Recent progress in syntheses and applications of Cu@Ag core-shell nanoparticles

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Abstract. Cu@Ag core-shell nanoparticles have attracted much attention over the past decade due to their unique electronic properties, and their potential use in a wide panel of applications ranging from catalyst to printed electronics. In this paper, we reviewed the preparation methods of Cu@Ag core-shell nanoparticles and their applications. Based on these literature reviews, the prospect have been presented in the end of this review.

1. Introduction
Nanotechnology, information technology and biotechnology are important pillars in the development of science and technology. Nanomaterials refer to materials that have at least one dimension in the nanoscale range (1–100nm) or are composed of such materials as basic units. With the continued development of nanotechnology, stricter requirements have been put forward for the preparation, properties and application of nanomaterials [1-3].

Metals are broadly applied in many fields, thus metallic materials at the nanometer scale have also been widely studied. Nanopowders, also known as superfine or ultrafine powders, generally refer to powders or particles with a particle size below 100 nm. They are characterized as a type of solid particle material with an intermediate state between an atom, a molecule and the macroscopic object. Core-shell metallic materials consist of two different kinds of metals, which individually form the core and shell. The shell coats the core nanoparticle via a physical or chemical interaction to form orderly assembled structures at the nanoscale [4,5]. Compared with a single metal, core-shell bimetallic nanoparticles have different catalytic properties, surface plasma energy, and magnetic and electrical properties. Because of the unique properties of core-shell nanomaterials and their magnetic, optical, electronic and medical applications, they have been extensively studied in recent years [6-9].

Silver nanoparticles are widely used in the electronic industry because of their high conductivity and oxidation resistance [10, 11]. However, because of the high cost of silver and its easy migration in humid environments, the application of silver nanoparticles on the industrial scale has been restricted. In the periodic table of elements, copper and silver are located in the same subgroup, and their extranuclear electron configurations are similar. Additionally, copper has a low cost, low mobility and excellent conductivity, thus it is feasible for copper to completely replace silver for applications in the electronics industry. However, as particles size of copper decreases and the specific surface area increases, copper nanoparticles can oxidize more easily [12], which limits the applications of nano-copper. Therefore, the formation of core-shell coated nanomaterials via silver coating the surface of copper nanoparticles not only improve the oxidation resistance of the copper nanoparticles, but also maintain its excellent conductivity [13], while simultaneously reducing the associated cost.
Although silver-coated copper nanoparticles with a core-shell structure have unique properties and great application potential in many fields, its preparation is still in the research stage [14, 15]. In this paper, the main synthetic methods and application fields for core-shell silver-coated copper nanoparticles are reviewed, and their future development prospects are investigated.

2. Coating mechanism for the core-shell structure
The coating mechanism of core-shell nanomaterials is complex, and current research on the formation mechanism is lacking [16]. There are several main mechanisms: chemical bonding, Coulomb electrostatic force, adsorption layer surface modification and supersaturation.

| Mechanism                 | Coating mechanism                                                                 |
|---------------------------|-----------------------------------------------------------------------------------|
| Chemical bonding          | The core-shell interaction occurs through functional groups on the polymer chain (e.g. -COOH, -OH, and -SH.), which form a coating layer between the substrate and the coating. |
| Coulomb force             | Because of the charges on the surface of the particles, a stable coating layer is produced via the Coulombic force. |
| Adsorption layer surface  | An organic adsorption layer is formed on the inner inorganic core particle by surface treatment, and the affinity between the core and shell is enhanced by the adsorption layer. |
| modification [17]         | When a solution exceeds supersaturation, a large number of nuclei are formed and deposited on the surface of the heterogeneous particles, and the concentration of the crystals is lower than that in the absence of heterogeneous particles. |
| Supersaturation.          |                                                                                   |

3. Preparation of silver-coated copper nanoparticles with core-shell structure

3.1. Liquid phase synthesis of core-shell silver-coated copper nanoparticles

3.1.1. Design ideas for the liquid phase synthesis of core-shell nanomaterials
At present, the liquid phase method is the primary one for the preparation of nanomaterials in the laboratory and industry [5, 14]. The basic idea for the classical liquid phase synthesis of core-shell nanometallic materials is mainly based on three aspects: first, the appropriate chemical reaction type and reactants are selected to produce the final target products; second, the solution system is chosen, including the choice of stabilizers (dispersants) and surfactants; third, the characteristics of the target products with a core-shell structure can be controlled by adjusting the thermodynamic and kinetic parameters.

