

Highly Exfoliated Graphene Oxide/Ag Nanocomposite via Supercritical Assisted Process for Efficient Visible-light Driven Photocatalyst

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ABSTRACT

A simple and effective supercritical route was developed to decorate silver nanoparticles (Ag NPs) on graphene oxide (GO) using glucose as a reducing agent. TEM, XRD and Raman analysis confirmed the formation of nanocomposite. The as-synthesized GO/Ag nanocomposite was used as an efficient visible-light driven photocatalyst for the degradation organic pollutants. The results showed that the photocatalytic performance of nanocomposite was greatly enhanced owing to the improved adsorption performance and separation efficiency of photo-generated carriers. In addition, antibacterial activity of the nanocomposite was studied.

INTRODUCTION

Silver (Ag) has been known as an antibacterial agent for centuries. Most commercially available Ag nanoparticles have limited control over the size, morphology and degree of aggregation [1,2] which are important parameters for determining the antibacterial activity of Ag nanoparticles. Graphene oxide (GO), a two-dimensional carbon material, has attracted a great deal of attention [3]. The presence of hydroxyl, epoxide, carbonyl and carboxyl groups not only allows the GO sheets to be well dispersed in water to yield a colloidal stable suspension, but also offers potential application as nanoscale substrates for the fabrication of flexible GO based composite materials. Recently, a number of studies have been reported based on the GO-metal nanoparticle composites in organic solvents [4,5]. However, processing of composites generally employs large quantity of organic solvents that are noxious and harmful to the environment. Thus, the processing with an environmentally benign supercritical fluid offers an attractive alternative to the conventional processing.

Supercritical fluid (SCF) technology has become an important tool for materials processing [6]. Among SCFs, supercritical carbon dioxide (scCO₂) is extensively employed. As a green solvent, scCO₂ is a substitute for conventional organic solvents because it is nontoxic, nonflammable, inexpensive, naturally abundant, and environmentally benign. Its low viscosity, high diffusivity, and negligible surface tension play important roles in preparing superior products of fine and uniform particles. These unique properties of scCO₂ make it an attractive medium for delivering solutes to small areas with complicated surfaces and poorly wettable substrates to attain a high uniformity and homogeneity.

In this work, Ag NPs decorated GO composite was fabricated via a facile and environmentally benign route with the assistance of scCO₂. The photocatalytic and antibacterial activities were tested. In addition, the nanocomposite is used as a catalyst for the reduction of potassium hexacyanoferrate(III).

MATERIALS AND METHODS

Graphite, silver nitrate (AgNO_3), glucose, methylene blue (MB), Titanium(IV) oxide (Degussa P25), potassium hexacyanoferrate(III) ($\text{K}_3[\text{Fe}(\text{CN})_6]$) and sodium borohydride (NaBH_4) were purchased from Aldrich and used as received.

Synthesis of GO/Ag nanocomposite

Experiment was carried out according to our previous procedure [7]. In a typical experiment, 20 mg of GO was dispersed in 1 mL of ethanol under ultrasonication for 2 h at room temperature to form a homogeneous suspension. 100 mg of AgNO_3 and 10 mg of glucose (reducing agent) were dissolved in 1 mL of ethanol. Immediately, the AgNO_3 solution was added to the above solution. The mixture was transferred quickly to a stainless steel reactor with a volume of 20 mL. CO_2 was then charged into the reactor. The temperature (65°C) and pressure (12 MPa) of the reactor was adjusted to the desired value and the scCO_2 condition was maintained for 3 h with magnetic stirring. The CO_2 was then vented slowly, and the sample was collected.

RESULTS

Raman spectrum of the nanocomposite showed two prominent peaks at around 1360 and 1600 cm^{-1} were assigned to the D and G bands, respectively. The G band represents the stretching motion of sp^2 carbon atoms (the E_{2g} phonons), whereas the D band corresponds to breathing modes of rings or K-point phonons of A_{1g} symmetry [8]. The intensities of these two bands were enhanced after coating the GO surface with Ag NPs, which is due to surface-enhanced Raman scattering from the intense local electromagnetic fields of Ag NPs that accompanies plasmon resonance [9].

XRD analysis confirmed both the patterns of GO and Ag NPs (JCPDS No. 04-0783). Diffraction peaks of Ag were indexed to the face-centered cubic structure.

TEM image (Figure 1) of the GO/Ag nanocomposite revealed that Ag NPs at the GO surface with a mean particle size of 5-15 nm. Nevertheless, few aggregated large particles could also be observed by TEM.

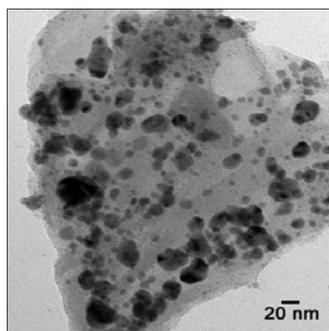


Figure 1. TEM image of nanocomposite.

