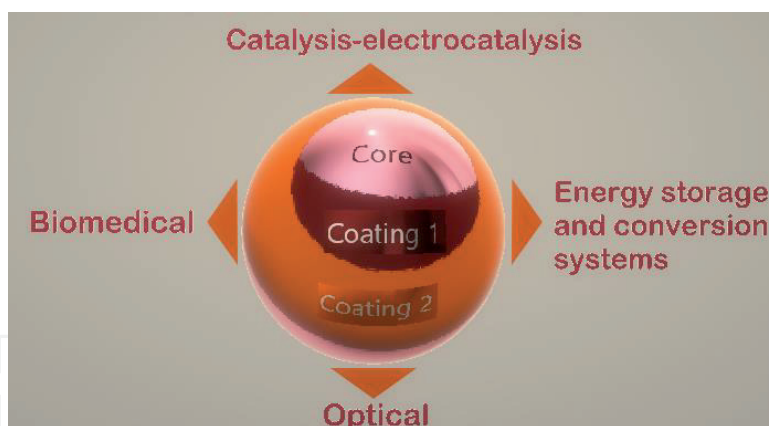


Figure 1.
Applications of multilayer coated-NMPs in advanced materials.

particles. Therefore, multilayer coated-NMPs structured have become one of the most popular research topics in recent years.

Nevertheless, synthesis of multilayer coated-NMPs has faced with concerns in terms of conformality and uniformity of coatings (shells). In one hand, the core particles might not only be considered as the spherical shape but also a variety of other shapes such as cube, prism, hexagon, octahedron, disk, wire, rod, tube, etc. can be employed. In the other side, fine particles are liable to clustering either by agglomeration (reversible) or aggregation (irreversible) processes due to the interparticle attractive force (IPF)-to-particle weight ratio (i.e., granular Bonding number) [9]. Therefore, to address such concerns, coating of fine particles as the synthesis of advanced materials needs a multidisciplinary understanding of powder technology and surface engineering.

In the present chapter, several multilayer coated-NMPs with different morphologies and compositions are discussed. The corresponding coated NMPs in various applications including catalytic, biomedical, energy, optical systems are reviewed (see **Figure 1**). Before digging into multilayer coated-NMPs, we found it quite necessary to make an applied understanding of particulate technology and classification. This would help to design the multilayered coating systems based on the corresponding powder characteristics. Indeed, the role of powder engineering cannot be ignored while particles are used as the substrate in a deposition system.

2. Particulate technology and classification

Powder technology is critically employed in the whole domains of particle processing and applications. Besides, a process involving solid particles cannot be conducted without the essential characterization of the particles of interest. Such characterizations encompass not only the intrinsic static parameters such as size, density, shape, and morphology) but also their dynamic properties attributed to the fluid flow, e.g., drag coefficient and terminal velocity. There are many techniques that can be employed to characterize particles, either simple or complicated. Namely, sieve analysis, imaging technique, dynamic light scattering (DLS) are used to directly characterize the particle size and shape. In addition, the physical gas adsorption technique based on the well-known BET (Brunauer–Emmett–Teller) method on monolayer coverage of adsorptives such as nitrogen is employed to measure the powder surface area and the pore size.

For a particle moving in a fluid (e.g., fluidization), the force acting on the surface of a particle depends only on the flow of the fluid in its immediate vicinity.

A widely used classification of particulate materials based on their fluidization properties has been long proposed by Geldart [10]. The empirical observations on fluidized particles in terms of particle size versus the relative density difference between the fluid phase and the solid particles are shown in **Figure 2** (classical Geldart's diagram). Such classification is in accordance with the behavior of powders as they are fluidized by dry air at ambient pressure and temperature.

Analogous to the Geldart classification typically used in the fluidized particles context, coated-particles can also be categorized based on the particle density and size. A useful nondimensional number to interpret the Geldart's diagram is the granular Bond number Bo_g , defined as the ratio of interparticle attractive force F_0 to particle weight W_p [11]. Fine cohesive particles ($Bo_g \gg 1$, typically $d_p \leq 20 \mu\text{m}$), possess the strong attractive forces existing between the particles when compared to their weight, are so-called Geldart C particles. For slightly cohesive particles ($Bo_g \sim 1$, $20 \mu\text{m} \leq d_p \leq 100 \mu\text{m}$, i.e., Geldart A particles), the particles are smoothly flowable. Therefore, Geldart A particles seem quite efficient for industrial applications. This might lead to an important criteria in terms of particles size and density when the coated-particles are needed to be utilized in the various industrial sectors. In addition, powders within the limit of noncohesive particles ($Bo_g \leq 1$, typically $d_p \geq 100 \mu\text{m}$ for dry particles,) are deemed in the group of Geldart B particles (i.e., granular materials).

2.1 Importance of multilayer deposition on particles

To utilize a synergistic properties of thin film coatings and the core particles, the thin film immobilized on fine particles can be a promising approach. The interaction between the thin films and the core fine particles result in adjustable properties of the coated particles. Therefore, such coated systems have been considered as an important class of emerging powder technology for a wide range of applications as it was mentioned above.

Coating the core materials successively with similar or different types of materials can result in so-called “core–multishell NMPs”, which have been

