



Carbon-encapsulated metal nanoparticles deposited by plasma enhanced magnetron sputtering

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ABSTRACT

Carbon-encapsulated gold nanoparticles (CEGNs) were synthesized by plasma enhanced magnetron sputtering using C₂H₂ and Ar mixtures as the precursor. The morphology, microstructure and optical property of the CEGNs were characterized using TEM, SEM, and UV–Vis absorption spectrum. The results show that the gold NPs with narrow size distribution ranging from 7 nm to 20 nm were encapsulated by amorphous carbon nanospheres. The fraction of C₂H₂ in the gas mixture of C₂H₂ and Ar seemed to have a significant influence on the gold particle size and distribution of the as-made CEGNs. As the fraction of the C₂H₂ increased from 5% to 10%, the average particle size decreased from about 13 nm to 7 nm and the carbon nanospheres with single gold NPs core evolved to the carbon chain with multi-cores. In addition, carbon-encapsulated silver nanoparticles (CESNs) were also prepared by the same method. This indicates that the plasma enhanced magnetron sputtering may be one of the best ways for the deposition of the carbon-encapsulated metal nanoparticles (CEMNs). The UV–Vis absorption spectra of the CEGNs and CESNs reveal strong absorption bands due to the surface plasma resonance of the nanoparticles, implying that the as-made CEMNs could be applied in optical limiting devices.

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1. Introduction

Metallic nanoparticles (NPs) have received tremendous scientific and practical interest due to their unique properties and novel applications that are different from bulk materials [1–4]. However, bare metal NPs are readily oxidized and agglomeration, which limits the potential use of these particles. Carbon encapsulated metal nanoparticles (CEMNs) represents a kind of composite materials with a core-and-shell structure on the nanoscale. The outside carbon shell can protect the metallic core (nanoparticle) against oxidation and further agglomeration to form bigger crystallites [5–7]. Accordingly, CEMNs have been found various prospective applications in catalysis, magnetic data storage, magnetic resonance imaging, biomedical application and in optical limiting devices [8–10].

CEMNs were first synthesized by decomposition of CO over a Ni catalyst twenty years ago [11]. In the last decade, many techniques have been developed to synthesize CEMNs, including physical vapor deposition (PVD) (e.g. arc-discharge [6] and sputtering [12]),

chemical vapor deposition [13], high-temperature heat treatment of carbon-metal mixtures [14], laser assisted irradiation [5], and wet-chemical route [15]. Among of these techniques, the arc-discharge method is one of the most popular and conductive PVD methods to large amount synthesis of CEMNs. However, the arc evaporation of the target materials with very high melting points is problematic or impossible. On the other hand, the arc evaporation of low melting point target materials tends to result in the formation of macro-particles during arc evaporation [16].

Recently, the magnetron sputtering technique was widely used to prepare metal NPs because of its advantages, such as, the relative ease for scaling up to larger dimensions, a good control of quantity, size uniformity and low temperature process used on the widest range of substrates including temperature sensitive substrates and polymers, etc [17–19]. Furthermore, the other important advantage of sputter deposition is that even materials with very high melting points are easily sputtered while evaporation of these materials is difficult. Accordingly, the magnetron sputtering may be one of the best methods to produce CEMNs. But very little work has been performed in CEMNs. Hayashi et al. [20] reported the cobalt NPs encapsulated in carbon cages obtained by magnetron and ion-beam co-sputtering. Babonneau et al. [21] deposited silver NPs

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encapsulated in carbon cages obtained by co-sputtering of the metal and graphite targets. However, in fact, both the structures they created were the metal NPs embedding in the dense carbon films rather than carbon encapsulating in nanocapsule structures. Therefore, although the formation of protective carbon films enhances the stability of the NPs and hinders clustering, some applications of such materials are limited due to their lack of porosity, such as chemical catalysis, where the porosity is need to increase contact area and improve the catalytic activity and stability of NPs.

In our previous works, we have reported that metal NPs embedded in carbon films deposited by magnetron sputtering combined with ion beam [22,23]. Recently, we found that carbon nanospheres with size of 50 nm could be produced by glow discharge in a relatively high deposition pressure [24]. Accordingly, we thought that CEMNs might be prepared using glow discharge combining with metal sputtering. So in this paper, CEMNs would be deposited using a plasma-enhanced magnetron sputtering and UV–Vis absorption of CEMNs was also characterized.

2. Experimental details

CEMNs including carbon-encapsulated gold nanoparticles (CEGNs) and carbon-encapsulated silver nanoparticles (CESNs) were deposited on silicon wafers (100) with a thickness of $525 \pm 15 \mu\text{m}$ using the plasma-enhanced magnetron sputtering in a discharge composed of a mixture of C_2H_2 and Ar gases (see Fig. 1). Si wafers were cleaned in an ultrasonic bath in acetone and ethanol and dried under nitrogen flow before being placed in a vacuum chamber. The chamber was evacuated to a base pressure of approximately 2×10^{-5} Torr. Gas mixtures of Ar and C_2H_2 were introduced into the chamber as the precursor. The deposition temperature of the samples placed on the cathode was held at room temperature by water cooling, and the work pressure was 500 mTorr. The magnetron sputter unit equipped with high purity (99.95%) Au or Ag target of diameter 5 cm was supplied with typical dc power of about 137 W (550 V, 0.25 A). The discharge was sustained at a radio frequency (RF) and power of 13.56 MHz and 400 W (500 V, 0.8 A), respectively. The total process period was 30 min.

