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Development of Ag dendrites-reduced graphene oxide composite catalysts via galvanic replacement reaction

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HIGHLIGHTS

- Silver dendrites/reduced graphene oxide composite was prepared via a novel galvanic replacement method.
- Formation of Ag dendrites and the reduction of graphene oxide were achieved simultaneously without adding any reductant.
- The prepared silver dendrites/reduced graphene oxide composite exhibited an outstanding catalytic performance.

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ABSTRACT

Silver dendrites/reduced graphene oxide (AgD/RGO) composites were synthesized via a facile galvanic replacement method. The successful formation of Ag dendrites and the graphene oxide reduction were proved by a series of characterization techniques. The possible formation mechanism of Ag dendrites during the galvanic replacement reaction was discussed. The catalytic activity of the as-synthesized AgD/RGO composite was evaluated by its performance on the chemical reduction of an organic dye methylene blue. The AgD/RGO composite showed a much higher catalytic performance and stability than that of Ag dendrites.

1. Introduction

Dendritic fractals of silver have attracted lots of attention due to their supermolecular structure and unique properties, which have many important applications in fields such as surface enhanced Raman Scattering [1,2], catalysis [3] and super-hydrophobic surface construction [4]. So far, a number of preparation methods have been developed to synthesize Ag dendrites during the past years including template assisted method, templateless direct growth, electrodeposition, photoreduction, microwave method and galvanic replacement, etc. [5–14]. It is possible to rapidly synthesize Ag dendrites with high yield and without using toxic reagents [5,15,16]. For example, Keita and co-workers reported a surfactant template-free, fully inorganic wet chemical route for the preparation of Ag dendrites [15]. However, there is still little study on the synthesis of silver dendrites based composites [17–22]. According to literatures, composites of Ag nanostructure and graphene possess combined effects in the enhancement of SERS signal [23], catalytic activity [24–27], sensing [28–30] and antimicrobial activity [31]. It is very possible that introducing graphene into Ag dendrite structures could potentially enhance the catalytic performance of silver. The present study reports the synthesis of Ag dendrites/reduced graphene oxide (AgD/RGO) composites using galvanic replacement. This one-step preparation process not only produces Ag dendrites on the Al foil, but also simultaneously induces the reduction of graphene oxide. The catalytic activity of the as-prepared AgD/RGO composite is then examined by its performance on the catalytic reduction of an organic dye methylene blue (MB).

2. Experimental

Silver nitrate ($AgNO_3$), methylene blue (MB), aluminum foils and ammonium hydroxide (28-30% NH_3 basis) were brought from

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Sigma. GO was bought from JCNANO, INC.

For the synthesis of AgD/RGO composites, first, 0.1 mL ammonia solution and 100 μL NaCl (0.1 M) were dropped into 2 mL of 20 mM $AgNO_3$ aqueous solution successively. After adding 2 mL GO dispersion (0.5 mg/mL), the solution was stirred for 10 min. A piece of commercial Al foil (cut into 1×1 cm^2) was then immersed to the mixture. The mixture was then filled into a stainless steel autoclave and heated at 120 °C for 2 h. After naturally cooled down, the precipitate was washed by water using centrifugation. The final sample was obtained after drying in an oven at 60 °C (denoted as AgD/RGO). The Ag dendrite sample without graphene was also obtained following the same procedure but not adding GO to the $AgNO_3$ solution.

A field emission scanning electron microscopy (SEM, ZEISS SUPRA 40VP) under secondary electron imaging mode was used for observing the morphology of the samples. The samples were directly deposited on an ITO slide and observed under SEM. A Halo RB-10 UV–vis spectrophotometer was used to collect the optical spectra of samples at 190–800 nm range. The functional groups of the sample was analyzed by a FTIR (Nicolet iS5, Thermo Scientific). An XRD (Bruker D8 Advance) at 40 kV and 30 mA employing Cu Kα radiation (λ=0.1541 nm) was used for analyzing the crystal phase of the samples. Raman spectroscopy was performed at room temperature using a Raman microscope (Renishaw, inVia) with 514 nm laser light.

The catalytic performances of the samples were measured as follows: the reduction of MB by $NaBH_4$ has been chosen as a model reaction. For a typical reaction, 0.1 mL of $NaBH_4$ (0.5 M) was mixed with 3 mL MB (15 mg/L) solution. After addition of 10 μL of catalyst (0.5 mg/mL), the catalytic reduction process was monitored by a UV–vis spectroscopy at regular intervals of time.

