Doctoral Dissertation (Shinshu University)

The fabrication and application of nanoparticle-based multifunctional composites

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Abstract

Nanoparticle composites have attracted scientific attention due to the distinguished set of properties and applications. The properties of nanoparticles are dependent on the component size and structure. Therefore, the synthesis of nanoparticle composites with well component size, nanostructure, and morphology have attracted great interest. However, the controllable fabrication, and particular desired shape of nanoparticle-based composites are still a challenge. This thesis focuses on exploring the size-controllable, shape-controllable, and applications of nanoparticle-based composites. The nanostructure formation, properties and applications of composites are well discussed. The most significant results achieved in this dissertation are given as follows:

In this work, owing to the large surface area, graphene oxide (GO) was used as the carrier to protect nanoparticles from aggregating, and the π-π continuous surface can provide abundant ways for nanoparticles transferring during their application.

Silver nanoparticles/graphene oxide nanoscroll composites (Ag/GO nanoscroll composites) were fabricated by a one-step method at room temperature. The GO sheets were cut into pieces by the silver nanoparticles (AgNPs) due to their catalytic activity, and then the GO pieces rolled up, resulting from the intermolecular hydrogen bonds. Transmission electron microscope images show that the Ag/GO nanoscroll composites have open-ended tubular hollow structures. The Escherichia coli (E. coli) was used to evaluate the antibacterial activity of synthesized nanoscroll composites. After against the

E. coli for 3 days, the inhibition rate of Ag/GO nanoscroll composites can still up to 99.99%. This attributes to the open-ended tubular hollow structures, providing abundant channels and space to prevent AgNPs from aggregating and oxidizing. The result exhibits that the Ag/GO nanoscroll composites have the potential for long-lasting antibacterial activity. So, the Ag/GO nanoscroll composites can be applied in antibacterial materials for long-lasting use. On the other hand, the Ag/GO nanoscroll composites were synthesized as a recyclable photocatalyst. The open-ended nanoscroll structures provide sufficient space to prevent the AgNPs from oxidizing and aggregating, and the π-π continuous surface provides an abundance of pathways for AgNPs transfer during photodegradation. To demonstrate the recyclability of the synthesized photocatalytic composites, methylene blue aqueous solution was photodegraded under optimal conditions over ten consecutive photocatalytic cycles. The result shows that the Ag/GO nanoscroll composites are able to mineralize methylene blue to colorless within 10 min in each cycle, and no decomposition was detected after ten cycles. The Ag/GO nanoscroll composites can be used as a recyclable photocatalyst in wastewater treatment applications.

Additionally, Copper nanoparticles (CuNPs) have been widely studied because they are cheap and easy to be obtained. However, it is challenging to be long-term storage because of their oxidation in the air easily. To prevent CuNPs oxidation, the sandwich structure composites (CuNPs intercalated into graphene oxide (GO) sheets - CuNPs@GO composites) were fabricated via the liquid-phase reduction method. The limited GO interlayer distance controls the size of CuNPs (~ 10 nm in diameter) during the reduction process, and the GO sheets serve as the protective cover to prevent CuNPs from oxidation. In addition, the large surface area of GO layer provides enough space for CuNPs against their aggregation. To confirm that the sandwich structure can protect CuNPs from oxidation, the air stability and high temperature stability of CuNPs@GO composites were evaluated. The result shows that the composites exhibit no oxidation sign following exposure to dry air for at least 21 weeks or 90 °C. Simultaneously, the conductivity result of the synthesized composites shows no change after exposure to dry air for at least 21 weeks. This sandwich structure provides a potential research direction for fabricating CuNPs with high antioxidant stability and stable conductivity.

Chapter 1

General introduction

Chapter 1: General introduction

1.1 Nanomaterials

Nanotechnology has gained huge attention in the past two decades, in which the nanomaterials are the primary and critical component. Nanomaterials are materials that have the size between 1 to 100 nm at least in one dimension and made up of carbon, metal, metal oxides, or organic matters [1]. Nanomaterials produce unique quality and capabilities by modifying the shape and size at the nanoscale level. Nanomaterials have different shapes, such as nanorods, nanoparticles, and nanosheets, based on their dimensionality [2]. The unique properties of nanomaterials, for example, high reactivity, strong sorption, etc., are explored for application in many fields like medicine [3-5], catalysis [6], renewable energy, and environmental remediation [7], and antibacterial material [8]. In this chapter, the classification, property, and application of nanomaterials are briefly introduced.