In order to investigate the photocatalytic activity of the nanocomposite, MB dye was employed. 20 mg of photocatalyst was added into 100 mL of 10 ppm dye solution. Prior to irradiation, the suspension was magnetically stirred in the dark for 30 min to establish the adsorption/desorption equilibrium of the dye. At a given time interval of irradiation, 5 mL aliquots were withdrawn. Before analysis, the suspension was centrifuged to remove any suspended solid catalyst particles. The intensity of UV-peak at around 665 nm corresponds to the dye decreases with increasing the visible-light irradiation time. Figure 2 clearly showed

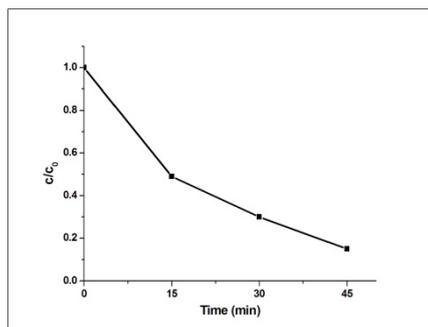
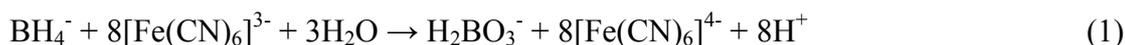


Figure 2. Photodegradation of the dye.

that about 85% of the dye was degraded within 45 min. Hence, we confirm that the photocatalytic activity of the composite on the degradation of dye.

The catalytic activity of as-synthesized GO/Ag nanocomposite was tested using a model reaction where hexacyanoferrate (III) is reduced by NaBH₄ into hexacyanoferrate(II) [10]. The redox reaction is depicted as:



In a typical experiment, 1 mL of distilled water, 0.5 mL of K₃Fe(CN)₆ solution (10 mM) and NaBH₄ in 0.1 M NaOH aqueous solution (30 mM, 1 mL) were added into the standard quartz cuvette. The alkaline solution could minimize the decomposition of borohydride. All the solutions were previously deaerated and purged with nitrogen. After two drops of GO/Ag in ethanol (1 mg/mL) was added into the above solution, the absorption spectra were recorded every 30 s up to 90 s. The progress of the reduction was monitored through changes in the UV-vis spectra of hexacyanoferrate(III). The characteristic hexacyanoferrate(III) absorption band at around 420 nm decreases with time as being reduced into ferrocyanide. Figure 3 showed the catalytic efficiency of nanocomposite in the conversion of hexacyanoferrate(III) into hexacyanoferrate(II) was found to be around 70%. The experimental data fit well with the first-order kinetics.

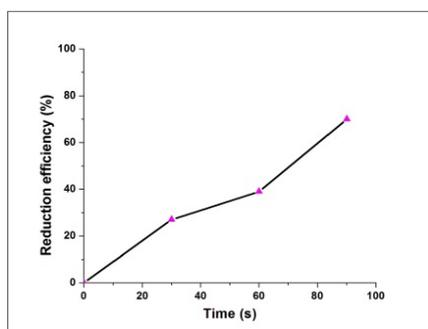


Figure 3. Reduction efficiency of photocatalyst.

As expected the Ag NPs coated on the GO exhibited significant antibacterial activity. The composite-free control showed no inhibition of bacterial growth. The antimicrobial activity depends on the permeability and penetration rate against the microbial cell wall.

CONCLUSION

We have successfully synthesized the GO/Ag nanocomposite by scCO₂ method. Ag NPs with an average diameter of around 5-15 nm were decorated on the GO. The simple, facile preparation method, appropriate dispersion and no residual impurities were significant aspects of this study. The photocatalytic degradation of MB dye showed that the nanocomposite had good visible-light driven photocatalytic property. The nanostructures exhibited good antimicrobial activity against gram-positive and gram-negative microorganisms. In addition, we have observed not only an enormous increase in the reaction rate, but also a change in the mechanism, from zero-order in hexacyanoferrate(III) reduction for the non-catalyzed reaction to first-order for the catalyzed reaction. In general, this method can be extended to the fabrication of other metal/GO composites.

REFERENCES

- [1] Vassilieff, T., Sutton, A., Kakkar, A. K., *Journal of Materials Chemistry*, 18, **2008**, 4031.
- [2] Fabrega, J., Fawcett, S. R., Renshaw J. C., Lead, J. R., *Environmental Science and Technology*, 43, **2009**, 285.
- [3] Zhang, L. L., Zhou, R., Zhao, X. S., *Journal of Materials Chemistry*, 20, **2010**, 5983.
- [4] Xu, C., Wang, X., Zhu, J., *Journal of Physical Chemistry C*, 112, **2008**, 19841.
- [5] Ma, J., Zhang, J., Xiong, Z., Yong, Y., Zhao, X. S., *Journal of Materials Chemistry*, 21, **2011**, 3350.
- [6] Ye, X. R., Lin, Y., Wai, C. M., *Chemical Communication*, **2003**, 642.
- [7] Haldorai, Y., Kim, B-K., Jo, Y-L., Shim, J-J., *Materials Chemistry and Physics*, 143, **2014**, 1452.
- [8] Zhou, H., Qiu, C., Yu, F., Yang, H., Chen, M., Hu, L., Sun, L., *Journal of Physical Chemistry C*, 115, **2011**, 11348.
- [9] Li, J., Liu, C.Y., *European Journal of Inorganic Chemistry*, 8, **2010**, 1244.
- [10] Pastoriza-Santos, I., Perez-Juste, J., Carregal-Romero, S., Herves, P., Liz-Marzan, L. M., *Chemistry-An Asian Journal*, 1, **2006**, 730.

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