3. Results and discussion

The morphology of the as-prepared Ag dendrites and AgD/RGO composite was observed using SEM. As shown in Fig. 1A, the Ag structure formed without GO has a typical dendritic shape, consisting one central stem and numerous side branches. The side branches present a nearly parallel pattern and almost emerged at 55° angles with the stem. After introducing GO into the galvanic replacement process, similar dendritic structures are observed with RGO sheets forming corrugated network around the Ag dendrites (Fig. 1B). The results indicate that the addition of GO sheets does not interrupt the formation of Ag dendritic structures. Figure 1C shows the XRD pattern of AgD/RGO composites. Five diffraction peaks observed at 38.1°, 44.4°, 64.8°, 77.7° and 80.1° are indexed to the face centered cubic silver. The (111) plane shows the highest intensity among all crystal planes, suggesting that silver is preferable to grow in (111) planes under the galvanic replacement condition. The (111) plane is also known as the most stable crystal plane of Ag. Elemental information of the as-synthesized AgD/RGO composite was collected using energy-dispersive X-ray spectroscopy (EDS). It can be seen that the composition of the AgD/RGO composite consists of carbon, oxygen, aluminum and silver. The strong peak of the element Ag implies the high content of Ag dendrites. Peaks of the element carbon indicate the presence of RGO while that of the element Al is from the Al foil.

Currently the exact growth mechanism of Ag dendrites is still not fully understood. The diffusion-limited aggregation (DLA) and the oriented attachment are the most commonly used models in the literature to explain the formation of Ag dendrites [32–35]. However, both mechanisms could not satisfactorily explain the construction of Ag dendrites during the galvanic replacement. Jiang et al. recently proposed the following mechanism for the construction of Ag dendrites during the galvanic replacement reaction [36]: The primary Ag nucleation occurs instantly when Al

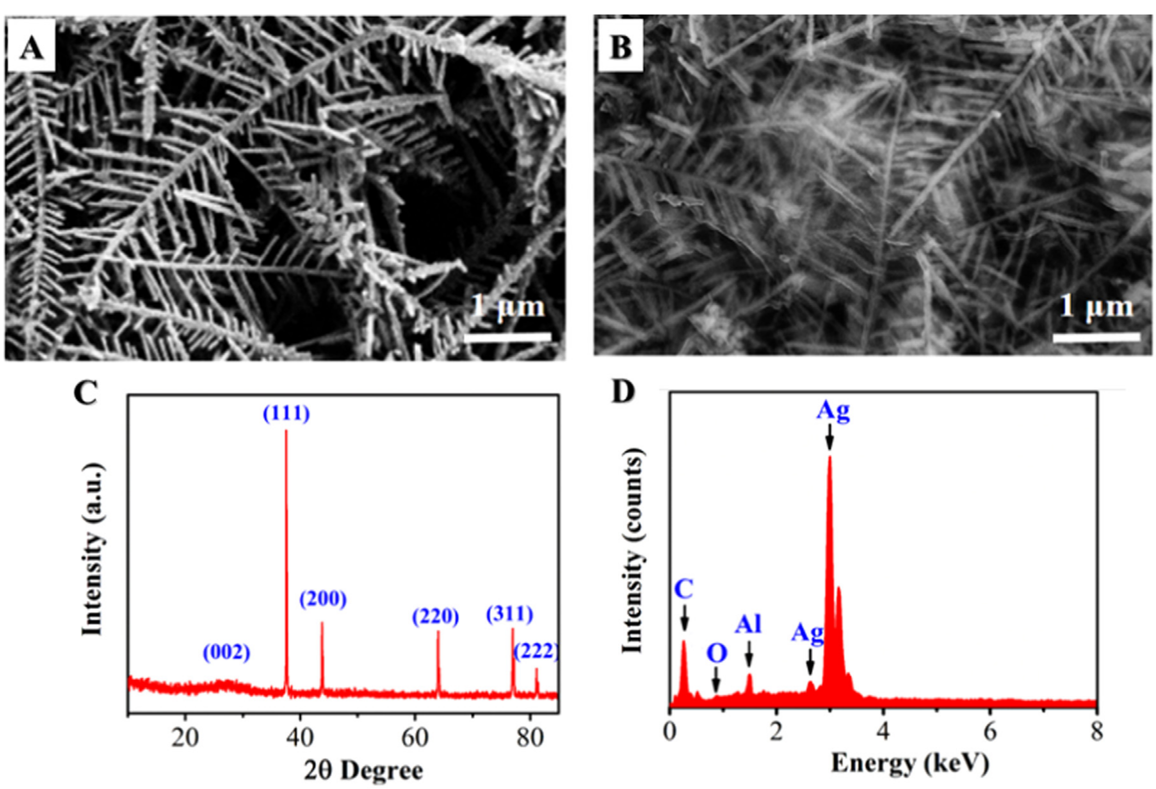

Fig. 1. SEM observations of (A) Ag dendrites and (B) AgD/RGO composite. (C) XRD pattern of the AgD/RGO composite. (D) EDS microanalysis of the AgD/RGO composite.