The nanomaterials are generally classified into the carbon-based nanomaterials, metal nanomaterials, nanocomposites, etc.

1.1.1 Carbon-based nanomaterials

The main constituent in this type of nanomaterials is carbon. They can be classified into graphene [9], carbon nanotubes (CNT) [10], carbon nanofibers [11, 12], fullerenes, and carbon dots [13]. Carbon-based nanomaterials are presented in Fig. 1-1.

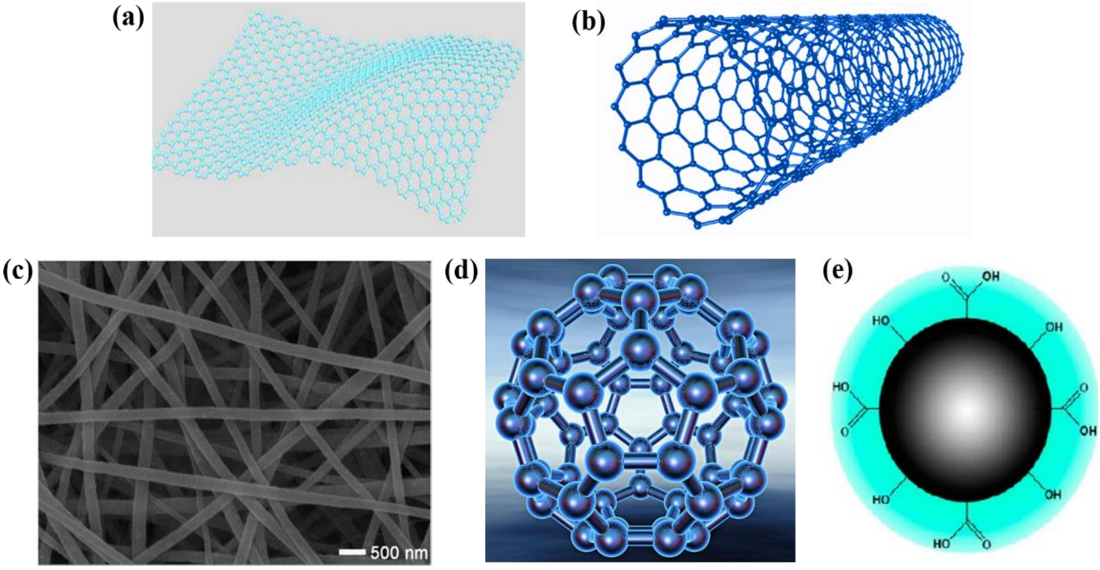

Fig. 1-1 Carbon-based nanoparticles. (a) graphene; (b) CNT; (c) carbon nanofibers; (d) fullerenes; (e) carbon dots.

Graphene, as one of the carbon-based nanomaterials, is the sheets of carbon atoms arranged in a hexagonal network. It was discovered in 2004 through a process of scotch tape peeling [14]. Owing to its properties such as high mobility of charge carriers, unique transport performance [15], high mechanical strength [16], and extremely high thermal conductivity and theoretically high surface area [17], graphene, as a 2D sheet of sp^2-hybridized carbon, suitable for many promising applications such as sensors [18], energy conversion devices [19], and catalysts [20]. The outstanding properties depend on the number of layers and dispersion performance of graphene sheets [21]. However, Van der Waals and π-π stacking interactions among individual graphene sheets result in their tendency to aggregate [22] when graphene dispersion solutions are dried. Therefore, preventing graphene agglomeration has become a significant research trend. A graphene layer interfacing with evenly distributed nanoparticles on the surface could lead to welldefined, novel graphene with an exceptional surface area. The nanoparticles can act as a stabilizer against the aggregation of individual graphene sheets, which is generally caused by a strong Van der Waals interaction between graphene layers. Moreover, the graphene sheets decorated with nanoparticles might can result in some particular properties because they combine the outstanding properties of nanoparticles and the synergetic effect between them. At the present, the various kinds of nanoparticles [23-25] have been synthesized and supported on graphene, including Ag, Au, Cu, TiO_2, ZnO, etc.

