

# Core–Shell Pigments Nanostructure

Subjects: Nanoscience & Nanotechnology

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Uses of novel technologies for improving the durability and lifespan of the construction materials have emerged as viable solutions toward the sustainable future wherein the coating industry plays a significant role in economy growth and better livelihoods. Thus, the continual innovation of various technologies to introduce diverse market products has become indispensable. Properties of materials like color stability under UV, elevated temperatures and aggressive environments, and skid and abrasion resistance are the main challenges faced by commercial coating materials, leading to more demand of natural materials as sustainable agents. Lately, nanostructured core–shell pigments with unique compositions have widely been utilized in composite materials to enhance their properties. Core–shell particles exhibit smart properties and have immense benefits when combined with building materials.

Keywords: nanotechnology ; core–shell pigments ; SiO<sub>2</sub> ; TiO<sub>2</sub> ; Fe<sub>2</sub>O<sub>3</sub> ; cyclist roads

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## 1. Introduction

In recent years, synthetically colored pigments have been introduced in various market products. Consequently, they have been the subject of extensive scientific investigation. The most common uses of pigments are in paints, varnishes, printing inks, plastics and textiles, leather decoration, building materials, rubber, paper, ceramic glazes, and so forth [1][2]. The durability of pigments refers to their capacity to withstand weathering processes and avoid deterioration when exposed to an external environment [3]. Studies have revealed that efficient uses of energy for construction materials production can protect the environment [4]. Thus, the development of durable and sustainable pigments has become fundamental in the construction industry. Diverse methods have been introduced to improve the durability of pigments, especially the core–shell approach for smart/functional materials preparation [5][6][7][8].

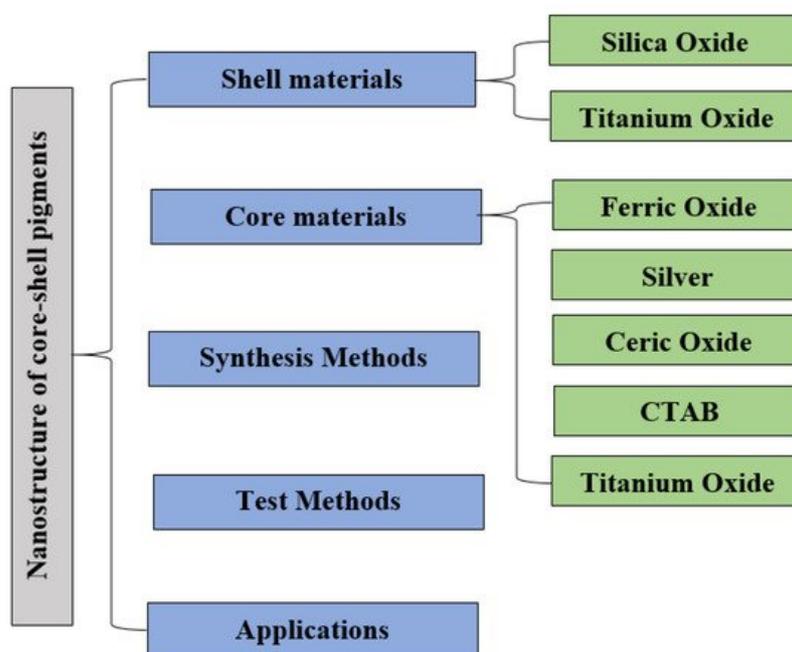
Earlier, different chemical techniques have been developed to prepare high-quality core–shell nanostructures. The multicomponent materials were shown to have better properties due to their diverse compositions and structures, making them versatile for widespread applications [9][10][11][12]. Owing to their distinct properties, core–shell structures have received intense research attention. These structures are more advantageous than other composite materials. For example, they can strengthen or generate new chemical and physical capabilities, facilitate the structural integrity desirable for self-maintenance, stop the core from breaking up into large particles, and ensure effective dispersion. In addition, they offer other benefits, like typical multifunctional compositions and structures. A higher performance can be achieved in the presence of synergy between the shells and cores [13].

The properties of materials obtained from core–shell particles can be finely tuned, making them fundamentally interesting in the fields of science and technology [1][14][15]. In every core/shell particle, there is a core structural domain cloaked by a shell domain. Various types of materials can constitute the core and shell domains, such as metals, polymers, and inorganic solids. It is easy to modify the structure, size, and composition of these particles to customize their mechanical, optical, magnetic, thermal, catalytic, electrical, and electro-optical attributes. To create hollow spheres and reduce the expenditure of these precious materials, core/shell morphology can be employed, in which the materials with relatively cheaper cores are coated with expensive materials [16][17].