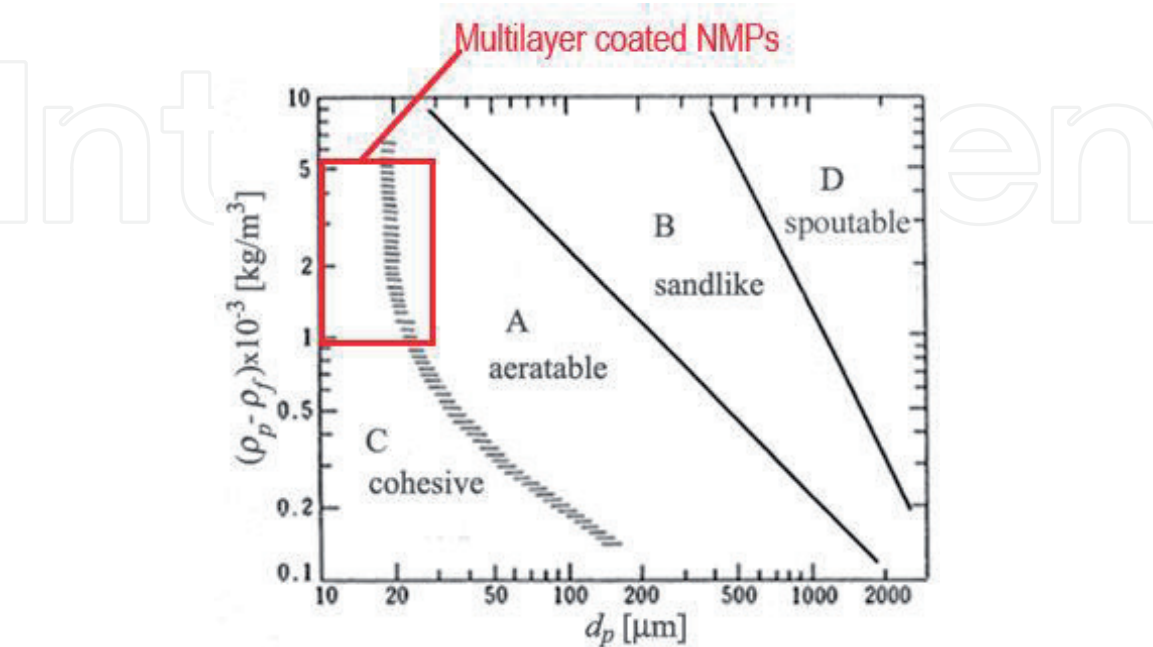


Figure 2. Classical Geldart's diagram for the types of behavior of powders fluidized by dry air at ambient conditions based on the difference between particle and gas density (vertical axis) and particle size (horizontal axis) [10].

explored recently for a number of applications ranging from catalysis to biology. The tunable construction of multilayer thin-film-based particulate has opened up new horizons in materials science and led to exciting new developments in many scientific areas during the past two decades. The multilayer coated particles benefit from the intrinsic potential for the combination of diverse building blocks through complementary interactions, i.e.: electrostatic interactions, hydrogen bonding, etc., to create thin films displaying functional groups and chemical entities at controlled sites in nanoscale arrangements [12]. In addition, a stepwise procedure is employed to utilize different functionalities of the multishell rather than just to protect the core materials. Furthermore, shielding the core from incompatible outer layers of such NMPs might be performed by the inner layers [13]. It should be noted that, traditionally, composite NMPs composed of inner material (core) and outer layer material (shells) are often defined as core-multishell NMPs (the notation of “@” represents the core-multishell structure, core @ shell_1 @ shell_2 @ ... @ shell_n).

Multilayer coating of powders can be applied by either wet chemical processes, such as sol-gel and impregnation [14, 15] or by dry techniques (i.e., the use of a reactive gas phase), including pyrolysis and chemical vapor deposition (CVD) [16]; however, most attention in the literature has been paid to the deposition on fine particles using wet chemical processes. This includes synthesis of core-shell particles or layer-by-layer (LbL) assembly [4]. Indeed, LbL technique initially employed the alternate deposition of oppositely charged polyelectrolytes to produce nanoscale films. Further, the LbL method was successfully applied to other building blocks. A broad variety of multilayer composite films have been constructed by replacing one or both polyelectrolyte counterparts with other charged building blocks such as proteins, dendrimers, lipids and colloidal nanoparticles [12].

2.1.1 Multilayer-coated particles in catalytic applications

Indeed, any advancement in the technology of powders can be employed to augment the catalytic reaction performance while working as a process engineer. In other words, multilayer structural features lead to designing a highly active and selective, low-cost and eco-friendly catalytic systems. This is due to the fact that the multilayer coated particles, i.e., catalysts, can synergistically take the advantages of the core (i.e., support) and the coated layers. For instance, a superior catalytic activity can be obtained by tuning the surface properties (surface area, porosity, etc.) of the core particles as the coating layers are properly engineered. In addition, combination of the properties of the core and shell might be utilized towards improved/combined applications (e.g. magnetically separable nanocatalysts with the possibility of the repetitive use without the loss of the catalytic efficiency).

$\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{TiO}_2$ coated-particles were developed through a hierarchical structure. The first layer of SiO_2 on the superparamagnetic Fe_3O_4 core was coated by a modified Stöber process. Subsequently, TiO_2 was deposited on top of the silica layer to obtain $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{TiO}_2$ composite. According to the x-ray diffraction (XRD) results, a uniform and well-defined morphologies with anatase crystalline TiO_2 was detected on the surface. However, the confirmation of the multilayer coatings of $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{TiO}_2$ with techniques other than microscopy has been yet a crucial challenge in the coated-NMPs context. In this study, the Fourier transform infrared spectroscopy (FTIR) spectrum was used to detect Si-O-Ti at the wave number around $940\text{--}960\text{ cm}^{-1}$. Moreover, decomposition of RhB under UV irradiation surpassed that of P25 composites, indicating good photocatalytic activity (see **Figure 3(d)**). Further, little drop in efficiency over 18 cycles together with the magnetic recoverability and good cyclability were reported [17].

Habibzadeh et al. deposited a multilayer film of $\text{TiO}_2/\text{SiO}_2/\text{TiO}_2$ on the surface of fine soda lime glass (SLG) particles by a fluidized bed chemical vapor deposition (FB CVD) technique (see **Figure 4(a)**). The optimal values of the gas velocity for different temperatures of the powder bed were obtained from the differential pressure measurements. Titanium dioxide was deposited at 300°C whereas the silicon dioxide deposition was implemented at room temperature. Focused ion beam