SEM (Nova 600, FEI) operated at an accelerating voltage of 5 keV was used to observe the porous carbon-encapsulated gold NPs networks. TEM (TecnaiG2, FEI) equipped with a cold-field emission gun and operated at 200 keV provided microscopic information

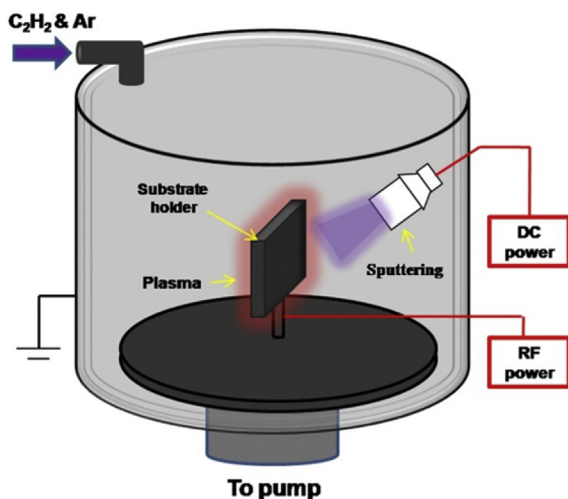


Fig. 1. Schematic diagram of the hybrid plasma-enhanced magnetron sputtering deposition process.

regarding the porous CEMNs networks. TEM specimens are prepared by dispersing the porous CEMNs in isopropanol and then dropping them onto a holey carbon films on Cu grid. UV–Vis absorption measurements were performed on a Jasco V530 UV–vis spectrophotometer. The specimens for UV–Vis absorption test were performed by dispersing the porous CEMNs in isopropanol through ultrasonication for 10 min. All measurements were baseline corrected using blank sample of isopropanol.

3. Results and discussion

Fig. 2 presents the SEM and TEM images of the carbon-encapsulated gold nanoparticles (CEGNs) deposited with the C_2H_2 fraction of 5% in the gas mixture of Ar and C_2H_2 . A typical TEM image of the CEGNs is shown in Fig. 2 (a). It is clear that all the gold NPs were encapsulated in carbon nanospheres with a diameter of approximately 30–50 nm to form a shell-core structure. The HRTEM image in Fig. 2(b) shows that the gold NPs have a lattice spacing of 0.23 nm which is consistent with a face-centered cubic (fcc) structure [25]. However, the carbon shell around the Au particle core exhibits a typical amorphous feature without any observable character. The diameter distribution of the gold NPs is given in Fig. 2(c), which reveals a narrow size distribution in the range of 7–20 nm. The average particle size is about 13 nm. On the other hand, from the normal and cross-sectional views of the SEM images (see Fig. 2(d) and (f)), it can be seen that the as-made CEGNs material presented a loose, sponge-like porous networks on the whole. The detail view indicates that the carbon nanospheres are connected to each other to form chains and networks, which is also reported in our previous work [24].

Fig. 3 shows the TEM images of the CEGNs materials deposited with the C_2H_2 fraction of 10% in the gas mixture of Ar and C_2H_2 . It should be noted that the carbon nanospheres adhered to each other like a chain. The diameter distribution of the gold NPs Fig. 2(c) also exhibits a narrow size distribution in the range of 5–15 nm. It is clear that the gold NPs in this is smaller than the one deposited with the C_2H_2 fraction of 10%. And the average size of the gold NPs encapsulated in carbon decreases from 13 nm to 7 nm, as the C_2H_2 fraction increases from 5% to 10% (see Fig. 3(d)). But the density of the gold NPs cores shows an increase in one carbon nanosphere. The HRTEM indicates that gold NPs also have the face-centered cubic (fcc) structure with the lattice spacing of 0.23 nm.

It is evident that the change of the ratio of Ar/ C_2H_2 affects the morphologies and size of the encapsulated gold NPs largely. The carbon plasma density will increase as the C_2H_2 fraction increases in the chamber while the density of metal plasma tends to decrease. This will increase the probability of the gold collision with carbon. As a result, each core of the gold NPs will be encapsulated fast by carbon. Then, the carbon shell will separate the gold NPs from each other and prevent the growth of the NPs. Similar phenomenon is also reported by Hao et al. [6], who prepared carbon encapsulated copper NPs by a modified arc plasma method with using He/ CH_4 as the gas source. On the other hand, the increase of carbon radicals diffused to the substrates, on which they deposited and played a role in gluing nanoparticles and provide adhesion among nanoparticles to form the chain-like structure [26]. Therefore, multi gold NPs are encapsulated in one carbon nanosphere or chain structure rather than single NP is encapsulated in one carbon nanosphere as shown in the sample deposited with the C_2H_2 fraction of 5%.

CESNs materials were also deposited by the same method using the Ag target with the C_2H_2 fraction of 5% in the sputtering gas mixture of Ar and C_2H_2 . Fig. 4 shows the TEM image and HRTEM (the insert in Fig. 4) of the CESNs. The HRTEM of the silver NPs reveals crystalline feature and ordered orientations of the lattice

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