Nanoparticles are defined as particles with diameters below 0.1  $\mu\text{m}$ , and such particles are attractive for diverse functional applications. In essence, these nanoparticles can be considered as smart materials due to their distinctive properties. Nanoscale systems are more advantageous than microscale, macroscale, and bulk materials because of their large surface area-to-volume ratios and quantum size effects [18][19]. The development of new and advanced synthesis methods has enabled the production of symmetrical (spherical) and various other shaped nanoparticles (e.g., cube, prism, hexagon, wire, rod, and tube) [20][21][22]. Nonetheless, the preparation and characterization of differently shaped nanoparticles have only been performed recently. Some reports have indicated that it is relatively easier to make non-spherical nanoparticles than other shapes [23][24][25]. It is important to note that the properties of these nanoparticles are both size- and shape-dependent. For instance, some properties of magnetic nanocrystals (including blocking

temperatures, permanent magnetization, and magnetic saturation) are determined by their particle size, whereas the coercivity of such a system is decided by their shape due to its impact on the surface anisotropy. For this reason, nanoparticles are often used to improve the pigment performance [26].

Nanotechnology has developed rapidly in recent years, and consequently, core-shell nanoparticles (NPs) have emerged as the key functional material. Currently, many researchers have been investigating core-shell NPs with different functional compositions. They find a wide range of applicability in various fields, including biomedicine, electronics, optics, catalysis, and pharmaceuticals [27]. Core-shell nanoparticles have distinct physiochemical traits and, thus, attract substantial research interests [22][28]. The key advantages of core-shell nanoparticles are enhanced levels of protection, encapsulation, and controlled release. Different types of core/shell nanoparticles have been identified and applied for various practical purposes. However, it remains challenging to classify all the available core/shell nanoparticles based on their industrial applications due to their wide varieties. Some studies were conducted on the pigments made from core-shell nanoparticles to outline their production methods and the nature of their core and shell materials, as well as their uses. Considering the immense benefits of core-shell nanostructures, this paper will analyze the key features and properties of such nanosystems. The features of inorganic materials and their fabrication methods and common uses are underscored. First, a brief overview of the different methods for the production of these particles is underlined. Next, different classes of existing core-shell materials and their uses are highlighted. Later, various latest techniques for the synthesis of core-shell pigment nanocapsules, followed by the use of core-shell nanoparticles in road paints, are explored. Finally, the paper is concluded, followed by some recommendations for further research and development within this field. **Figure 1** provides the overall structure of this paper.



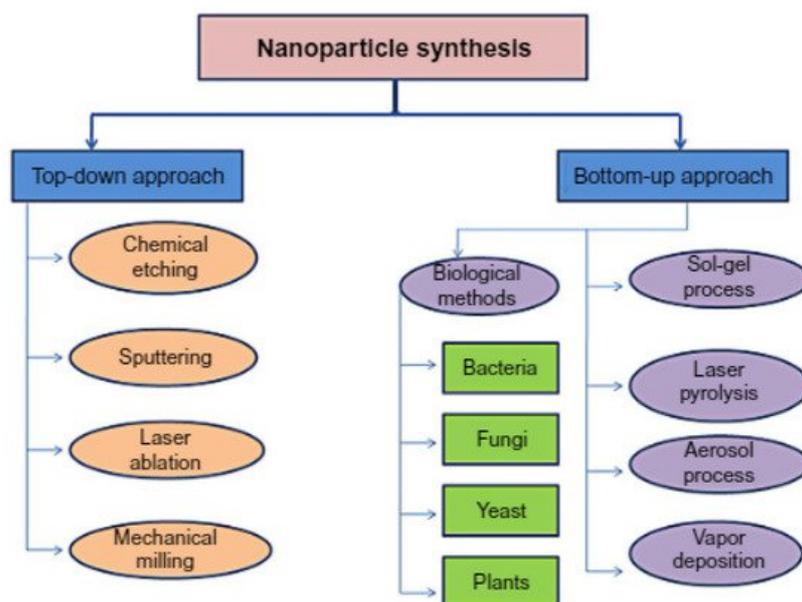
**Figure 1.** Flow chart of core-shell pigment materials, synthesis, test methods, and applications. CTAB: Cetrimonium bromide  $[(C_{16}H_{33})N(CH_3)_3]Br$ .