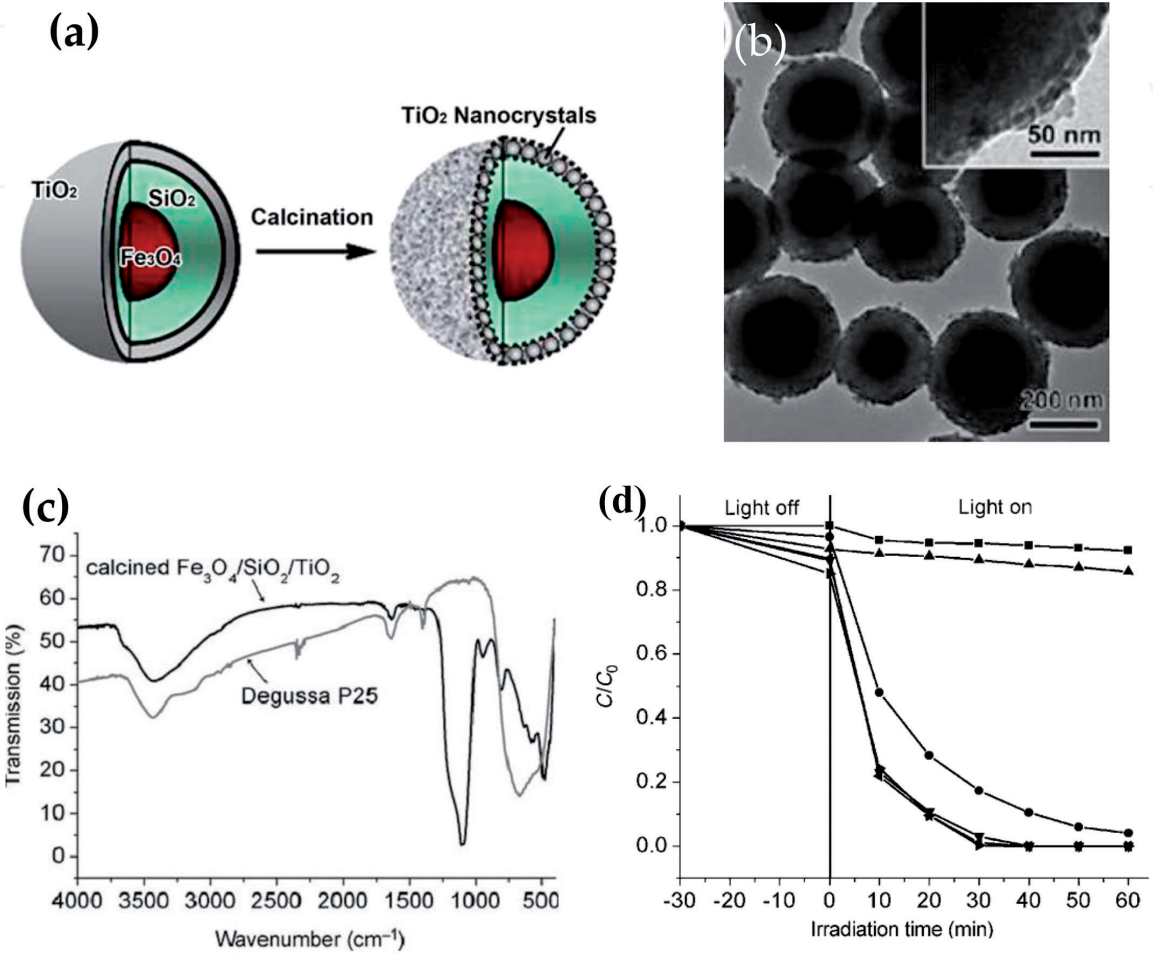


Figure 3. (a) Scheme of as-synthesized composite structure, (b) TEM images of calcined $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{TiO}_2$ particles (inset in TEM image is the magnified ones of the composite particles showing the morphological change in the TiO_2 shell due to calcination), (c) FTIR spectra of the calcined $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{TiO}_2$ structures and Degussa P25 (commercial TiO_2) and (d) Photocatalytic performance of various samples of catalysts (\blacksquare = UV, \bullet = TiO_2 spheres, Δ = $\text{Fe}_3\text{O}_4/\text{SiO}_2$, ∇ = $\text{SiO}_2/\text{TiO}_2$, \times = $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{TiO}_2$, \circ = P25) [17].

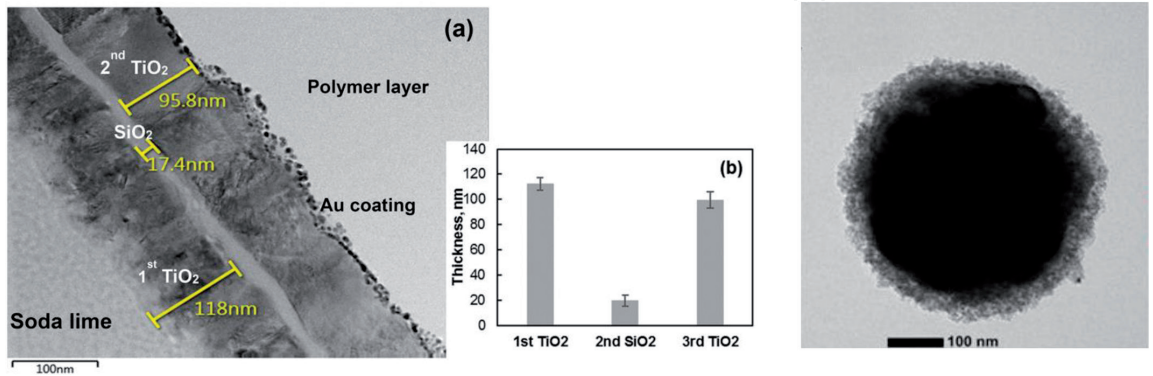


Figure 4. (a) FIB cross-sectional TEM image and (b) the average film thicknesses of the $\text{TiO}_2/\text{SiO}_2/\text{TiO}_2$ system on the surface of SLG fine particles. The gold and polymer layers are added during the preparation of the TEM sample (c) HRTEM images of $\text{CdS}/\text{PDA}/\text{TiO}_2$ core/shell hybrids [4, 18].

(FIB) cross-sectional transition electron microscopy (TEM) images (**Figure 4(a)**) showed a thickness of ~ 110 and ~ 20 nm for titanium and silicon dioxide deposited layers, respectively.

X-ray photoelectron spectroscopy (XPS) results confirmed pinhole-free and uniform multilayer coatings on the surface of silica microspheres. Moreover, the anatase crystalline and amorphous structures of TiO_2 and SiO_2 , respectively, were detected by XRD of the multilayer-coated particles. Uniform distribution of Ti and Si were also observed by energy-dispersive x-ray spectroscopy (EDS) elemental mapping analysis. In addition, it was found that the multilayer coatings developed in this study can be effectively employed as a photocatalyst in wastewater treatments [4].

The photocatalytic activity of the multilayer coatings, $\text{CdS/polydopamine/TiO}_2$ (CdS/PDA/TiO_2 -**Figure 4(b)**) was determined. The ternary coated-particles were synthesized where dopamine self-polymerization and titanium (IV) butoxide hydrolysis were conducted on CdS nanospheres through hydrothermal processes. A considerable increase in the reaction rate constants of such ternary hybrids (more than three times) towards the degradation of RhB, methylene blue (MB) and phenol as the pollutants were seen as compared to CdS/TiO_2 hybrids. The amended photocatalytic degradation was credited to the greater light absorption and charge carrier separation efficiency together with the introduction of PDA [18].

Xiong et al. [1] showed an enhanced catalytic activity of 3D ordered meso-macroporous $\text{Ce}_{0.3}\text{Zr}_{0.7}\text{O}_2$ -supported PdAu@CeO_2 nanoparticles for soot oxidation. The multilayered structure catalyst found to improve the activation property for gaseous reactants. In addition, the synergetic effect of Pd-Au- CeO_2 could promote the rate determining step. Yi et al. [19] reported the synthesis of a nanocomposite of $\text{Pd/SiO}_2/\text{Fe}_2\text{O}_3$ catalyst system utilized in hydrogenation of nitrobenzene. First, monodisperse silica-coated Fe_2O_3 nanoparticles ($\text{SiO}_2/\text{Fe}_2\text{O}_3$) were obtained in water-in-cyclohexane reverse microemulsion. Then, they were functionalized with mercapto and amine functionalities, which have been known to have strong affinity with transition metal nanoclusters, such as Pd, Fe_3O_4 , and Au. The multilayer coated catalyst resulted in five times higher conversion rate as compared to the commercial Pd/C.

