Synthesis and applications of silver nanocomposites: A review

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Abstract. Nanomaterials refer to materials whose structural unit size is between 1 nanometer and 100 nanometers. Since nanoparticles' size is close to the coherence length of electrons, their properties have also changed greatly due to the self-organization brought about by strong coherence. Therefore, noble metal nanoparticles have unique physical, chemical, and biological properties. This paper mainly studies the silver nanoparticle material, one of the precious metal nanoparticles. The silver nanoparticle is modified to graphene, metal materials, fiber materials, ceramic materials, and polymers to form a silver-based composite material, which improves its antibacterial, electrical conductivity, and Chemical durability, photocatalysis, and other capabilities. They can be applied to medical, environmental, industrial, biological, food and other fields, providing a reference for in-depth research on the properties of nano-silver particles and the continuous development of their application prospects.

1. Introduction
Nanomaterials are suchlike materials whose particle size is in the range of 1 nanometer to 100 nanometers. There are numerous species of nanomaterial, and noble metal nanomaterials are widely used in the abundant applying fields, such as for anti-microbial, creating anti-cancer drugs, healing the wound and bioimaging because of having remarkable compatibility with biological materials in the medical field [1], for sewage treatment due to its strong adsorption capacity [2] to absorb metal and organic pollutants and antibacterial properties for treatment of microorganisms[3], and for super-capacitor for energy storage [4] on account of its stability, high mechanical strength and low specific density[5]. Furthermore, there are still some facing noble metal nanomaterials problems, such as the high price of raw materials and manufacturing cost and the harm of toxicity for creatures or environment not being observed [1].

The composite nanomaterials are devoted to a number of applications because of their broad structure due to more complex combination methods for materials and functional performance [6]. They can be applied in catalysis, such as for accelerating photodegradation [7] and decomposing pollutants [8], generating packaging because of good barrier property [6], producing sophisticated materials field,
such as manufacturing supercapacitor electrode with high capacity and stability [9], and the nanocomposite material generating via plants synthesis are also fully used in carriers or as medicines in the medical field. Silver nanocomposites combine function between silver nanoparticles and other mixed materials via other material enhancing the useful abilities or decreasing the harmful part of silver material. Therefore, they have more widespread or extensive applications than single silver nanoparticles. Silver nanoparticles can be compounded by physical, chemical [10], or biological methods, which are always combined with pure silver nanoparticles, showing high abilities to strengthen the performance of silver nanoparticles. For instance, silver nanocomposites having antioxidant and anti-cancer abilities are as medicines [11] and having loading ability are as carriers in the medical field. Silver nanoparticles decorated by chemistry agents or plants can be applied in purification via photocatalytic [12] and sensor development [13] in industrial sectors.

Therefore, this report will organize the articles about the synthesis methods and widely applications of silver nanocomposite to provide a reference value for future research, which might useful to improve the insufficient of silver nanocomposites and push the silver nanoparticles to widespread of practical applications.

2. Modification of nanosilver onto different materials

2.1 Modification of nanosilver onto graphene

Kim et al. [14] used hydrazine as a reducing agent in a graphene oxide aqueous solution in the presence of stabilizers and coupling agents (PVP (polypyrrolidone) and APTMS (3-aminopropylytrimethoxysiloxane)) to prepare φ2~5 nm graphene-silver nanoparticle composites. Shen et al. [15] prepared graphene-silver nanoparticle composites using a mixed reducing agent of sodium borohydride and ethylene glycol. Manash et al. [16] used Sodium borohydride simultaneously reduced silver ions and graphite oxide to prepare graphene-silver nanoparticle composites. Pasricha et al. [17] loaded silver nanoparticles on graphene oxide in a heated KOH solution without reducing agents.

At present, the specific mechanism of nanosilver modification to graphene is not clear. Still, several speculations are as follows: (1) The presence of oxygen functionalities at the graphene surface provides reactive sites for the nucleation of silver nanoparticles. (2) When Ag⁺ is reduced by adding a mixture of ethylene glycol and NaBH₄, the growth of Ag particles begins, and they will stay attached to the graphene oxides (GOS). (3) The additional reduction of GOS to the chemically converted graphene (CCG) is observed, provided that the reducing agent is strong enough, forming Ag-CCG nanocomposites.