## 2. Core-Shell Nanoparticle: Synthesis Approach and Importance

Nanotechnology refers to the atomic-level manipulation of materials that can be performed by combining the engineering, chemical, and biological approaches. Several techniques can be used to synthesize nanoparticles, like chemical, biological, physical, and even hybrid approaches (**Figure 2**). Generally, two key types of approaches are used for the production of nanostructures: “top-down” and “bottom-up”. In the former (“top-down”) approach, traditional workshops and microfabrication techniques are used in addition to externally controlled equipment to cut, mill, shape, and mold materials into their desired forms. The most common top-down methods are the lithographic techniques (e.g., UV, electron or ion beam, optical near-field scanning, laser beam processing, and scan probing) and mechanical methods (i.e., machining, grinding, and polishing) [29][30][31][32]. Conversely, the “bottom-up” approaches focus on the manipulation of the chemical properties of molecules, forcing them to self-assemble into a new and more beneficial form with emergent traits. The most commonly employed bottom-up approaches include chemical synthesis, laser-induced assembly, chemical vapor deposition, colloidal aggregation, self-assembly, and film deposition and growth [33][34]. Both approaches have strengths and weaknesses. Nonetheless, one key advantage of the bottom-up approach is that it can create much smaller particles and may be more cost-effective than the top-down approach due to its absolute precision, minimal energy loss, and

complete control over the whole process. With regards to the synthesis of core/shell nanoparticles, ultimate control is needed to create a uniform coating around the core materials while the particles are forming. In this respect, a bottom-up approach would be more appropriate. In addition, a hybrid approach can also be used. For example, a top-down approach may be used to make the core, and a bottom-up approach can be subsequently employed to maintain the shell's thickness. As water droplets can serve as nanoreactors, the use of microemulsion is also recommended to regulate the size and thickness of shells.

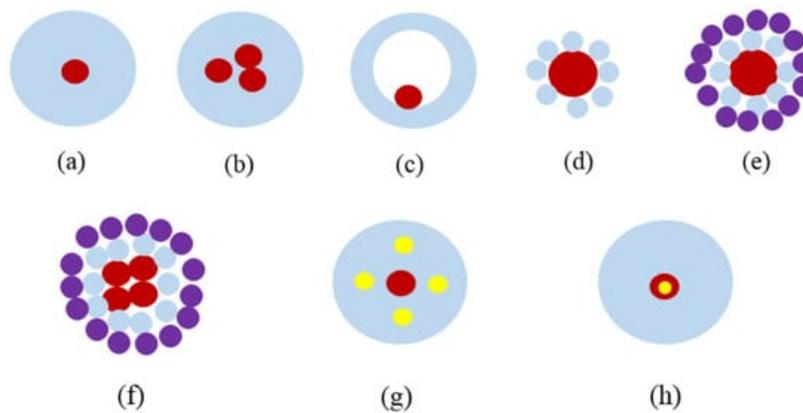
Nowadays, several researchers are turning their attention towards core/shell nanostructures because of their great benefits in a raft of fields, including chemistry, electronics, pharmaceuticals, optics, biomedicine, and catalysis. Additionally, these nanoparticles are highly functional and show specialized properties, wherein the characteristics of the core or shell materials can be entirely different. It is possible to modify these properties by altering the materials or the core-to-shell ratio [35]. Interestingly, the reactivity and thermal stability of the core materials can be changed by modifying the shell coating, thereby enhancing the stability and dispersion of the core particles. This, in turn, results in unique properties of each material employed, wherein the resultant product has an inherent ability to modify the surface functions based on the environment when implemented [36]. Some benefits of coating the core particles include the facilitation of surface modifications; enhanced functionality, stability, and dispersion of core particles; the significant reduction of expensive material consumption; and controlled release of the core.