Moreover, Pd@CdS@ZnO multilayer nanorods (NRs) showed a superior catalytic activity for the degradation of toxic organic pollutants due to the effective separation of electrons-hole pairs. The excitation-wavelength-dependent catalytic performance of Pd@CdS@ZnO NRs showed significant enhancement at the wavelengths equivalent to the CdS layer. The recyclability results revealed a strong ability with favorable reusable photocatalytic efficiency. Besides, electrochemical impedance and photocurrent detection analysis further confirmed a reduced in the charge transfer resistance of Pd@CdS@ZnO NRs owing to embedded Pd NPs and coating of a CdS layer on ZnO NRs [20].

2.1.2 Multilayer-coated particles in biomedical applications

The smaller size and high surface to volume ratio of fine particles are the key features which render them useful in the biomedical fields. In addition, multilayer-coated NMPs can be employed in the development of many new properties, ease of functionalization, conjugation of biomolecules, etc. In particular, the application of novel nanomaterials in the biomedical engineering has directed to the development of the new contrast agent and drug delivery vehicle, which are of great importance in the area of health care [7]. The discrepancy of nanoparticles has been applied in several researches attributed to disease diagnostics, early detection studies, and better contrast agents for enhanced imaging techniques.

Owing to greater bio- and cyto-compatibility as well as increased circulation time of new drug delivery vehicles the load of the drugs along with the efficacy of the drug in the system have been reduced. Thus, the appearance of nanoparticles has revolutionized all the matters related to the medical biotechnology and biomedical engineering. This results in improving the conventional techniques together with the experimentation of new and advanced techniques for drug delivery and its monitoring.

In biological applications multilayer-coated NMPs have major advantages over individual particles leading to the improvement of properties such as less cytotoxicity, more dispersibility, bio- and cyto-compatibility, better conjugation with other bioactive molecules, greater thermal and chemical stability and so on [21]. In other words, when the particles of interest are toxic which may cause plenty of issues to the host tissues and organs, the multilayer coatings of benign materials on top of the core render the nanoparticles much less toxic and bio-compatible.

Sometimes the coating layers not only act as nontoxic layers, but also improve the core material property. Moreover, hydrophilicity of particles is quite important to disperse them in biological systems (aqueous). The increase in biodispersivity, bio- and cyto-compatibility makes it a useful alternative to conventional drug delivery vehicle. In addition, many bio-applications are dependent upon the conjugation of biomolecules on the surface of particles. In particular, coating of a suitable bio-compatible material can help to conjugate a particular type of biomolecules with the surface of particles. Further, coating of an inert material generally enhances the stability of core particles when the core materials are susceptible to chemical or thermal change during exposure to surrounding environment. Thus, coated NMPs are more appropriate for biological applications than single nanoparticles.

In an in vivo experiment, dual imaging contrast agent for MRI and optical imaging purpose Gadolinium tetraazacyclododecanetetraacetic acid (Gd-DOTA) is covalently linked with silanized nanoparticle to form Gd-DOTA, and then attached to SiO₂ coated CdS/ZnS quantum dots (QDs) [22]. In fact, excitons (electron and hole) in a QDs (i.e., semiconductor nanoparticles) can restrict the movement of conduction band electrons, valence band holes and excitons in all three spatial directions. However, The main problem associated with QDs is its high toxicity, because of the presence of heavy metals in its core, which causes cell death due to leaching out to the external environment. The deposition of outer layers or employing another metal in place of toxic cadmium, from the respective QDs might lead to addressing the problems caused by cadmium. Kim et al. [23] performed cell labeling in Hela cells, a human cervical cancer cell line by CTAB to prepare CdSe/CdS/ZnS (core/shell/shell) QDs. Apart from CdSe@CdS@ZnS QDs which has been widely applied in cell labeling, multilayer coated-QDs such as CdSe@ZnSe@ZnS [24] and CdSe@Zn_{0.5}Cd_{0.5}Se@ZnSe@ZnS [25] have been used for imaging applications. In addition, CdSe@ZnS@SiO₂ nanoparticles [26] which gave stronger emissions with consistent fluorescence intensity than bare CdSe–ZnS nanoparticles alone, leading to improve imaging applications. Besides, the silica shell renders it suitable for conjugating with bioactive agents, needed for targeted delivery to the concerned imaging site [27].

The other aspect of coated-NMPs research revolves around targeted drug delivery. Namely, the cancer therapy and treatment of static tumors due to a low therapeutic index (ratio of therapeutic efficacy to side effects) of medication causes severe deterioration in health [28]. Therefore, the effects of these drugs should be target-oriented where the disorder of vulnerable cells is critical. Next, diabetes and cardiovascular diseases are regarded after cancer therapy considering medical importance; indeed, malfunctioning of certain tissue regions, or cells result in

such diseases. For instance, malfunctioning of pancreatic β cells leads to diabetes. Hence, a precise and permanent cure by targeting these cells particularly for drug therapy may eliminate the problem once and for all. Chitosan/B-lactoglobulin core/shell particles were successfully synthesized as nutraceutical carriers for nutrient delivery increasing permeability of the molecules, increasing gastric residence time. This subsequently provides the environmental stability (that it lacked in normal food processing). This encapsulated nutrient system rendered the oral administration safe [29].

As mentioned above, most particles-based drug delivery research is focused on cancer therapy. The material comprising the particles plays a significant role on the working mechanism. In the category of particle-based drug delivery carriers, two types are the most important; first, magnetic materials (i.e., iron and its oxides and sulfides), and secondly, noble metals such as gold and silver. The former materials, i.e. the magnetic, are mostly used as core materials since the corresponding surface exposure because is not required to exploit their properties. However, Au owing to its efficient surface functionalization of different ligands, might be used as a shell material.

In addition, most inorganic materials are toxic to the living system. Other metal oxide particles, i.e., TiO_2 , SiO_2 , ZnO have also been studied for drug delivery. Gold nanorods/mesoporous silica/hydroxyapatite (Au/ SiO_2 /HAP) hybrid nanoparticles with AuNR core and SiO_2 /HAP hybrid inorganic shell for multi-responsive drug delivery had been prepared. According to the in vitro results of the drug release, Au/ SiO_2 /HAP nanoparticles showed high drug loading efficiency, superb near-infrared (NIR)- and pH-responsive drug release properties. In addition, Au/ SiO_2 /HAP nanoparticles displayed a higher drug release of 37.62% upon NIR irradiation at pH 4.5 as compared to the drug release of Au/ SiO_2 nanoparticles over 12 h (about 6.35%). This is due to the NIR-responsiveness of AuNRs and the pH-responsiveness of HAP in acid media. Noticeable biocompatibility of the Au/ SiO_2 /HAP nanoparticles was shown based on the cell viability results [30].