Graphene oxide (GO) as a type of graphene is the product of chemical exfoliation of graphite and has been known for more than a century. GO has been known to disperse well in water since its first discovery over a century ago and thus has been routinely described as hydrophilic. The GO is the ideal alternative for the production of solution processable graphene, as it can be synthesized in large quantities from inexpensive graphite powder and can readily yield stable dispersions in various solvents. GO is an oxidized graphene sheet having its basal planes decorated mostly with epoxide and hydroxyl groups, in addition to carbonyl and carboxyl groups located at the edged.

1.1.2 Metal nanomaterials

There are different methods for the preparation of metal nanoparticles like chemical or photochemical methods. By using reducing agents, the metal ions are reduced to the metal nanoparticles. Almost all the metals can be synthesized into their nanoparticles [26]. The commonly used metals for nanoparticle synthesis are cobalt (Co), silver (Ag), copper

(Cu), gold (Au), iron (Fe), lead (Pb), zinc (Zn), etc. The nanoparticles have distinctive properties such sizes as low as 10 to 100nm, surface characteristics like a high surface area to volume ratio, pore size, surface charge and surface charge density, crystalline and amorphous structures, shapes like spherical and cylindrical and color, reactivity and sensitivity to environmental factors such as air, moisture, heat and sunlight etc. [27, 28]. Not only a single nanoparticle but also the mixing of two or more nanoparticles with size control can also be achieved. They are widely used in different research areas, environmental and bioimaging studies.

Among various metal nanomaterials, silver nanoparticles are obtained particular interests due to their unique properties, which could be used in broad-spectrum antimicrobial materials [29-31], chemical/biological sensors and biomedicine materials [32-34], and biomarker [35] and so on. They have unique optical, electrical, and thermal properties and are incorporated into the industrial application of electronics, catalysis, and photonics. Silver nanoparticles are one of the most attractive nanomaterials for commercialization applications. They have been used extensively as electronic products in the industry, antibacterial agents in the health industry, food storage, textile coatings, and environmental applications. As antibacterial agents, silver nanoparticles were used for a wide range of applications, from disinfecting medical devices and home appliances to water treatment [36-38]. However, the bare silver nanoparticles are prone to oxidize and aggregate while they are exposed to air or water at room temperature [39]. Therefore, the silver nanoparticles-based composite nanomaterials have become the current research trend.

Since 1990s, copper nanoparticles have attracted much attention from scientists. Many techniques, such as chemical reduction [40], reduction of copper ions with supercritical fluids [41], and laser irradiation of copper oxide powders, are developed to synthesize copper nanoparticles [42, 43]. Copper nanoparticles have been pulled in extensive consideration because of their optical, catalytic, mechanical, and electrical properties [44, 45]. They have also been used as a substitute for gold, silver and platinum in different areas (e.g., thermal conducting materials and microelectronics applications) [46, 47]. However, copper nanoparticles have a large specific surface area and high chemical activity, which can be easily oxidized into dark red cuprous oxide and black copper oxide in the air, losing their original physical and chemical properties. In addition, the copper nanoparticles have low dispersion in the absence of modified stabilizers, which limits their application in many fields. Therefore, suitable base materials decorating copper nanoparticles to form nanocomposites point out a new direction for research.

1.1.3 Nanocomposites

The nanocomposite is a polyphase solid material where one of the phases has one, two, or three dimensions of less than 100 nm. Over recent years, nanocomposites have become a hot topic very fast by the reason of the quick development of nanofillers (nanoparticles, nanotubes, nano-whiskers, nanofibers, nanolayers and nanosheets) as well as the excellent material performances resulted from the great specific surface area, high surface energy, small size effect, quantum benefit and macroscopic quantum tunneling of nanofillers. In them, the graphene-based nanocomposites are developing in recent days to a large extent. The single-layer carbon atoms are arranged in a hexagonal matrix, with zero band gap. The electrons are almost as the massless particles that consist of the good electrical medium in 2D [48]. The oxidation product of graphene is graphene oxide, whose electronic conductivity is excellent [49]. The different types of graphene oxide family nanocomposites are metal/graphene oxide nanoparticles, metal oxide /graphene oxide nanocomposites, metal chalcogenide/graphene oxide nanocomposites. The metal and metal oxides possess a variety of applications. Among of them, Ag [50], Cu [51], Au [52], ZnO [53], TiO_2 [54], and Fe_2O_3 [55] show the photocatalytic, photovoltaic, drug delivery [56], gas sensors [2], batteries [57] and cytotoxicity activities [58].