**Figure 2.** The synthesis of nanoparticles using different approaches [37].

### 3. Core–Shell Synthesis Methods

As aforementioned, core–shell particles are particles that consist of a shell and a core, wherein both can be made using the same or different materials [38][39][40]. **Figure 3** shows various core/shell particles, wherein the core and shell are marked in different colors. The core can be in the form of a single sphere (**Figure 3a**) or a collection of many small spheres (**Figure 3b**). Moreover, there may be a hollow shell with a small sphere inside, which appears in a yolk–shell structure (**Figure 3c**) [41]. The shell structure may be in the form of a continuous layer (**Figure 3a–c**), multiple smaller spheres accumulated onto a larger core sphere (**Figure 3d,e**), or a simple collection of core spheres (**Figure 3f**) [42]. In fact, the insertion of smaller spheres into the shell can be performed to produce more intricate core/shell structures (**Figure 3g**) [43]. Alternatively, the same process can be carried out using multiple shells (**Figure 3h**) [44][45]. Varieties of chemical or physical methods can be used to synthesize core/shell nanoparticles, including wet chemistry and chemical/physical vapor deposition. Generally, multiple steps are involved in core–shell particle production. Typically, core particles are synthesized first; after which, a shell is created around the particle. However, the methods used to achieve these nanoparticles vary according to the type of core and shell materials under consideration [21]. The primary objective of core–shell particle preparation is to bring together the desired properties of diverse materials and structures to produce a synergistic effect, stabilize the active particles, and generate biocompatible properties [46]. **Figure 3** illustrates various types of core–shell structures, depending on the type of core and shell materials, preparation method, and applications.



**Figure 3.** Schematic representation of different types of core–shell particles (a) single sphere (b) several small spheres (c) yolk-shell (d) small spheres onto small cores (e) small spheres onto big core (f) core spheres (g) smaller spheres into the shell (h) multiple shells.

Core–shell nanoparticles have become a fundamental nanomaterial for various industrial usages. During the preparation of core–shell NPs, it is important to identify a simple, quick, and cost-efficient method with the least-possible negative impacts on the environment. To meet this target, several methods have been developed, including the microemulsion, sol–gel, microwave synthesis, multistep reduction, epitaxial growth, electrochemical dealloying, sonochemical processing, and Stöber methods. Alternatively, these methods can be combined to create a hybrid method. Amongst all these approaches, the sol–gel method is most common for core–shell NP preparation. This method is a relatively new approach for preparing nanoparticles that allows for more control over the reaction processes involved in synthesizing solid materials. Homogenous multicomponent systems are easy to acquire, especially homogenous mixed oxides that can be prepared through the mixing of molecular precursor solutions. The sol–gel method is used in materials science to transform small molecules into solid materials. It is often applied to produce metal oxides like SiO<sub>2</sub> and TiO<sub>2</sub>. To achieve this, the monomer must be converted into a colloidal solution (sol), which then serves as a precursor for a combined network consisting of network polymers or discrete particles. Generally, the metal alkoxides are used as precursors. During the chemical reaction, a colloidal solution called a “sol” is produced and gradually forms a gel-like diphasic substance consisting of a liquid and a solid phase. The morphologies of these phases can be in the form of discrete particles or continuous polymer networks. With regards to the colloid, it may be necessary to remove vast amounts of liquid if the volume fraction of the particles (or particle density) is extremely low in order to evoke the gel-like properties. It can be achieved in several ways, wherein the easiest one is to allow sufficient time for the sedimentation to occur. Subsequently, the remaining fluid can be poured away. Conversely, phase separation can be sped up through a process called centrifugation. As a wet chemical process, the sol–gel method is widely applied to produce core–shell nanoparticles [47][48][49].

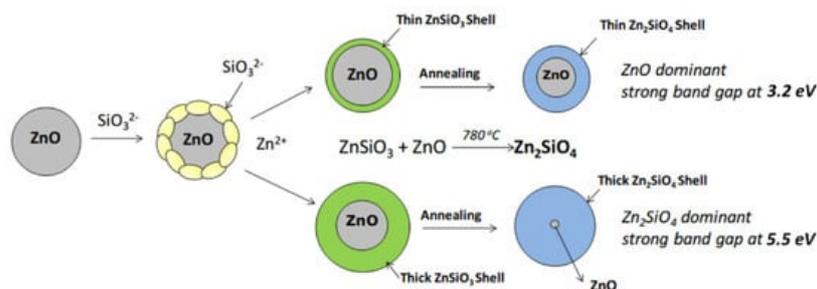
Microemulsions are isotropic liquid mixtures consisting of water, surfactant, oil, and often, cosurfactants thermodynamically stable and clear in appearance. There may be salt present in the aqueous phase, as well as various other ingredients. The “oil” may actually be an intricate mix of various different hydrocarbons. As opposed to normal emulsions, microemulsions are created by mixing components, and no high shear conditions are required to produce them. There are three main types of microemulsions—namely, direct (oil dispersed in water, o/w), reversed (water dispersed in oil, w/o), and bi-continuous. Microemulsions are ternary systems in which two separate immiscible phases (water and “oil”) occur with a surfactant, and the surfactant molecules can create a monolayer between the oil and water. Additionally, the surfactant molecules have hydrophobic tails that dissolve during the oil phase, whilst hydrophilic head groups dissolve in the liquid phase. To synthesize gold and silver core–shell bimetallic nanoparticles quickly, two-step microwave irradiation is often used. This strategy requires the creation of a bilayer organic barrier around the core, which is achieved using citrate and ascorbic acids, which serve as capping agents. In turn, this enables a well-defined boundary layer to be established between the core and the shell materials. The boundary layer plays a vital role in the process of synthesizing various core–shell particles, which results in the production of modifiable bimetallic NPs with clearly defined core/shell structures. These nanoparticles may have spherical or triangular seed cores.