Compared with pure silver nanoparticles, Ag@RGO (reduced graphene oxide) nanocomposites have many excellent characteristics. First of all, silver nanoparticles exist in the graphene sheet layer and the middle of each sheet layer in the composite material, which prevents agglomeration. Due to the introduction of silver nanoparticles into the composite material, the Raman signal intensity in the graphene is increased by 7 times. The silver nanoparticles maintain high surface activity; besides, graphene provides a good non-specific adsorption platform for bacteria, which is beneficial to the sterilization of the silver nanoparticles loaded on it.

2.2 Modification of nanosilver onto metals

Bosetti et al. [18] prepared silver film by ion-beam-assisted deposition of silver from the vapor-phase and then coated with silver by the SPI-ARGENTTM method to prepare stainless steel-silver nanoparticle composites. Lizhi Zhang et al. [19] synthesized silver nanoparticles by reducing [Ag(NH₃)₂]⁺ ions in ethanol through triblock copolymers under ambient light irradiation and anchored silver nanoclusters with a size of about 2nm with high dispersion. Set on TiO₂ nanoparticles. Ang Gao et al. [20] used pulsed DC magnetron sputtering to deposit TiAg coating on Ti with TiAg target at room temperature. Lingzhou Zhao [21] fabricated titanium dioxide nanotubes (TiO₂-NTs) doped with silver (Ag) nanoparticles. The TiO₂-NT was immersed in a silver nitrate solution and then irradiated with ultraviolet rays to make the Ag nanoparticles adhere to the wall tightly.

Compared with stainless steel widely used as metal implants, stainless steel-nano-silver composites...
have neither genetic toxicity nor cytotoxicity and have good cytocompatibility. Compared with uncoated TiO$_2$, TiO$_2$-silver nanocomposite material shows stronger photocatalytic (nano-silver loading can effectively reduce the recombination of photogenerated electron-hole pairs) and bactericidal activity (enzyme inhibition and antibacterial activity against a variety of microorganisms).

2.3 Modification of nanosilver onto fiber
Chou et al. [22] spun silver-loaded asymmetric cellulose acetate (CA) hollow fiber membranes through dry-jet wet spinning technology. The spinning solution was prepared by dissolving AgNO$_3$ and CA in N, N-dimethylformamide (DMF). Minwoo Park et al. [23] produced a conductive composite made of silver nanoparticles and rubber fibers. The silver nanoparticle precursor is absorbed by electrospun poly(styrene-block-butadiene-block-styrene) (SBS) rubber fibers and then directly converted into silver nanoparticles in the fiber mat (Fig. 1).

![Fig 1. Highly stretchable circuit made of silver nanoparticle and elastic fiber composite material [23]](image)

Linghui Peng et al. [24] used dopamine as a binder and reducing agent, synthesized silver nanoparticles on bamboo pulp fabric under microwave radiation, and prepared a uniformly covered silver nanoparticle/bamboo pulp fabric composite material. (Fig.2)
There are two main methods for preparing nanoparticle/polymer composite fibers: One is to perform surface post-treatment on the fiber, such as dipping or padding the colloidal solution of nanoparticles or the nanoparticles adsorbed by the carrier to make it compound on the surface of the fiber. The other is to blend and spin the nanoparticles with the polymer matrix so that the nano-particles are compounded inside or on the fiber’s surface, and the particles are firmly combined with the polymer fiber through the bond between the matrix and the particles.

The silver nanoparticle/polymer composite has a dense structure in the sublayer. No obvious pores are observed on the outer surface and the inner surface at a magnification of 50k, so the polymer matrix (i.e., hollow fiber) can retain antibacterial agent (i.e., silver nanoparticles). Furthermore, the use of dopamine and silver coating provides bamboo pulp fabric with excellent UV radiation protection and hydrophobicity.