1.2 Antibacterial materials

Bacterial contamination has become a crucial problem due to many infections in food storage, medical implants, hospital settings, biosensors, and public health events [59]. Therefore, antibacterial materials have been widely researched. Antibacterial material refers to a new type of functional material that kills or inhibits bacteria. Many substances have good bactericidal or antimicrobial functions, such as some organic compounds with specific groups, some inorganic metal materials and their compounds, and some minerals. However, antibacterial materials are functional materials that can inhibit or kill surface bacteria by adding individual antibacterial agents, such as antibacterial plastics, antibacterial fibers, and fabrics, antibacterial Ceramics, antibacterial metal materials, etc.

1.2.1 Organic antibacterial agents

The main varieties of organic antibacterial agents are vanillin or ethyl vanillin compounds, which are often used in polyethylene food packaging films to have an antibacterial effect. In addition, the acylanilides, imidazoles, thiazoles, isothiazolone derivatives, quaternary ammonium salts, bisquats, phenols, etc. are also used as antibacterial agents. Generally, organic antibacterial agents have low heat resistance, are easily hydrolyzed, and have a short validity period. Simultaneously, the safety of organic antibacterial agents is still under research.

1.2.2 Inorganic antibacterial agents

There are many types of inorganic antibacterial agents, such as Ag, Cu, and ZnO, which can bring antibacterial activity to materials. Sevinc etc. [60] have demonstrated that the blending 10 wt.% ZnO nanoparticles into dental composites displays antibacterial activity and reduces the growth of bacterial biofilms against Streptococcus subrings by roughly 80% for a single-species model dental biofilm. In addition, a variety of metallic biocides used for mold inhibition are only operative for the short-term. Therefore, the development of simple, low-cost, and long-term effective antibacterial methods is significant.

1.2.3 Nano antibacterial agents

Nano antibacterial materials are the treatment of inorganic antibacterial agents with high-tech nanotechnology so that they have more extensive and excellent antibacterial and sterilization functions; it improves the long-term antibacterial effect through the slow release. Nanoparticles are widely used as antibacterial activities mainly through two reactions. The first one is called the contact reaction, which relies on Cullen's gravity to attach nano ions to cell walls firmly, then the nano ions can break through the cell walls and enter the cells to solidify the bacterial protein [61, 62]; eventually the cells die due to loss of the ability to divide and multiply. When the bacteria lose their activity, nano ions are freed out from the bacteria, repeated sterilization, so their antibacterial effect can last a long time. The second one is called the photocatalytic reaction, meaning that under the action of light, nano ions activate the water and air of oxygen adsorbed to the surface of the powder, producing OH^- and O_2^-, which can decrease the ability of bacteria to multiply and destroy bacteria in a short period of time.

Among all the nanoparticles, silver nanoparticles with a high bactericidal activity [63, 64] have been widely applied in medicine to prohibit colonization of bacteria on prostheses [65], wound-dressing [66], and to reduce infections in burn treatment [67]. However, the bare silver nanoparticles are prone to oxidize and aggregate while exposed to air or water [39]. To overcome the shortcomings, many other materials, such as carbon nanotubes (CNTs), graphene oxide (GO), and so forth, have been employed as potential support materials to increase the stability and antibacterial activity of silver nanoparticles

[68-73]. Among these materials, the one-dimensional CNTs have been widely used as adsorbents to remove various environmental pollutants due to their unique structures and high super physical and chemical properties. CNTs have high electron transfer property, making them have better photocatalytic performance and yield an efficient antibacterial activity level. However, the CNTs tend to agglomerate due to their hydrophobic nature, limiting some applications. In contrast, GO has received significant interest due to a large number of oxygen bonds, such as hydroxyl, carboxyl and epoxide groups, which stabilize the aqueous dispersion of GO [74-76] can be a suitable support material to increase the stability of silver nanoparticles.

1.3 Photocatalytic materials

1.3.1 History of photocatalytic materials

The history of photocatalysis can be traced back to the 1960s. The discovery of water photolysis on a TiO_2 electrode by Fujishima [77] and Honda in 1972 has been recognized as the landmark event that stimulated the investigation of photonic energy conversion by photocatalytic methods [78, 79]. Since then, intense research has been carried out on TiO_2 photocatalysis, which focused on understanding the fundamental principles, enhancing the photocatalytic efficiency, and expanding the scope of applications [80]. Unfortunately, TiO_2 is not ideal for all purposes and performs relatively poorly in processes associated with solar photocatalysis. In principle, TiO_2 can utilize no more than 5% of the total solar energy impinging on the earth' surface due to its wide bandgap (3.2 eV). Therefore, during the past decade, much effort has been devoted to modifying TiO_2 and investigated possible alternatives to TiO_2.