Another technique that can be used to create core–shell materials such as carbon nanotubes is high-pressure chemical vapor deposition. This method was developed by Nikolaev et al. [50] with the main focus of creating a single-wall carbon nanotube by combing CO with a small quantity of Fe(CO)<sub>5</sub> and passing the mixture through a heated reactor. El-Gendy et al. [51] synthesized carbon-coated Fe, Co, Ni, FeRu, CoRu, NiRu, NiPt, and CoPt nanoparticles using high-pressure chemical vapor deposition and manipulating the temperature and pressure inside the reactor. In these experiments, metal–organic precursors known as metallocenes (carbon-rich metal elements) were used. The precursors were inserted

into a thermostatic sublimation chamber; after which, argon gas was passed through the chamber to push the vapor into the reactor's hot zone. The precursors could then break down the nanoparticles in the cooling finger. The precursor entered the gas phase in the hot zone to perform a supersaturation. Subsequently, the nanoparticles were nucleated when the supersaturation was achieved. The extent of a supersaturation can be changed by controlling the temperature inside the sublimation chambers and the pressure/temperature inside the chemical vapor deposition reactor. High pressure increases collisions between gas atoms, which ultimately reduces the rate at which atoms diffuse away from the original location. However, it is important to note that supersaturation cannot be achieved if the diffusion rate is poor, and this will result in single atoms or tiny clusters of atoms being deposited on the cooling finger.

The wet chemical technique was used [52] to synthesize Fe<sub>2</sub>O<sub>3</sub> coated with graphene shells. A solution containing oleic acid and 1-octadecene was heated to 320 °C in a reflux reactor to dissolve purified iron oleate. Subsequently, ethanol and acetone were applied to wash the solution in order to generate iron oxide particles. Additionally, the Stöber process is commonly used to prepare silica (SiO<sub>2</sub>) particles [53] of controllable and uniform size [54], and these particles can be used for many purposes in the field of material science. This method was proposed by Werner Stöber et al. in 1968 [53] and is still the most common wet chemistry synthetic approach employed to prepare silica nanoparticles [55]. This technique is a sol-gel process, in which a molecular precursor (typically tetraethylorthosilicate) is placed in water and reacted with an alcoholic solution. This causes the newly produced molecules to join together and create bigger structures.

Du et al. [56] used a sol-gel reaction to coat Fe<sub>3</sub>O<sub>4</sub> nanoparticles with a SiO<sub>2</sub> shell, yielding a core/shell structure. To synthesize the core/shell nanocomposites, a two-step procedure was used. First, the coprecipitation method was used to acquire Fe<sub>3</sub>O<sub>4</sub> nanoparticles; after which, electrostatic interactions with tetramethylammonium hydroxide (TMAOH) were performed to disperse the particles in a liquid solution. Secondly, the produced SiO<sub>2</sub> during the hydrolyzation of tetraethyl orthosilicate (TEOS) was used to cap Fe<sub>3</sub>O<sub>4</sub>. **Figure 4** presents the sol-gel technique used by Li et al. [57] to produce ZnSiO<sub>3</sub>/ZnO core-shell nanoparticles. In this experiment, they combined the sol-gel with an annealing technique to synthesize zinc silicate-zinc oxide (Zn<sub>2</sub>SiO<sub>4</sub>@ZnO) core-shell nanoparticles with a high band gap energy. First, the concentrations of the Na<sub>2</sub>SiO<sub>3</sub>/ZnCl<sub>2</sub> precursors were modified to coat ZnO nanoparticles with ZnSiO<sub>3</sub> shells of various thicknesses; after which, a low annealing temperature (780 °C) was set. This caused the amorphous ZnSiO<sub>3</sub> to react with ZnO and to produce a crystalline Zn<sub>2</sub>SiO<sub>4</sub> shell. The sol-gel technique was also used by Chai et al. [47] to produce core/shell-structured Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> nanoparticles. They employed a two-step process to create silica-coated magnetite (Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>) core-shell nanoparticles. Firstly, they used a solvothermal technique to fabricate Fe<sub>3</sub>O<sub>4</sub> nanoparticles. Subsequently, SiO<sub>2</sub> produced during the hydrolyzation of tetraethyl orthosilicate was used to coat the Fe<sub>3</sub>O<sub>4</sub> nanoparticles.