2.4 Modification of nanosilver onto ceramic materials

Jeon et al. [25] and M. Kawashita et al. [26] prepared silver-doped silica film and antibacterial silver-containing silica glass by sol-gel method. Thananchai Piroonpan et al. [27] modified silica nanoparticles (SiO$_2$NPs) with poly 2-(dimethyl amino) ethyl methacrylate (PDMAEMA) brushes for template synthesis and immobilization of AgNPs using electron beam assisted grafting and reduction reactions. Weiqiang Yang et al. [28] encapsulated carbon dots (CD) in silica spheres and then modified these spheres with amino groups (CD @ SiO$_2$-NH$_2$). Based on the silver mirror reaction (Silver mirror reaction: aldehydes can reduce the silver ammonium complex to generate metallic silver, Ag$^+$ assembled on the surface of CD@SiO2-NH2 is reduced to silver nanoparticles (AgNPs) by formaldehyde(Fig.3).
Fig 3. Schematic diagram for (a) preparation of fluorescent CD@SiO$_2$-NH$_2$-Ag$^+$, b in-situ grown AgNPs on silica-encapsulated CDs induced MEF for a formaldehyde gas assay [28]

Lv et al. [29] produced silver nanoparticle-decorated porous ceramic composites by overnight exposure to a silver nanoparticle colloidal solution of a porous ceramic modified with an aminosilane coupling agent 3-aminopropyltriethoxysilane (APTES)(Fig.4).

Fig 4. Reaction mechanism between porous ceramic and Ag nanoparticles through APTES as a connection part[29]
Padilla et al. [30] used electroless plating and cathodic electrodeposition techniques to coat the Ag film on the Porous ceramics' surface.

At present, the main method for manufacturing silica-nanosilver composites is the sol-gel method. The method is to solidify compounds containing highly chemically active ingredients with solutions, sols, and gels and then heat-treat them into composite solids. Also, chemical methods can also prepare silica-nanosilver composites. The connection between silver nanoparticles and ceramics depends on the coordination bond between the \(-\text{NH}_2\) group on the top of the APTES molecule and the silver atom on the nanoparticle's surface. The other end of the silane coupling agent is connected to the silicon atom in the ceramic through the Si-O-Si bond.

Ceramic-nano-silver composite materials have higher antibacterial activity, chemical durability, and economic effects. (1) It can gradually release silver ions at a controlled rate over a long period. (2) The porous ceramic composite material is durable and can be stored for a long time. Even under ultrasonic irradiation, there will be no loss of nanoparticles. (3) The materials involved in preparing porous ceramic composite materials are generally readily available, cheap, and non-toxic, so the preparation process is simple, convenient, and low in cost.

2.5 Modification of nanosilver onto polymer

Daeyeon Lee et al. [31] utilized nanoreactor chemistry combined with the layer-by-layer assembly of weak polyelectrolytes to synthesize nanometer-sized metal particles in LbL assembled thin films. Jinhua Da et al. [32] used the alternate adsorption of polyethyleneimine-metal ion complexes and polyanions to form a multilayer polyelectrolyte film. The post-deposition reduction of metal ions is performed by heating or exposure to NaBH₄, and then a composite film containing metal nanoparticles is obtained(Fig.5).

![Scheme 1](image)

Fig 5. Reduction after the deposition of silver ions [32]

Jin-Woong Kim et al. [33] reduced AgNO₃ in the aqueous dispersion to deposit colloidal Ag onto poly(EGDMAco-AN) microspheres(Fig.6).
Fig 6. Nanoparticles are deposited uniformly onto surface functional porous poly(ethylene glycol dimethacrylate-co-acrylonitrile) (poly(EGDMA-co-AN)) microspheres.[33]

Hongyong Luo et al. [34] used polydopamine spheres (PDS) to reduce silver nitrate without surface modification or adding other reducing agents to prepare a submicron dopamine sphere loaded with silver nanoparticles (Ag@PDS)(Fig. 7)

Polymer is a good carrier for nanosilver. First of all, layer-by-layer (LbL) assembly of polymers (e.g., synthetic polyelectrolytes and natural polyelectrolytes such as proteins) presents opportunities for creating conformal and robust coatings with molecular-scale precision and a wide range of physical properties. Secondly, the methods for preparing silver/polymer nanomaterials include in-situ polymerization and in-situ generation. The former is to first synthesize silver nanoparticles, then mix the nanoparticles and monomers uniformly, and initiate the monomers' polymerization under appropriate conditions. The in-situ generation method simultaneously generates silver nanoparticles during the polymerization process of the polymerization reaction monomer.