3.1.2. The selection of stabilizers
Choosing suitable stabilizers is mainly based on the requirements of the target nanomaterial products [14], and modification by polymer dispersants is similar to surfactants and contains two main components [15].

Figure 1 (a) and (b) show the basic principle of the stabilizer. The stabilizer is adsorbed on the surface of nanoparticles mainly through physical, chemical and electrostatic interaction of the ions, which makes the nanoparticles repel and disperse each other, and they do not easily agglomerate. Figure 1 (c) and (d) are schematic diagrams using surfactant molecules and polymers as stabilizers.

3.1.3. Preparation of core-shell silver-coated copper nanoparticles via the liquid Phase method
(1) Displacement reaction method
The displacement method is one of the commonly used ones for the preparation of metal nanomaterials [18]. The principle of the displacement method is relatively simple and there are numerous reports on the preparation of core-shell silver-coated copper nanoparticles via the displacement method [19]. For this, the pretreated copper powder is added to a silver ammonia solution and the main reactions are as follows:

\[
\begin{align*}
\text{[Ag(NH$_3$)$_2$]$^\text{+}$} + e^- & = \text{Ag$\downarrow$} + 2\text{NH}_3 \quad E^\theta = +0.373 \\
\text{Cu} + 4\text{NH}_3^- - 2e^- & = \text{[Cu(NH$_3$)$_4$]$^{2+}$} \quad E^\theta = -0.05 \\
\text{[Ag(NH$_3$)$_2$]$^\text{+}$} & = \text{[Cu(NH$_3$)$_4$]$^{2+}$} + 2\text{Ag$\downarrow$} \quad E^\theta = +0.423
\end{align*}
\]

As a reducing agent, Cu replaces Ag in \([\text{Ag(NH$_3$)$_2$}]^\text{+}\) in the solution to form \([\text{Cu(NH$_3$)$_4$}]^{2+}\). Because of the high Gibbs free energy on the surface of the copper powder, the complete aggregation of Ag takes precedence over the aggregation of \([\text{Cu(NH$_3$)$_4$}]^{2+}\).

Luo et al. prepared silver-coated copper powder with an average particle size of 70nm by coating silver nanoparticles on the copper powder with a particle size of ~35-50nm via the displacement method [20]. Tang et al. used the displacement method to reduce complex silver ions and deposit silver on the surface of the copper powder particles [21]. The degree of silver coating, bonding strength of the silver and copper and the oxidation resistance of the composite powders were analyzed. Cao et al. prepared a copper-silver bimetallic powder via the displacement reaction [22]. They used EDTA instead of ammonia as the complexing agent to prepare a bimetallic powder at room-temperature in one step. Studies have shown that the displacement reaction system has a large influence on silver-coated copper nanoparticles depending on the kinds of additives and the amount of reagents in the system [23]. Zhao et al. adopted the composite method of displacement and chemical deposition [24]. Sun prepared silver-coated copper powder via a composite method of displacement and chemical deposition [25].

Figure 1. Coating mechanism of the stabilizer [14]. (a) Stabilization through the electrostatic adsorption layer, (b) Stabilization through other adsorption layers, (c) Schematic diagram of surfactant molecularly stabilized nanoparticles, (d) schematic diagram of polymer stabilized and dispersed nanoparticles.

(2) Surface Deposition method (Chemical Reduction Plating method )

The surface deposition method is also known as the heterogeneous co-precipitation method or the chemical reduction plating method [11, 17, 19]. Grouchko et al. synthesized core-shell nano-silver-coated copper via a step-by-step reduction process [26], shown in figure 2. The first step was to use hydrazine hydrate as a reducing agent and sodium polyacrylate as stabilizer to prepare the copper nanoparticles in a copper sulfate solution. The second step was the addition of a nitrate solution to the copper nanoparticle solution. The nano-silver was then reduced and deposited on the surface of the nano-copper to produce the silver-coated copper nanoparticles with a core-shell structure. It was found that the strong reducibility of hydrazine hydrate could reduce some silver ions to silver and affect the coating process. To address this, acetaldehyde (C$_2$H$_4$O) was added to the nano-copper solution to remove hydrazine hydrate from the solution before adding the nitrate solution. The results of the HR-TEM, SEM, EDS, and XRD analysis show that the prepared nano-copper had a particle size of 40 nm and a thickness of ~2 nm. with good dispersion and oxidation resistance, as shown in figure 3.
Figure 2. Schematic diagram of the synthesis route of nano-silver-coated copper [26]