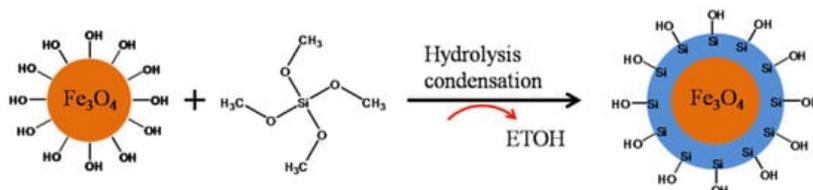


**Figure 4.** Sol-gel method for the fabrication of core-shell particles [57].

A two-step reduction method was used [58] to produce epitaxial Au@Ni core/shell nanocrystals. The first step involved mixing octahedral, triangular and hexagonal platelike, decahedral, and icosahedral crystals; after which, HAuCl<sub>4</sub> was reduced in ethylene glycol (EG) and heated in a microwave with polyvinylpyrrolidone (PVP) added as a polymer surfactant. This enabled the core seeds to be produced. After this, oil bath heating was carried out to reduce Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O in EG with NaOH and PVP using oil bath heating in order to overgrow the Ni shells on the Au core seeds. Similarly, Fan et al. [59] employed a two-step seed-mediated growth technique using Au cores to test the synthesis of bimetallic core-shell nanocubes in liquid phases. The formation of heterogeneous core/shell structures for four typical noble metals (i.e., Au, Ag, Pd, and Pt) was systematically assessed. The findings of these experiments highlighted the growth modes and general requirements for achieving conformal epitaxial growth, as well as the heterogeneous nucleation and formation of different noble metals. It identified two types of growth for heterogeneous metal shells on gold cores—namely, conformal epitaxial growth (Au@Pd and Au@Ag nanocubes) and heterogeneous nucleation and island growth (Au@Pt nanospheres). Based on their findings, it was concluded that the two metals should have comparable lattice constants, with mismatches being below 5%. Other researchers also confirmed the validity of these findings (Au@Ag (lattice mismatch, 0.2%), Au@Pd (4.7%), and Pt@Pd (0.85%)) [60][61][62].

Tsuji et al. [63] used a one-pot polyol technique to synthesize Ag@Cu core-shell nanoparticles with a high yield. In this method, bubbling Ar gas was used. Chemical reagents such as AgNO<sub>3</sub> and Cu(OAc)<sub>2</sub>·H<sub>2</sub>O were added to serve as the reagents. First, AgNO<sub>3</sub> was reduced in ethylene glycol (EG) to synthesize Ag@Cu particles via a two-step process. To start, Ag cores particles were separated from AgNO<sub>3</sub>; after which, Cu(OAc)<sub>2</sub>·H<sub>2</sub>O was added to create Cu shells. However, this was ineffective and produced no Cu@Ag core-shell particles; rather, Cu/Ag bi-compartmentalized particles were produced. In this work, Ag@Cu particles were prepared using different methods at various reaction temperatures and heating times. It was observed that adding the two reagents in reverse was the most effective way of producing Ag@Cu particles. To start the process, 8 mL of 15.9-mM Cu (OAc)<sub>2</sub>·H<sub>2</sub>O in EG and 8 mL of 477-mM poly(vinylpyrrolidone) (PVP; MW: 55,000 monomer units) were placed in EG, and the solution was mixed in a 100-mL three-necked flask. To eliminate all of the oxygen from the solution, Ar gas was bubbled for 10 min at room temperature. The solution was soaked in an oil bath at 180 °C. Subsequently, the temperature was increased to 175 °C, and the solution was left to bubble in Ar for several minutes; after which, 2 mL of 15.7-mM AgNO<sub>3</sub> was added to the reagent solution and kept for 20 min at 175 °C. The concentrations of the final yields were 7.0 mM for Cu (OAc)<sub>2</sub>·H<sub>2</sub>O, 1.7 mM for AgNO<sub>3</sub>, and 212 mM for PVP. The influence of different reaction times was tested on the reagent solution to further investigate the Ag@Cu growth process.