The polymer-nano-silver composite material solves the aggregation problem of silver particles. Because silver ions can be well distributed along the polymer chain, so that silver nanoparticles are dispersed throughout the film, thereby forming a film on the surface. Moreover, the polymer impregnated with silver nanoparticles exhibits hydrophilic surface properties, which helps prevent microorganisms from adhering to the surface, preventing the formation of biofilms and the deposition of corrosion-causing proteins and electrolytes.

3. Application of Nano Silver

3.1 Application for the medical field
3.1.1 Applying as medicine
Silver nanocomposite materials are widely used in the medical field mainly because of their anti-ability. For inoxidizability, according to Chinnathambi, Nasif and Alharbi, silver nanoparticles are synthetic with *zingiber officinale* leaf aqueous extract to form a kind of anticancer medicine, no toxicity for normal cells and the ability of inoxidizability and anti-cancer increasing because of plants, which can detect pancreatic cancer in humans on account of the ability of oxidation resistance for free radicals which can cause abnormal cells growth rapid by damaging DNA and RNA [11]. In addition, there is another application for the inoxidizability of silver nanoparticles. As a report goes by Gauthami et al., silver nanoparticles mediate with cissampelous pairera. This kind of silver nanocomposite material can be anti-diabetic via inhibiting α-Amylase, antibacterial and antioxidant by removing 1,1-diphenyl-2-picrylhydrazyl (DPPH), a type of stable free radicals [10]. For antibacterial, it is reported by Zhang et al. that silver nanoparticles are decorated on graphene oxide (GO) with polydopamine immobilizing by biological blending method and growing by themselves, named Ag-DA/BC (rGO) composite film, which is used in wound dressing to cure in the biomedical field, depending on electric conduction to generate the heat to improve the wound cells moving, promote curing speed and prevent the harmful objects away from the wound [35]. For anti-cancer ability, according to Pathak et al., silver nanoparticles is forming by extracting polygonatum verticillatum rhizome to embed into the silver nanoparticles (Pv-AgNPs), which are mainly used for resisting the breast and hepatic, [36, 37] and the primly extracting plant compounds are absorbed in the surface of silver nanoparticles, which can prevent the signal propagating for anti-breast and anti-hepatic ability. Through the testing, the effect of Pv-AgNPs extract curing cancer is better than polygonatum verticillatum rhizome [36].

3.1.2 Applying as a carrier
Silver materials are not only applying in medicine but also can be used as a carrier. For instance, silver nanoparticles can also be used to treat breast cancer, reported by Pandey, Ali, and Negi. Silver nanoparticles are loaded in amygdalin by reducing reaction and putting this composite into the folate functionalized chitosan microcapsules (Amy/AgNP/CS) used to treat breast cancer. The mechanism of this application is that amygdalin is widely applied for the medical field, which is extracted from apricot blossom, silver nanocomposite materials are helpful for signal delivering, causing cell death by disrupting cell cycle, and chitosan has biodegrability, biocompatibility, modification, and low toxicity, which offers convenience to be microcapsules [38].