Figure 3. TEM and HR-TEM images of nano-copper (a) and core-shell Cu@Ag (b) [26]

Peng et al. [27] and Zhao et al. [28] used environmentally friendly methods to synthesize a uniform silver-coated copper powder. The uniformity of the silver-coated copper was further confirmed by FE-SEM, TEM and selected area electron diffraction (SAED). As shown in figure 4, the surface of the large particles were covered with a layer of small spheres of ~20nm, which is consistent with the diffraction spots of the TEM that have different light and dark diffraction contrasts. Ag (111), (200), (220), (311), and (420) diffraction rings were observed via SAED of the spherical powders. The improvement of the oxidation resistance of the silver-coated copper powder was also further confirmed. Xu et al. used potassium tartrate as a reductant to coat silver on the surface of the copper powder [29]. Hai et al. prepared silver-coated copper powder via electroless plating [30].

Figure 4. SEM, TEM and SAED of the silver-coated copper powder [28]

(3) Polyol reduction method
For the polyol reduction method [31-33], metal salts are dispersed in the liquid-phase polyol system (commonly used polyols are ethylene glycol, triethylene glycol and tetraethylene glycol). The metal atoms are reduced by increasing the temperature, and the metal atoms aggregate to form metal particles in the system. Polyol reduction is a simple process and the raw materials are highly adaptable. The alcohol system, as a solvent, can be used as a metal precursor and dispersant.

3.1.4. PWE synthesis method
The pulse wire evaporation (PWE) method is an alternate method for the preparation of core-shell nanoparticles, as shown in figure. 5. The following figure shows an improved PWE system for preparing nanoscale core-shell silver-coated copper. The equipment consisted of a pulse power generator, a wire feeding system, a reaction chamber and a filtering/collecting part. Copper wire with a diameter of 0.4mm
and a mass fraction of >99% was used as the starting material. The feeding length of the copper wire to the reaction chamber was 100mm, and the applied voltage was 26kV. When a high density current pulse passes through the wire, the copper wire is heated and evaporates, forming a vapor in a few microseconds. Then, the copper vapor was cooled and condensed into nanoparticles in the presence of argon. To collect the silver-coated copper nanoparticles without polluting their surface, the synthesized copper nanoparticles were fed into the filter, and then contacted directly with the AgNO₃ in an ethylene glycol solution in the collector. The chemical reactions between the copper nanoparticles and silver ions is as follows:

\[ \text{Cu} + 2\text{Ag}^+ \rightarrow 2\text{Ag} + \text{Cu}^{+} \]  

The silver film is coated on the surface of nano-copper through the above metal displacement reaction. Core-shell silver-coated copper nanoparticles with Ag uniformly coated on the surface of Cu can be synthesized by changing the molar ratio of [Cu]/[Ag].

**Figure 5.** Schematic diagram of modified pulsed wire evaporation (PWE) system

### 3.1.5. Thermal decomposition-dip plating method

Although the crystal seed growth method can be used to synthesize silver-coated copper nanoparticles with good oxidation stability, the nanoparticles have a broad size distribution and are relatively large. For some industrial applications, a suitable size and a uniform size distribution are needed, such as for conductive inks made of nano-silver-coated copper, which requires appropriately sized nanoparticles that do not block the printing nozzles. Therefore, the application of the crystal seed growth method is restricted. The combined reduction method is a very simple and effective one for reducing two metal salts to produce silver-coated copper nanoparticles; however, it is difficult to control the reduction and nucleation process of the two metals because of their different oxidation-reducing properties and chemical behaviors.

Dip plating is an electrochemical process that involves the oxidation of highly reducible metal ions. This method is widely used to synthesize bimetallic nanoparticles with various structures, such as alloys, core-shell structures and hollow structures. However, the reaction time required for synthesizing the silver-coated copper nanoparticles by this method is very long (>29 h) for the production of a very small weight of product particles (~0.01 g), which does not meet the requirements for the production of conductive ink. Therefore, the thermal decomposition-dip plating method was developed.