Furthermore, applying an external magnetic field facilitates conducting the drug towards specific target cells while employing magnetic nanoparticles such as ferrites because of their biocompatibility and superparamagnetic behavior [31]. Although such magnetic core particles have been employed as the potential drug carriers through in vitro systems (i.e., simulating human physiological systems), one must take into caution the toxicity of the bare Fe particles. This can be attributed to the thrombosis formation (aggregation of Fe particles), induction of free radicals in bloodstream and their facile oxidizability. However, encapsulating of these ferrite particles with a noble metal layer, leading to better surface chemistry between the drug and the carrier and thus the corresponding structural stabilization. Namely, a shell of gold has been used in anticancer drugs such as doxorubicin. Such layer can effectively adsorb amine-groups, thus reducing particle aggregation by steric hindrance [32]. The adsorbed drug can be released to the target sites in response to ionic, pH stimuli or externally controlled mechanism (magnetic or thermal). Moreover, magnetic core/mesoporous silica shell structures have been studied for in-vitro drug carrier application [33]. While Fe/Au core/shell nanocomposites [34], $\text{Fe}_3\text{O}_4/\text{CaCO}_3/\text{PMMA}$ [35], Au/poly(L-aspartate-doxorubicin)-b-poly(ethylene glycol) copolymer [36] may also find similar biomedical applications in the near future.

2.1.3 Multilayer-coated particles in energy and other applications

Developing low-cost, eco-friendly systems with large energy conversion and storage efficiency have been recently addressed by emerging intricate

nanocomposites. Such structure with multilayer coatings can revolutionize the energy storage systems, i.e., supercapacitors, li-ions batteries and hydrogen storage as well as the corresponding energy conversion technologies including quantum dot solar cells, dye-sensitized solar cells, silicon/organic solar cells and fuel cell.

Supercapacitors (SCs) are typical energy storage devices encompassing electrochemical double layer capacitors (EDLCs), pseudocapacitors and asymmetric capacitors. The electrode materials of EDLCs can be used in mobile and stationary systems while high power pulses are required. EDLCs based on carbon materials have attracted much attention due to its high power density and long cycling life [37], which is attributed to the good electronic conductivity of carbon materials together with their high chemical stability and large specific surface areas. However, simultaneous fast charging/discharging rate, high energy density, and long cycle performance cannot be practically obtained through a single nano-structured electrode material owing to some inherent limitations of individual composition. For instance, carbon materials have excellent cyclical stability and high rate capability while faced with low specific capacitance. In general, the ideal multilayer coating structured nanomaterials in supercapacitors should meet a few critical requirements for coating materials. First, such coatings maintain structural integrity and limit volume expansion. It can protect the core particle from being affected by outside environmental and causes a rapid transport of electrons and ions.

As the second category of SCs, pseudocapacitors which store charges through a Faradaic process possess higher energy density compared to EDLCs [38]. Metal oxides and conducting polymers are employed as the promising materials for pseudocapacitors. Namely, metal oxides such as, ruthenium, manganese, nickel and iron oxides with two or more oxidation states and good conductivity as well as conducting polymers, e.g., polythiophene (PTh), polypyrrole (PPy), polyaniline (PANI) and their derivatives with high storage capacity/porosity and high potential window are considered as outstanding candidates for pseudocapacitors.

A hierarchical ZnO@MnO₂@PPy multilayer arrays (see **Figure 5(a–c)**) fabricated through layer-by-layer process as an active material for energy storage showed an enhanced electrochemical performance. Specific capacitance of 1281 F g⁻¹ at a current density of 2.5 A g⁻¹ associated with a significant areal capacitance of 1.793 F cm⁻² at a current density of 3.5 mA cm⁻² were resulted from such electrodes. Furthermore, excellent cycling stability of the ZnO@MnO₂@PPy ternary core-shell electrode (**Figure 5(d)**) with a capacitance retention of 90% after 5000 charge-discharge cycles at 5 A g⁻¹ was obtained [39].

Apart from the application of multilayer coatings in different types of supercapacitors, such coatings can be well employed as the electrode materials for lithium ion batteries (LIBs). Indeed, many impediments, such as the slow Li⁺ diffusion and high resistance at the electrolyte/electrode interface can be addressed by improving the reactivity and conductivity of Li⁺ ion/electron, accelerating charge across the electrolyte/electrode interface and shortening the Li⁺ extraction/insertion pathway. One of the most significant roles of the coatings on the cathodic and anodic LIBs' active materials is attributed to the electronic conductivity enhancement. This has typically been conducted by employing carbon material such as graphite or metal/metal oxides as well as conductive polymers. Zhang et al. [40] synthesized graphene@Fe₃O₄@C core-shell nanosheets (**Figure 6(a, b)**) have been rationally designed and fabricated by a solvothermal method, which have been demonstrated as a high-performance LIB anode material with a capacitance of 1200 mAh g⁻¹ after almost 100 cycles, indicating the great stability and usability of this modern structure. The obtained graphene@Fe₃O₄@C nanosheets contains Fe₃O₄ nanoparticles