3.2 Application for sewage detection
Silver nanoparticles can be used in environmental treatment, such as sewage detection based on the reaction between silver nanocomposites and harmful substances with color change for convenient observing. Sharma reported that using *terminalia bellirica* extract silver nanoparticles through reducing silver ions, which enhances the photocatalytic and antibacterial ability of silver nanoparticles. This silver nanomaterial can detect wastewater from textile industries by diagnosing methylene blue, a sort of harmful material that might cause skin irritation, via observing the color change, dark blue for no methylene blue and Cambridge blue for having it [12]. Another example is about detecting mercury ions. According to Yilmaz, silver nanoparticles are functionalized by chlorophyll (Chl-AgNPs), a colorimetric sensor. This nanocomposite material can detect mercury ions in the water, which is showed by color change, brown for no mercury ions, and colorless for having mercury ions. The mechanism of this application is an oxidizing reaction between silver nanoparticles and mercury ion [39], mercury ions reacted with a methyl group to form methyl mercury ([CH₃Hg]⁺), which react with silver nanoparticles to cause aggregation to change color [40], and the different size of silver nanoparticle and distance between reactants causing the different color to test concentration, which is easy being observed by eyes [39].

3.3 Application for industrial engineering field
3.3.1 Catalytic
There are widely applying industrial aspects for silver nanocomposites materials, such as catalyzing, sensor devices, and fuel cells field [41]. According to Alula, silver nanoparticles are formed into Fe$_3$O$_4$ magnetic nanoparticles (AgNPs/Fe$_3$O$_4$) by ultrasonication, the first nano-composite material with catalytic reduction capacity and peroxidase activity. There are two main applications aspects for it. The first one is the catalyst in chemical reactions to degrade the methylene blue and rhodamine 6G, depending on the synergetic effect between the metal and oxide support to increase the catalytic activity of silver nanoparticles, which is more efficient than Fe$_3$O$_4$ aggregation and is re-utilization due to the magnetism in favor of gathering. [42]. The second aspect is being catalytic to enhance the peroxidase activity. The oxidation of peroxidase substrate (OPD) can be oxidized to 2, 3-diaminophenazine (DAP) with H$_2$O$_2$ by AgNPs/Fe$_3$O$_4$ nanoparticles [13]. AnotPaul reports another example silver nanoparticles are embedded into in-vitro biomineralized vaterite (Ag NPs / Vaterite). This nano-catalytic is used for improving the catalytic performance of 4-nitrophenol reducing reaction [43]. The mechanism is that there are porous in the spherical surface of vaterite of CaCO$_3$, which is the carrier to take silver nanoparticles [44]. Biomineralized vaterite enhances the contact area of silver nanoparticles to prevent aggregation, which helps achieve high catalytic performance maximization and control the size. In detail, silver nanoparticles inserted vaterite seem like spheres, which causes nearly perfect catalytic ability [43].

3.3.2 Auxiliary
Silver nanocomposite materials are also widely used as auxiliaries. For instant, according to a report by Paturi et al., silver nanoparticles are added into water-based Tween 80 emulsifier oil to form AgNP-GCF. The application of AgNP-GCF is being cutting fluid for cooling, lubricating, and reducing friction during machining surfaces with the minimum quantity lubrication (MQL), which is environment friendly. This application's mechanism is that Ag nanoparticles loaded in Tween 80 base cutting fluid reduces the friction by enhancing the heat transfer. Specifically, using nearly 1% AgNP-GCF for similar dry and MQL machining has improved the machined surface to be less rough. The efficiency has been improved by almost thirty percent, compared with dry or MQL machining traditional cutting fluid. [45]

3.4 Application for creatures

3.4.1 Acting on plants
Silver nanocomposites materials can be acting on creatures, plants, and animals. For plants, as the report goes of Raja et al., silver nanoparticles, having strong surface oxidation activity to control the growth of microbial, are synthetic with trichoderma harzianum Th3, whose application is biological control type for the complex pathogen of groundnut root rot [46, 47]. Additionally, silver nanocomposites material likewise can be used in the detection field. A study showed by Su et al. raised that silver nanoparticles functionalized by fluorescein to be sensing probes (F-AgNPs) can be applied for sensing tricyclazole from pesticide in the rice, an effective, simple, rapid, and low-cost method. This nanomaterial mechanism is that the tricyclazole from pesticide can react with the sulfur in F-AgNPs, which cause F-AgNPs to easily gather in the surface of the pesticide to lead the color changing from yellow to gray, yellow for clean, and gray for being polluted. [48]