To synthesize highly dispersed silver-coated copper nanoparticles, the thermal decomposition-dip plating method consists of two steps. The first step is the thermal decomposition: for this, 3.33g copper diacetylacetonate and 200mL oleamide are added to a 500 mL three-neck flask and continuously stirred at 100°C for 30min under the protection of high purity argon. Then the flask was heated to 235°C and maintained at this temperature for 3h to synthesize the copper nanoparticles. The second step is the dipping one: 0.52g AgNO₃ and 150mL oleamide are added to the flask and maintained at 80°C for 2h. Finally, the silver-coated copper nanoparticles were synthesized via centrifugation at 10000rpm for
30min and washed three times with hexane. The nanoparticles were dried for 24h at 40℃ in vacuum to finally obtain the desired powdered nanoparticles.

4. Application of silver-coated copper nanoparticles with core-shell structure

Silver-coated copper nanoparticles with a core-shell structure not only maintain the excellent properties of the core and shell materials but also effectively overcome the defects of the individual materials. They have unique advantages in application and great application prospects in the electronics industry [34], as antimicrobial materials and as catalysts.

4.1. Application of conductive adhesives

Conductive adhesives are generally used in printed circuit boards, microelectronic packaging, conductive circuit bonding and other electronic fields. The conductivity is an important criterion for evaluating the performance of these adhesives. It is generally believed that the volume resistivity of the conductive adhesives for electronic packaging should be less than $1 \times 10^{-4} \Omega \cdot \text{cm}$. Because the conductivity of the adhesives mainly come from their fillers, the morphology, particle size and type of conductive fillers have a large influence on the conductivity of the adhesives. As a conductive filler, silver-coated copper nanoparticles can not only solve the migration problem of silver (its anti-migration ability is nearly 100 times higher than that of a common silver powder conductive coating), but can also improve the conductivity and anti-oxidation performance of copper powder. Compared with pure silver powder, the production cost is markedly lower [35]. New conductive adhesives with silver-coated copper nanoparticles as a conductive filler can not only overcome the instability of copper powder-based conductive adhesives, but also has the advantage of a lower price than silver powder-based conductive adhesive.

Zhao studied the conductivity of silver-coated copper powder with different morphologies as a conductive adhesive fillers [36]. The results showed that the properties of the silver-coated copper conductive adhesives are almost the same as those of silver powder based conductive adhesives.. Wong et al studied the sintering process of silver nanoparticles [37, 38]. Their results showed that when the conductive adhesives were cured by heating, the silver nanopowder manifested a self-sintering phenomenon, which not only improved the interfacial contact between conductive fillers, but also greatly improved the interfacial contact between the fillers and the resin matrix, thus reducing the resistivity of the conductive adhesives. Jiang et al. made a conductive filler by mixing silver flakes and nano-silver powder, which were influenced by surface interactions and formed conductive network by sintering [39]. Park et al. added nano-silver with a diameter of 20–50nm to the conductive adhesives prepared with spherical micropowder [40]. With the increase of the nano-silver content, the properties of the nano-silver improved while the total amount of silver remained unchanged.

4.2. Application of conductive paste

Conductive paste is a basic functional material of the modern electronics industry, and currently, silver conductive paste is the most extensively applied one and is mainly used for applications such as displays and hybrid integrated circuits. Therefore, silver powder has important applications in capacitors, solar electrode materials, membrane switches, electronic sensitive components, LED light sources and other electronic components [41]. Grouchko et al. prepared conductive ink with conductive silver-coated copper nanoparticles, it had a viscosity of 1.9 centipaste (cP) and a surface tension of 23.0mN·m·1 [26]. A pattern was printed using the prepared conductive ink with a micro single nozzle printer. The printed pattern was heated from room temperature to 150℃, and XRD spectra confirmed the absence of copper oxide and the color of the pattern remained unchanged; however, when the temperature reached 200℃, the silver layer coated on the surface of the copper nanoparticles was destroyed, resulting in oxidation of the nano-copper. Jillek et al. also proposed methods related to the preparation of nano-copper and nano-silver conductive ink [42].

The conductive silver paste used for solar cells is mainly a mechanically mixed paste composed of silver powder, glass powder, an organic carrier and other additives (accessories) in certain proportions
[43]. Huang et al. prepared silver powder and core-shell silver-coated copper powder as pastes for solar cell applications [44]. Their paste was printed on a silicon wafer by screen printing and sintered, and the resulting film could meet the electrical performance requirements of solar cells. Li et al. significantly improved the performance of photovoltaic solar cells using silver coated glass powder to prepare the silver paste [45].