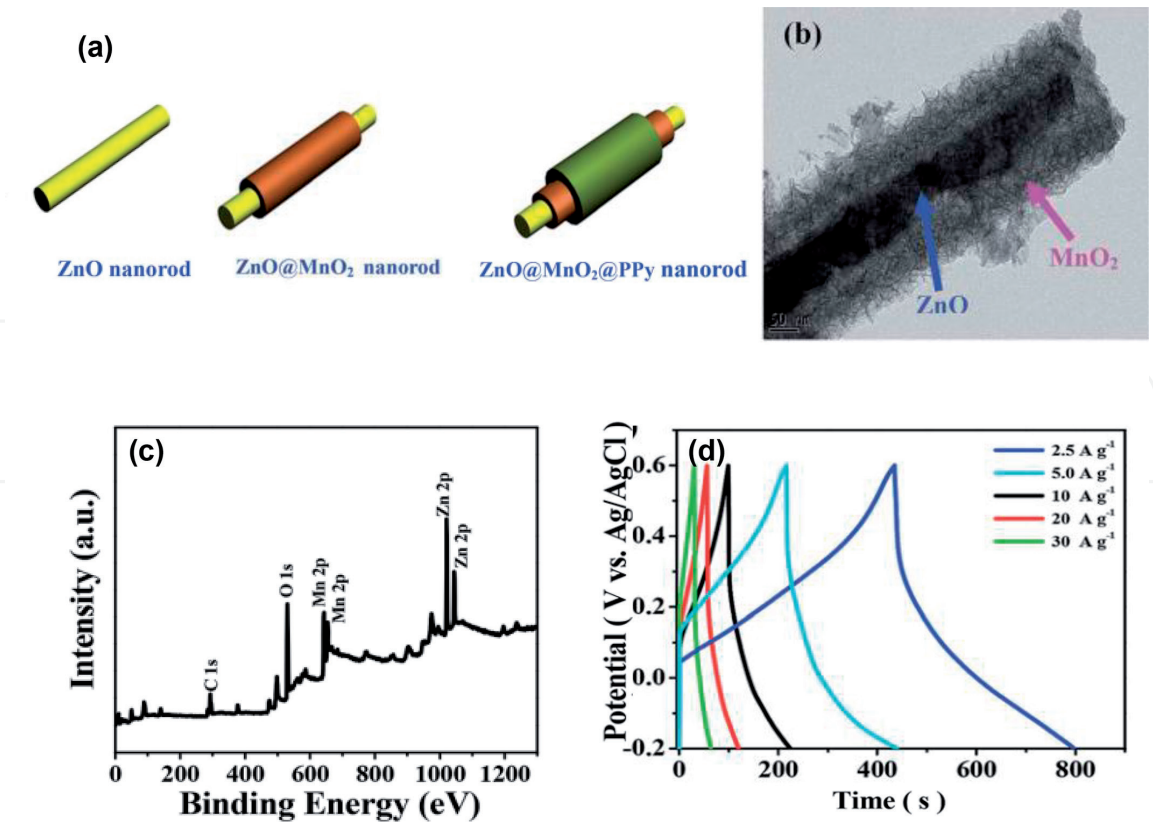


Figure 5. (a) Schematic illustration of the formation process for ZnO@MnO₂@PPy ternary core-shell nanorod arrays, (b) typical TEM images of ZnO@MnO₂@PPy nanorod arrays, (c) XPS survey spectrum of the ZnO@MnO₂ nanorod arrays, (d) the galvanostatic charge-discharge (GCD) plots at various current densities of ZnO@MnO₂ (c) and ZnO@MnO₂@PPy [39].

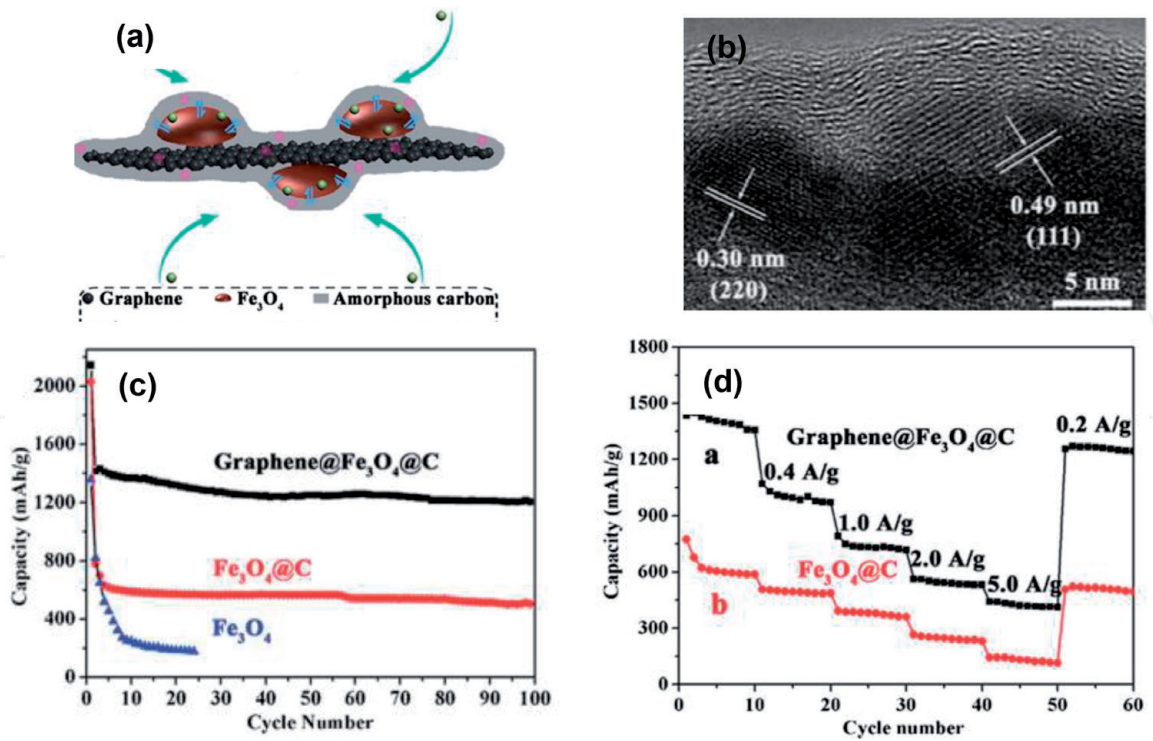


Figure 6. (a) Schematic representation of the electrochemical reaction path on the graphene@Fe₃O₄@C core-shell nanosheet electrode (b) HRTEM image of the graphene@Fe₃O₄@C core-shell nanosheet. (c) Cycling performance of the graphene@Fe₃O₄@C core-shell nanosheet, Fe₃O₄@C core-shell nanosphere, and Fe₃O₄ nanosphere electrodes at a constant current density of 200 mA g⁻¹, (d) cycling performance of the graphene@Fe₃O₄@C core-shell nanosheet (a) and Fe₃O₄@C core-shell nanospheres (b) at different current densities [40].

(6 nm) on the graphene sheets and coated by a uniform flexible carbon shell, as well as show a high surface area of $136 \text{ m}^2 \text{ g}^{-1}$.