1.3.2 Semiconductor photocatalytic materials

Semiconductor photocatalytic materials have received much attention as a potential solution to the world energy shortage and counteract environmental degradation. In semiconductors, the conduction-band electrons (e_{cb}^-) have a chemical potential of + 0.5 to -1.5 V versus the normal hydrogen electrode (NHE); hence they can act as reductants. The valence-band holes (h_{vb}^+) exhibit a strong oxidative potential of + 1.0 to + 3.5 V versus NHE [81]. The energy of the incident photons is stored in the semiconductor by photoexcitation, then converted into chemical form by a series of electronic processes and surface/interface reactions.

TiO_2 photocatalyst, as one of the traditional semiconductor materials, is widely used in a variety of applications and products in the environmental and energy fields, including self-cleaning surfaces, air and water purification systems, sterilization, hydrogen evolution, and photoelectrochemical conversion. The photocatalytic properties of TiO_2 are derived from the formation of photogenerated charge carriers (hole and electron), which occurs upon the absorption of ultraviolet light corresponding to the band gap [82, 83]. The photogenerated holes in the valence band diffuse to the TiO_2 surface and react with adsorbed water molecules, forming hydroxyl radicals (•OH). The photogenerated holes and the hydroxyl radicals oxidize nearby organic molecules on the TiO_2 surface. Electrons in the conduction band typically participate in reduction processes, which typically react with molecular oxygen in the air to produce superoxide radical anions ($•O_2^-$). However, only a small proportion of the holes is trapped at lattice oxygen sites and may react with TiO_2, which weakens the bonds between the lattice titanium and oxygen ions. As a result, the effect achieved by TiO_2 photocatalysis is not very significant. ZnO photocatalyst presents higher photocatalytic activity than TiO_2 in the photodegradation of some organic compounds, so it is a suitable alternative to TiO_2 [84]. However, the photocatalytic activity of ZnO is still not high enough because the low separating efficiency of the photoelectron hole pairs and the structure of the ZnO crystal would be destroyed after consecutive use due to the photo corrosion effect.

1.3.3 Novel photocatalytic materials

In order to overcome these drawbacks, a lot of efforts have been made to improve or replace the traditional semiconductor photocatalysts. Recently, the introduction of noble metal nanoparticles (e.g., Ag, Au) onto semiconductor surfaces contributes to expanding the light-harvesting scope of UV and visible light, due to their potent surface plasmon resonance (SPR) effects [85]. In addition, owing to their low Fermi levels, noble metal nanoparticles might serve as electron trappers, reducing the photogenerated electron-hole recombination rate [86]. Among the noble metals, Ag is considered to be the most economical raw material with the most potent SPR effect. Ag as a co-catalyst could enhance the separation of electron-hole. Thus, the photocatalytic activity of the semiconductor increased. It can be inferred that Ag can be a potential candidate for photocatalysis.

1.4 Purpose of this research

Nanotechnology is one of the most active research areas with both novel science and useful applications. Nanotechnology is a multidisciplinary science which deals with physics, chemistry, materials science, and other engineering sciences. The applications of nanotechnology are spreading in almost all branches of science and technology. So far, the research of nanotechnology has made specific achievements; however, nanoparticle composites with controllable shape and size are still challenging in the present study. In this thesis, thence, three different types of nanoparticle-based composites with controlled shapes and sizes were investigated. (1): The Ag/GO nanoscroll composites were synthesized using a one-step method at room temperature, where the GO sheets were cut into pieces by AgNPs (4 - 10 nm), and then rolled up to nanoscrolls due to the force of intermolecular hydrogen bonds. The synthesized the Ag/GO nanoscroll composites can be applied as an antibacterial material and a recyclable photocatalyst for long-lasting use. (2): The sandwich shaped CuNPs@GO composites were fabricated via the liquid-phase reduction method, in which the limited GO interlayer distance controls the CuNPs growth (~ 10 nm diameter) during the reduction process, and the GO sheets serve as the protective cover to prevent CuNPs from oxidation. The sandwich composites exhibit no sign of oxidation after exposure to dry air for at least 21 weeks or 90 °C heat and show stable conductivity after at least 21 weeks' exposure to dry air.