A modified Stöber technique was used by Chae et al. [47] to produce Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>. A sol-gel method was employed to prepare the Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> nanoparticles. The synthesis method involved the addition of 4 g of Fe<sub>3</sub>O<sub>4</sub> particles and 4 mL of tetraethyl orthosilicate to 40 mL of deionized water, followed by ultrasonication to mix the solution, forming a stable emulsion. Thereafter, the emulsion was inserted into a mixture containing 50 mL of ethanol and 12 mL of NH<sub>3</sub>·H<sub>2</sub>O. The resultant solution was stirred for 4 h at room temperature at a rate of 400 rpm, followed by centrifugation to separate the core-shell structure of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>. **Figure 5** demonstrates the procedure for Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> synthesis.



**Figure 5.** The Stöber method for Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> nanoparticle synthesis [47].

Sharma et al. [64] showed that core/shell particles can be fabricated through precipitation without a surfactant. They investigated the impacts of different surfactants and various concentrations on core-shell particle development. To investigate this, anionic and nonionic surfactants were tested. Additionally, fly ash was employed to create nanoTiO<sub>2</sub> for shell coating [64]. The main purpose of using surfactants was to enhance nanotitania shells' adhesion to fly ash core. It was concluded that, to determine the optimum impacts of TiO<sub>2</sub> adhesion onto fly ash, various surfactants must be tested. One test was carried out without a surfactant, whilst other tests employed anionic and nonionic surfactants. The particles produced with the addition of an anionic surfactant were found to have better pigment properties and reflectance in the near-infrared area than the one obtained without a surfactant. Thus, such systems were claimed to be used effectively as a pigment in cool coatings. Fly ash was placed in a solution containing 70% ethanol supplemented with an anionic (SDS) or nonionic surfactant (TX-100). Next, titanium isopropoxide was added to the solution, followed by stirring for two hours. After two hours, the solution was dried in the range of 50–600 °C, and the resultant dry powder was collected. An experiment was conducted [65] using the semi-batch emulsion polymerization method to synthesize PUA hybrid emulsion PA/PU with a ratio of 20/80. A 250-mL four-neck glass flask containing a reflux condenser, digital thermometer, nitrogen gas inlet, and mechanical stirrer was used in this synthesis process. To prepare the pre-emulsion, SDS (2.0 g per 100 g of the acrylic and PU content) was dissolved in water. Subsequently, 5.0 g of MMA, 5.0 g of BA, and 0.015 g of AA (0.15 wt% of the overall MMA and BA weights) were added gradually to the emulsifier mixture and constantly stirred. The emulsion was then mixed for another 0.5 h. First, the reactor vessel was charged to achieve 111.3-g PU emulsion dispersion and 10% of the monomers. Then, it was set at 80 °C with constant stirring. Later, 10% of the initiator solution (0.4 g of KPS per 100-g acrylic monomers) was added to the solution and stirred for half an hour. Then, at a constant flow rate, the leftover monomer pre-emulsion and initiator solution was poured into the flask for a total of 4 h while the temperature was increased by 5 °C, keeping the solution at 85 °C for half an hour. The emulsion was then stirred continuously while left to cool. After adding NaHCO<sub>3</sub>, the pH value was kept within the predetermined range.

In brief, all the developed methods to date have aimed for the green and effective synthesis of core-shell NPs with controllable sizes, compositions, architectures, and properties through rational molecular design and material preparations. Despite substantial advances in the methods of preparation of core-shell nanostructures, the one-step/pot strategy in the preparation of core-shell nanostructures is still in its infancy and remains challenging. For example, the

facet control of metal@metal oxide crystalline nanoparticles in a one-step co-reduction is limited compared to those prepared through a two-step seed-coating process.

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