The three-dimensional graphene foams encapsulated hollow $\text{SnO}_2@\text{Co}_3\text{O}_4$ were synthesized using 300 nm spherical SiO_2 particles as a template. The multilayer coated spheres fabricated through self-assembly in hydrothermal process from graphene oxide nanosheets and metal oxide hollow spheres. The encapsulated architectures could considerably enhance the capacity, cycling stability and rate capability of hollow $\text{SnO}_2@\text{Co}_3\text{O}_4$ spheres electrodes as the supercapacitor. This was because of the highly conductive networks and flexible buffering matrix [41]. Furthermore, the 3D $\text{h-SnO}_2@\text{Co}_3\text{O}_4@\text{GF}$ electrode was also evaluated as LIBs (Figure 7(a-c)). The lithium storage properties were conducted by using the as-synthesized products as anode materials and Li metal as the cathode. Figure 7(d) shows the discharge capacities of the different electrodes at current rates of 200, 500, 800 and 1000 mA g^{-1} , then returns to 200 mA g^{-1} . Obviously, the 3D $\text{h-SnO}_2@\text{Co}_3\text{O}_4@\text{GF}$ electrodes reveal superbly high rate capability relative to the other electrodes. For example, at a large current density of 1000 mA g^{-1} , 3D $\text{h-SnO}_2@\text{Co}_3\text{O}_4@\text{GF}$ electrode still delivers favorable capacity of about 380 mAh g^{-1} , while $\text{h-SnO}_2@\text{Co}_3\text{O}_4$ electrode only exhibits capacity of about 120 mAh g^{-1} , 3D $\text{h-SnO}_2@\text{GF}$ electrode retains 160.7 mAh g^{-1} and h-SnO_2 electrode retains only 56.4 mAh g^{-1} . When the current rate is returned to 200 mA g^{-1} , the stable capacity of 3D $\text{h-SnO}_2@\text{Co}_3\text{O}_4@\text{GF}$ is 676.6 mAh g^{-1} , which is 86.9% of the initial reversible capacity at 200 mA g^{-1} (Figure 7(e)). The values are much larger than these of 3D $\text{h-SnO}_2@\text{GF}$ (362 mAh g^{-1} and 57% retention), $\text{h-SnO}_2@\text{Co}_3\text{O}_4$ (287.9 mAh g^{-1} and 32.5% retention) and h-SnO_2 (165.2 mAh g^{-1} and 16.5% retention) [41].

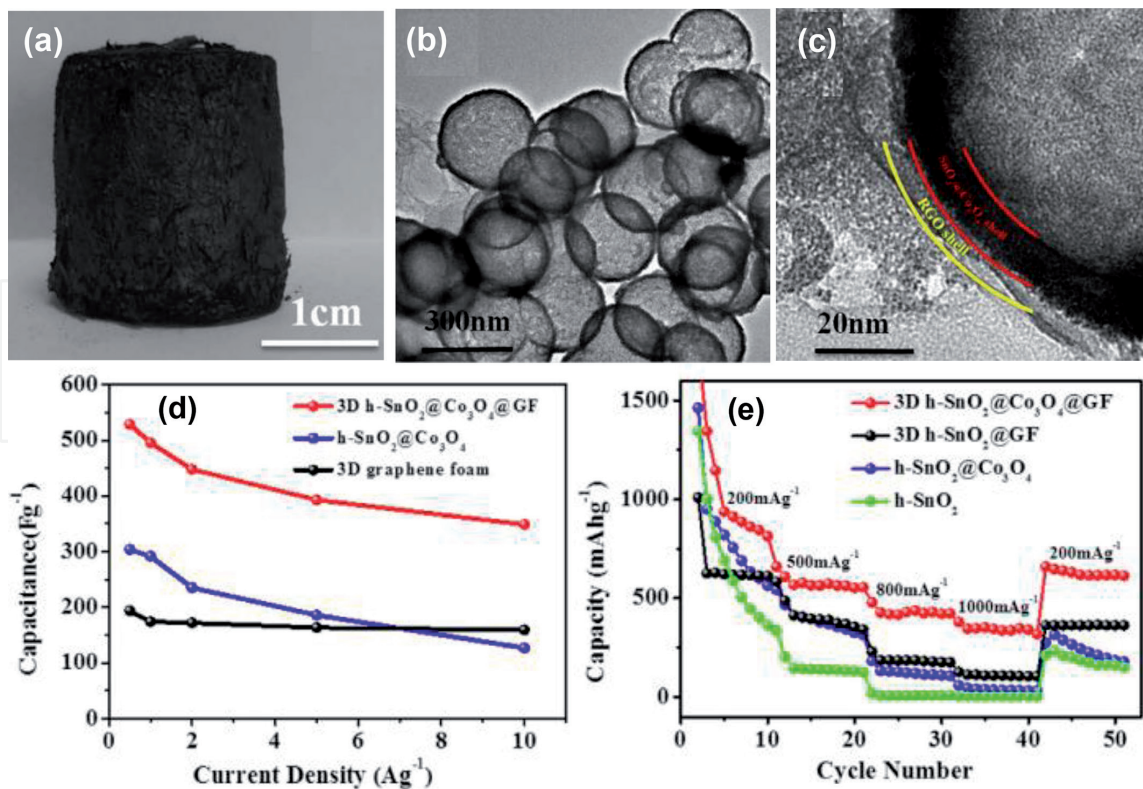


Figure 7. (a) Digital photograph of 3D $\text{h-SnO}_2@\text{Co}_3\text{O}_4@\text{GF}$, (b) 3D graphene foams encapsulated hollow $\text{SnO}_2@\text{Co}_3\text{O}_4$ spheres, (c) HR-TEM of 3D $\text{h-SnO}_2@\text{Co}_3\text{O}_4@\text{GF}$ structure (d) specific capacitance of 3D graphene foams, $\text{h-SnO}_2@\text{Co}_3\text{O}_4$ and 3D $\text{h-SnO}_2@\text{Co}_3\text{O}_4@\text{GF}$ electrodes, (e) cycling performance at various rates (from 200, 500, 800, 1000 to 200 mA g^{-1}) for the h-SnO_2 , 3D $\text{h-SnO}_2@\text{GF}$, $\text{h-SnO}_2@\text{Co}_3\text{O}_4$ and 3D $\text{h-SnO}_2@\text{Co}_3\text{O}_4@\text{GF}$ [41].

Xie et al. reported a core@double-shell structure to synthesize barium titanate (BT)-based high performance polymer nanocomposites. The first layer of hyper-branched aromatic polyamide (HBP) and the second one of poly (methyl methacrylate) (PMMA) were deposited on top of the core particles. The synergistic effect of both polymer shells, resulting in superior dielectric property. This cannot be obtained in nanocomposites prepared by the conventional blending methods. The energy densities of BT@HBP@PMMA nanocomposites were higher than that of BT/PMMA nanocomposites accordingly. The analyses of the dielectric response of the nanocomposites together with the mechanisms resulting in the higher dielectric constant and lower dielectric loss in BT@HBP@PMMA nanocomposites. As a result, the core@double-shell structure polymer nanocomposites can be considered a newly-designed architecture with desirable dielectric properties [42].

The role of multilayer coatings NMPs in the optical application is mostly dependent upon the shell layers' material and thickness. By varying the core and shell thicknesses, the color of such shells can be varied across a broad range of the optical spectrum spanning the visible and the near infrared spectral regions. The use of semiconductors either as the core or shells (multilayer coatings) have been much raised. The typical band gap for semiconductor particles is normally less than 4 eV, which are those normally found in insulating materials. In comparison with other fluorescent probes (organic dye or proteins), semiconductor nanoparticles or quantum dots as a new class of fluorescently labeled compounds render exceptional properties. In addition, since the fluorescent emission spectra of these particles can be tuned by changing the particle size, such semiconductor materials are preferably used in photoluminescence (PL) applications [43].