3.4.2 Acting on human being
Another aspect is for the animal, taking human beings as an example. According to Jesus et al., acetylated cashew-gum-based modify silver nanoparticles (ACG-AgNPs) by acetylation reaction. The application is that ACG-AgNPs are used to detect fingerprints, especially for forensic investigation [41]. For the mechanism of fingerprint detection, the porous surface of ACG-AgNPs, which transforms the latent form of fingerprints to visible form, is useful for displaying the fingerprints rapidly, and the multifunctionality of surface modification causes the precise targeting. Additionally, silver nanocomposites stabilizer is a biodegradable and biocompatible non-toxic material, acetylated cashew gum, which is environment friendly compared with traditional technologies [49-52]
3.5 Application for food packaging
Silver nanocomposites materials can be used to produce the packing bags, such as food packages. It is reported by Gu et al., using graphene oxide (GO) as a template, silver nanoparticles are reduced by chitosan (CS) to form sandwich-like film, CS/rGO@AgNPs, which depends on the high quality of antimicrobial activity to yield food packaging [45, 53, 54]. The mechanism of this adhibition is that the form of sandwich-like film is helpful to control the silver nanoparticles releasing slowly to keep antimicrobial activity in the long-term, which is reducing the shortage of silver nanoparticles, such as high-cost, toxic, and low-stability [45, 55], and this film has the effective ability of oxygen barrier and the water vapor transmission rate is lower than traditional PE or CS film. After the experiment, the most effective result form has been tested out, amount of silver nanoparticles releasing almost 2% after 2 weeks [45]. The other kind of nanomaterial is that silver nanoparticles coated onto the dextran are scattered into the cellulose nanofibrils film (Ag-CN), which can be used to produce the environmental protection film of food anticorrosive packaging material. The mechanism is that dextran can control silver nanoparticle releasing, reduce oxygen passage rate to prevent food spoilage, and reduce the thickness of CNF with the highest oxygen permeability. Additionally, silver nanoparticles have a high antibacterial ability on account of the reaction between silver ions and amino and carboxyl groups of peptidoglycan in the cell wall. The production process is simple and green, which solve the excessive releasing of silver ion. [56]

4. Suggestion
Metal nanoparticles can be synthesized through biosynthetic pathways, have broad application prospects, and can achieve the purpose of commercialization [1]. However, metal nanoparticles also have weaknesses such as toxicity, which may damage beneficial microorganisms or marine organisms, or soil organisms, and are harmful to human health. If these weaknesses continue to be addressed, silver nanomaterials and even metal nanomaterials can be used in a wider range of fields and used on a large scale.

When silver nanoparticles enter biological receptors, it is not clear whether they will adversely affect the organism. Therefore, it is necessary to study the toxicity mechanism of silver nanoparticles. Whether the toxicity comes from the silver nanoparticles themselves or the dissolved silver ions released by the silver nanoparticles. There is currently no mature silver nanoparticle detection method, and the nanoparticles' safety is still unclear.

5. Conclusion
This article summarizes the preparation process and unique properties of some silver-based composite materials. This thesis mainly studies the silver-based composites composed of nano-silver modified on graphene, metal materials, fiber materials, ceramic materials, and polymers. At present, there are three main methods for preparing nano-silver composites: physical, chemical, and biological methods. The physical method is suitable for industrial preparation that does not require high requirements for the size and shape of silver nanoparticles. The chemical method is used in fields that require high nanoparticle performance, such as optics, electric power, and biomedicine. The biological method has low cost, mild reaction conditions, and no additives are required during the reaction. The prepared silver-based composite materials are widely used in medical, environmental, industrial, biological, food, and other fields due to their excellent antibacterial properties, electrical conductivity, chemical durability, photocatalysis, and other abilities. However, the toxicity mechanism of nano-silver has not yet been studied, and the safety of nano-silver remains to be discussed. Therefore, this article hopes to provide a basis for future research on silver nanocomposites.

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