4.2.1. Application as antibacterial materials
Inorganic copper and silver antimicrobial agents have a long history for medical antimicrobial application, and there are many related studies on the antimicrobial mechanisms of copper and silver [46-49]. Kaviya et al. prepared two kinds of silver nanoparticles with a diameter of 35nm and 10nm from citrus peel extract and tested their antimicrobial properties [50]. Their results showed that the two nanoparticles had good antimicrobial properties against Gram-negative bacteria and Gram-positive bacteria. Wei prepared high-stability spherical and rod-like copper nanocrystals by modifying the surface of their fabricated copper nanoparticles [51]. Antibacterial experiments demonstrated that they had good bactericidal effect on stachybotrys with a minimum bactericidal concentration of 40μg/mL.

4.3. Catalytic applications
As a catalyst [52], nanoparticles have many advantages. The research and application of nanoparticles in the field of catalysis has significantly increased because of the benefits of their small particle size and large specific surface area. In the metallurgical and petrochemical industries, copper nanopowder and nano-silver have been widely used as excellent catalysts [52-55]. The core-shell structure of silver-coated copper nanoparticles not only has the characteristics of nano-copper and nano-silver, but also exhibits novel properties. Hence, it is an efficient catalyst with great application prospects.

5. Development prospects of nano-silver-coated copper
Because of the excellent properties of both copper and silver powders, silver-coated copper powder is increasingly used in electronic pastes (conductive coatings and conductive adhesives), electrode materials, electric brushes and other products [56-58]. Because precious metal powders are scarce and expensive, the demand for the more economical silver-coated copper powders has increased year over year. In 2008, the development and market-oriented production of silver-coated copper powder was carried out in Europe, America and Japan, while China's research in this field had been in the nascent stage. Currently, the main international producers of silver-coated copper powder are American SCM, German Ecka, Belgian Nano and Japanese Fukuda, while only a few Chinese companies are capable of producing a small amount of silver-coated copper powder with uneven quality. According to a market demand survey in 2014, it was found that the domestic demand for high quality silver-coated copper powder was mainly met by imports, and only a small amount was provided by domestic manufacturers. Therefore, the domestic market has an urgent need of the development and promotion of high-quality silver-coated copper nanopowder.

From the technical perspective of nanoscale silver-coated copper powder, these nanoparticles not only maintain the physical properties of the original copper core, but also has the excellent metallic properties of the silver coating layer, improved the oxidation resistance and thermal stability of pure copper powder, while maintaining the high conductivity of copper and silver. Moreover, the copper in the coated powder can inhibit the dissolution of silver, overcome the defects of silver migration in conductive silver adhesives, and realize the economic use of precious metals and environmental protection. In addition, the coating process for silver-coated copper powders with a core-shell structure can be used as a model system to study the interaction and stability of composite nano-particles; thus, obtaining valuable information on their dispersion. Presently, with the rapid development of electronics and the information and communication industry, the processes of chip miniaturization and the use of multi-layer electronic components have accelerated. There is an increasing demand for electronic pastes (conductive coatings and conductive adhesives) with gold, silver, nickel, copper and other metallic...
powders. Therefore, the development of nanoscale silver-coated copper powder, which has a strong practical applicability, is of great value for the future market-oriented development of novel materials.

6. Conclusion
In summary, as a new type of core-shell composite material, nanoscale silver-coated copper powder has attracted significant global research interest towards the further exploration of the synthetic methods and potential application prospects. At present, this material has been applied in the electronics industry, as catalysts and for antimicrobial applications, but research of the material is still in the initial stages. Therefore, to encourage the broad application of core-shell nanometer silver-coated, further in-depth research is needed. According to the current state-of-the-art, the urgent problems that need to be addressed are as follows:

(1) During the preparation of silver-coated copper, hydrolysis can easily occur in an alkaline environment. This inhibits the formation of the silver nucleus, resulting in an uneven distribution of the silver nuclei on the surface of the copper particles, and even decreases the number of surface nuclei. Hence, issues such as the incomplete coating and poor dispersion after coating, as well as effectively controlling the thickness, and the nucleation and growth process, the particle size distribution and the final yield of silver coating need to be addressed.

(2) The agglomeration of copper nanopowders occurs easily during the preparation, collection and preservation stages, and the oxidation of the copper powders can also occur during the process of activation and washing, which affects the purity and coating structure of the silver-coated copper powders.

(3) The synthetic and coating mechanisms of the nanomaterials are very complex. At present, the synthetic method and mechanism are still in the exploratory stage, and the coating mechanism needs to be further studied.

(4) Further research and development should focus on new systems, the improvement and optimization of the synthetic routes, and the search for facile, controllable, high-yield synthetic methods and processes References

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