It should be mentioned that the main advantages of multilayer semiconductor NMPs are ascribed to the corresponding higher quantum yield, higher photoluminescence efficiency, improved optical properties, increased half-life times. In addition, facile detection of emission spectra of the semiconductor coated-NMPs is owing to their higher wavelength shift in the visible range, photo-oxidation stability, improved appropriate electronic properties (band gap, band alignment), and finally better structural (lattice mismatch) properties than unlayered fine particles. Moreover, lattice mismatch between the core and shell material can improve the luminescence properties no matter how significant is the shell thickness. Lattice mismatch refers to "the situation where two materials having different lattice constants are brought together by deposition of one material on top of another". It should be noted that the band gap as well as the lattice structure of the material are employed to form the semiconductor core particles and the multilayer coatings. Namely, CdSe/HgTe/CdTe [44], CdS/HgS/CdS [45] CdSe/ZnTe/ZnS [46] and etc. are the common multilayered coating structures applied.

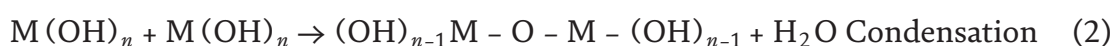
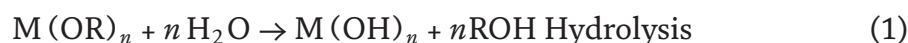
Kim et al. reported a multilayered core-shell composite particles with a high reflective efficiency and durability. The multilayer SiO_2 and TiO_2 were deposited onto the Fe/Ag microspheres by the corresponding precursors of tetraethyl orthosilicate (TEOS) and titanium n-butoxide (TBOT), respectively. The coating of shell layers were conducted through a sol-gel process. It was shown that the SiO_2 and TiO_2 multilayered shells render the Fe/Ag microspheres high efficient for preserving the reflectivity and increasing the durability of the core particles [47].

3. Synthesis and characterization of multilayer-coated particles

Conformal and uniform multilayer coatings NMPs are considered as an enormous challenge in the fine particles deposition. In particular, the situation would be more severe when the coating layer thickness must be controlled. Some of the

various synthetic methods for multilayer coated- NMPs used by different research groups are categorized into dry techniques (i.e., the use of a reactive gas phase), such as pyrolysis, chemical vapor deposition (CVD) [16] and atomic layer deposition (ALD) [48] onto particles or wet chemical techniques including precipitation, polymerization, microemulsion, impregnation and sol–gel condensation [8, 14, 15], layer by layer adsorption techniques [12], etc.

In order to conduct the synthesis of multilayer coated-NMPs, the techniques used to synthesize one of the most applied multilayer coatings, i.e., metal oxides, will be next discussed. Namely, the sol–gel technique is widely used as a wet chemical process when metal oxides are employed as the multilayer coatings. Indeed, this synthesis process encompasses three different routes. The reaction pathway might go through the gelation of solutions of a colloidal powder. The other pathway might be the hydrolysis Eq. (1) and polycondensation of metal alkoxides or metal salt precursors Eq. (2) followed by hypercritical drying of the gels. Apart from such two pathways, the commonly-used route for the synthesis of multilayer metal oxide coatings has been implemented by hydrolysis and polycondensation of metal alkoxide precursors followed by aging and drying under ambient atmosphere. It would be worth mentioning that the sol–gel process has preferentially been employed to synthesize the multilayer of silicon and titanium oxides.



Furthermore, most of the various types of oxides can be synthesized through the coprecipitation techniques. This is particularly applied for the metals which form the hydroxide precipitate in alkaline pH. In fact, a precipitation reaction results in at least one water insoluble salt which precipitates from the precursor media (i.e., two or more water-soluble salts). Such a precipitation reaction is significantly dependent upon the solubility product of the precipitated compound. Namely, the particle formation would begin as the concentration of the product goes beyond the solubility product value of the respective compound in the reaction media. The mechanism of multilayer coating formation via precipitation would follow the process of nucleation and growth (i.e., molecular addition, Ostwald ripening and aggregation) [8, 49, 50].

The characterization of multilayer coated-nanoparticles is not as straightforward as that of multilayer coatings on the common substrates with macro-dimension, e.g., silicon, steel, plastic, etc. In addition, it would be somewhat troublesome to distinguish the various coated layers on the fine particles; therefore, a reliable characterization technique is always necessary for the core and multilayer coatings. A similar approach for characterization of single particles can be applied for multilayer coated-NMPs; however one technique may not be sufficient. The characterization techniques for the measurement of size, shell thickness, elemental and surface analysis, optical properties, and thermal stability play more important role for multilayer coated-nanoparticles. Therefore, dynamic light scattering (DLS), scanning electron microscopy (SEM) or much higher magnification - FESEM (field-emission SEM) SEM, transmission electron microscopy (TEM), thermal gravimetric analysis (TGA), X-ray photoelectron spectroscopy (XPS), photoluminescence (PL), and UV-vis spectroscopy are the ones most often used [4, 8, 51–55].

Among the electron microscopy techniques (SEM, TEM), TEM provides much more important information. Namely, TEM can result in corroboration of core/multilayer coatings through contrast difference, overall particle size, core

size, shell thickness, uniform or nonuniform shell coating, lattice fringes of the coating material, etc. Besides, the size and morphology of the particles can be determined from the contrast difference of the core and shell materials. In order to reach the resolution even at the molecular level, much higher magnification, HR-TEM (high-resolution TEM) is used. Images can release valuable outcomes on crystallinity, lattice fringes, and even the d-spacing of the multilayer coated-NMPs. Nevertheless, two-dimensional images of the surface cannot be obtained by these electron microscopy techniques (SEM, TEM); thus, it is difficult to understand the roughness of the surface. Therefore, additional information can be found through the scanning probe microscopy (STM, AFM, etc.) techniques. Besides, the diameter and height of the particles can be obtained using such microscopy techniques.

More importantly, XPS is a useful spectroscopic technique to reveal surface information including elemental composition, chemical status, and electronic state or binding modes of surface ligands, and depth analysis or atomic composition with depth. The kinetic energy (KE) and/or binding energy (BE) together with the number of electrons escaping from a 1–10 nm thick layer of the surface is possible to measure using this technique. The main disadvantages of XPS are the maintenance and operating costs. Namely, it requires an ultrahigh vacuum (UHV) chamber and characterization is only possible to a depth 10 nm from the particle surface [4].

4. Conclusions

This chapter reviewed a newly-emerged topic in the coating research area. Multilayer coated NMPs have been showed to render the powder technology more room to grow. The new properties of the coated particles can be employed to develop multicomponent nano/micro particles in the various applications. Particulate technology together with the surface engineering concepts was properly discussed to address the current advancement and challenges in the particle deposition technology.

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