GREEN SYNTHESIS OF GRAPHENE-METAL OXIDE NANOCOMPOSITES USING SUPERCRITICAL CARBON DIOXIDE

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ABSTRACT

Several methods have been carried out to produce graphene/metal oxide nanocomposites. Fabrication of these nanocomposites normally requires solution approaches, which are solvent-dependent. However, ideally 'green' synthetic approaches should be examined towards the new field of sustainable nanotechnology, where green solvents and one-pot synthesis approaches are preferable to conventional organic solvents containing many reaction steps. Therefore, processing with green solvents has attracted considerable interest as an alternative to the conventional processing. Herein we report the synthesis of graphene/metal oxide composites using supercritical fluid solvents.

INTRODUCTION

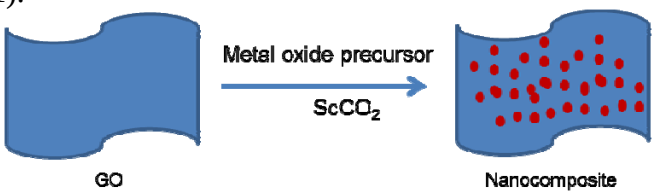
Due to supercritical carbon dioxide ($scCO_2$) has a zero heat of vaporization and it can be removed easily and completely by depressurization, thereby eliminating the energy-intensive drying processes generally used to remove traditional solvents. The special properties of $scCO_2$ have been used to fabricate nanomaterials that are difficult to prepare by traditional techniques. The low viscosity, high diffusivity, and negligible surface tension of $scCO_2$ play important roles in preparing superior products of fine and uniform particles [1]. These unique properties of $scCO_2$ also make it an attractive medium for delivering solutes to small areas with complicated surfaces and poorly wettable substrates to achieve high uniformity and homogeneity [2]. Recently, $scCO_2$ has been used in the exfoliation of graphene sheets [3] as well as the preparation of graphene from GO [4], providing tremendous potential for producing new materials. This paper reports an in-situ method for the growth of ZnO, Al_2O_3, Co_3O_4 NPs on RGO using $scCO_2$. The superior advantages of this $scCO_2$ chemical deposition technique lay in its flexibility, simplicity, green properties, and efficiency in material science and chemical processing.

MATERIALS AND METHOD

GO was prepared from natural graphite using a modified Hummers method [5]. In a typical experiment, GO was dispersed in 1 mL of ethanol to form a homogeneous suspension. A proper amount of metal oxide precursor was added to the above solution. The mixture was transferred quickly to a 20 mL stainless steel reactor. CO_2 was then charged into the reactor. The temperature and pressure of the reactor were adjusted to the desired values, and the $scCO_2$ conditions were maintained for 6 h with magnetic stirring. The CO_2 was then vented slowly, and the product was collected.

RESULTS AND DISCUSSIONS

The nanocomposites were synthesized by an environmentally-friendly approach using scCO2 (Scheme 1). In this study, $scCO_2$ played a key role in the coating of metal oxide NPs on the GO or RGO surface. First, $scCO_2$ is miscible with ethanol under suitable conditions. When ethanol acts as a solvent for the precursor, the zero surface tension of $scCO_2$ allows ethanol to wet the GO surface during the entire experimental process. Consequently, $scCO_2$ helps the precursor adsorb easily on the surface of GO and enhances the physical attraction of the two substances. In the composite, the metal oxide NPs were distributed densely on the RGO sheets (Figure 1).



Scheme 1. Illustration for preparation of graphene/metal oxide nanocomposites in $scCO_2$.

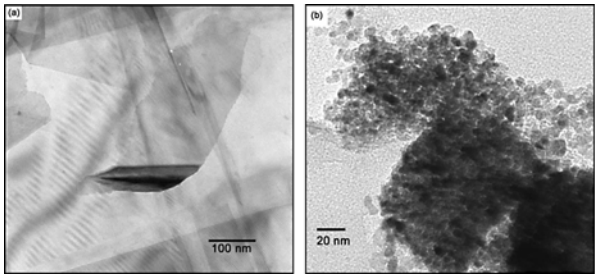


Figure 1. TEM images of the (a) RGO, (b) ZnO/RGO nanocomposite.

CONCLUSION

We successfully fabricated the metal oxide-RGO nanocomposite by a one-step green approach using $scCO_2$. $ScCO_2$ helped to debundle the RGO nanosheets and the densely dispersed metal oxide NPs on RGO prevented restacking of the nanosheets, and improved the electrochemical properties of obtained nanocomposites. The synthetic approach presents not only an environmentally-friendly option, but also relatively mild processing conditions that would be important for many techno-logical applications.

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