The research schematic for this work is shown in Fig. 1-2.

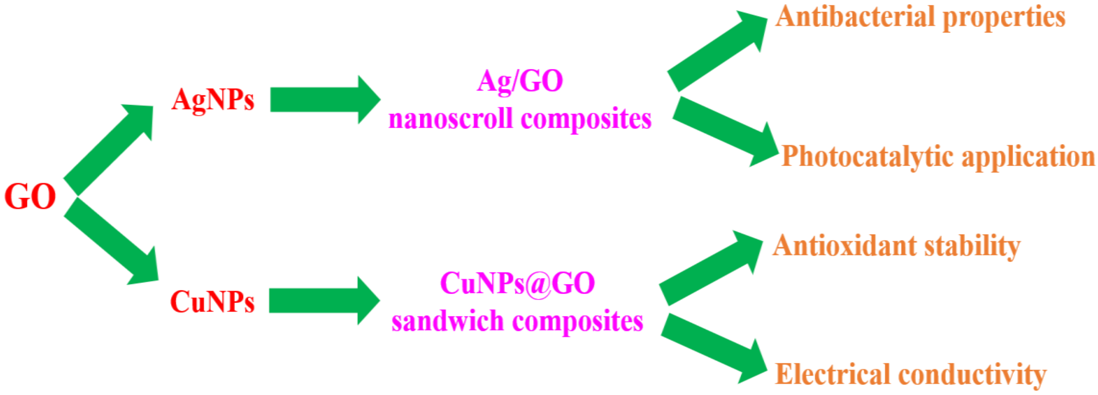

Fig. 1-2 The research schematic

Chapter 2

The synthesis and antibacterial activity of silver nanoparticles/graphene oxide nanoscroll composites

Chapter 2: The synthesis and antibacterial activity of silver nanoparticles/graphene oxide nanoscroll composites

2.1 Abstract

In this work, silver nanoparticles/graphene oxide nanoscroll composites (Ag/GO nanoscroll composites) were fabricated by a one-step method at room temperature. The GO sheets were cut into pieces by the silver nanoparticles (AgNPs) due to their catalytic activity, and then the GO pieces rolled up resulting from the intermolecular hydrogen bonds. Transmission electron microscope images show that the Ag/GO nanoscroll composites have open-ended tubular hollow structures. The Escherichia coli (E. coli) was used to evaluate the antibacterial activity of synthesized nanoscroll composites. After against the E. coli for 3 days, the inhibition rate of Ag/GO nanoscroll composites can still up to 99.99%. This attributes to the open-ended tubular hollow structures, providing abundant channels and space to prevent AgNPs from aggregating and oxidizing. The result exhibits that the Ag/GO nanoscroll composites have the potential for long-lasting antibacterial activity. So, the Ag/GO nanoscroll composites can be applied in antibacterial materials for long-lasting use.

Chapter 3

The photocatalytic application of silver nanoparticles/graphene oxide nanoscroll composites

Chapter 3: The photocatalytic application of silver nanoparticles/graphene oxide nanoscroll composites

3.1 Abstract

In this work, silver nanoparticles/graphene oxide nanoscroll composites (AgNPs/GO nanoscroll composites) with open-ended nanoscroll structures were synthesized as a recyclable photocatalyst. The open-ended nanoscroll structures provide sufficient space to prevent the AgNPs from oxidizing and aggregating, and the π-π continuous surface provides an abundance of pathways for AgNPs transfer during photodegradation. To demonstrate the recyclability of the synthesized photocatalytic composites, methylene blue aqueous solution was photodegraded under optimal conditions over ten consecutive photocatalytic cycles. The result shows that the AgNPs/GO nanoscroll composites are able to mineralize methylene blue to colorless within 10 min in each cycle, and no decomposition was detected after ten cycles. The AgNPs/GO nanoscroll composites could be used as a recyclable photocatalyst in wastewater treatment applications.

Chapter 4

Synthesis and antioxidant stability of “sandwich” copper nanoparticle @ graphene oxide composites

Chapter 4: Synthesis and antioxidant stability of "sandwich" copper nanoparticle @ graphene oxide composites

4.1 Abstract

Copper nanoparticles (CuNPs) have been widely studied because they are cheap and easy to be obtained. However, it is difficult to be long-term storage because of their oxidation in the air easily. To prevent CuNPs oxidation, the sandwich structure composites (CuNPs intercalated into graphene oxide (GO) sheets - CuNPs@GO composites) were fabricated via the liquid-phase reduction method. The limited GO interlayer distance controls the CuNPs growth (~ 10 nm diameter) during the reduction process, and the GO sheets serve as the protective cover to prevent CuNPs from oxidation. In addition, the large surface area of GO layer provides enough space for CuNPs to against their aggregation. To confirm that the sandwich structure can protect CuNPs from oxidation, the air stability and high temperature stability of CuNPs@GO composites were evaluated. The result shows that the composites exhibit no sign of oxidation following exposure to dry air for at least 21 weeks or 90 °C heat. Simultaneously, the conductivity result of the synthesized composites shows no change after exposing to dry air for at least 21 weeks. This sandwich structure provides a potential research direction for fabricating CuNPs with high antioxidant stability and stable conductivity.

Chapter 5

Overall conclusions

Chapter 5: Overall conclusions

This thesis was mainly devoted to studies on the fabrication of nanoparticle-based functional composites, and their properties and applications. Three kinds of shape-controlled, size-controlled nanocomposites were successfully fabricated, and their structural and functional properties were investigated and discussed in detail. The brief summaries are as follows:

Chapter 1 reviewed references and provided brief summaries of functional composites, including to nanomaterials, antibacterial materials, and photocatalytic materials.

In chapter 2, the Ag/GO nanoscroll composites were fabricated, and their antibacterial activity was investigated in detail. Three different molar ratios were carried out to study the optimal condition of the rolling up process. The result shows that when the $AgNO_3$ of 5.88 mmol was added into the GO solution of 42 mL at room temperature, the GO sheets were cut into pieces, Then, the Ag/GO nanoscroll composites with 100 nm in diameter are fabricated by the force of intermolecular hydrogen bonds, attached by lots of AgNPs (4 - 10 nm). The Ag/GO nanoscroll composites were proved to have long-lasting antibacterial activity. The result shows that after against the E. coli for 3 days, the inhibition rate of Ag/GO nanoscroll composites can still up to 99.99%. This is due to their open-ended tubular structures, and the composites provide abundant continuous channels and space to prevent the AgNPs from aggregating and oxidizing, which enhance the antibacterial activity of the composites to use for a long time.

In chapter 3, the photocatalytic application of Ag/GO nanoscroll composites was addressed. Ten consecutive cycles of MB mineralization were used to demonstrate the recyclable photocatalytic properties of synthesized nanoscroll composites. The results show that under the optimal conditions (bath ratio of Ag/GO nanoscroll composites to MB of 1:100, initial MB concentration of 100 mg/L, and UV light irradiation), the nanoscroll composites can mineralize MB to colorless within 10 min in all cycles, and no loss was exhibited after ten cycles. This performance is attributed to the open-ended nanoscroll structures, which provide not only enough space for the AgNPs to prevent aggregation and oxidization, but also abundant pathways for AgNPs to transfer during photodegradation.

In chapter 4, the fabrication and conductivity of CuNPs@GO composites were studied. The L-ascorbic acid was used as an eco-friendly reducing agent, and its strong polarity efficiently reduced Cu^{2+} to Cu^0. Owing to the limited interlayer distance of the GO sheets, controlled the growth of CuNPs during the reducing process, the CuNPs were uniformly generated with a diameter of about 10 nm. To verify that the sandwich structure protected the CuNPs from oxidation, the air stability and high- temperature stability of CuNPs@GO composites was evaluated. The combined results show that the CuNPs@GO composites exhibit no sign of oxidation after exposure to air for 21 weeks. Additionally, after heating the composites at temperatures up to 90 °C for 30 min, the CuNPs still maintain their metallic nanoparticle form, and the GO is not reduced. The conductivity result of the synthesized composites shows no change after exposure to dry air for at least 21 weeks. These results indicate new potential research directions based on fabricating highly stable CuNPs with enhanced conductivity.

In summary, three types of nanoparticle-based composites have been successfully fabricated and their properties, structural analysis, and applications have been well discussed.

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