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Phase transferring of silver nanoparticles to organic solvents using modified graphene oxide as carrier

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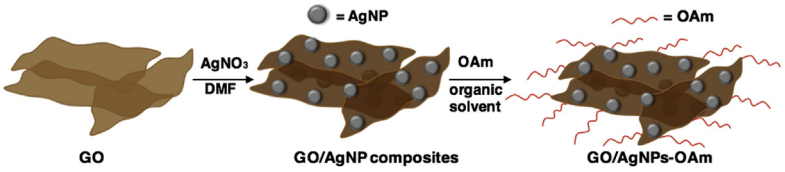
HIGHLIGHTS

- Innovative phase transfer process of anisotropic silver nanoparticles is proposed.
- Phase transferring process using graphene oxide as carrier is presented.
- Dispersive behaviors of the GO/AgNP composite in various organic solvents.

GRAPHICAL ABSTRACT



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ABSTRACT

An innovative phase transferring process of anisotropic silver nanoparticles (AgNPs) from aqueous to a wide range of organic solvents (e.g. toluene, n-butanol, iso-butyl acetate, ethyl-acetate, acetonitrile and ethylene glycol) was described. In the developed process, AgNPs were transferred to the organic solvents by using graphene oxide (GO) as a carrier. The transferring process was utilized by only two straightforward steps. Firstly, the composite of graphene oxide-silver nanoparticles (GO/AgNPs) were synthesized using N,N′ dimethylformamide (DMF) as a reducing agent. The existence, purity and stability of AgNPs on the GO sheets were examined by UV–visible spectroscopy, FTIR spectroscopy, XRD, and TEM. Secondly, the composite GO/AgNP were modified with oleylamine (OAm) in order to improve hydrophobicity. To reach the maximum phase transfer efficiency, an appropriate amount of OAm was carefully optimized. The dispersion behaviors of the composite GO/AgNP modified with OAm (GO/AgNP-OAm) in the organic solvents were investigated. It was found that the GO/AgNP-OAm are uniformly dispersed in the organic solvents for at least 18 h after sonication. The developed phase transfer method has the features of simplicity and high efficiency, moreover, it suitable to be scaled up for the industrial application.

1. Introduction

Noble metal nanoparticles especially silver nanoparticles (AgNPs) is a promising class of functional materials which have tremendous applications in several practical fields including nanomedicide as antibacterial agents [1–3], catalysis as a promising heterogeneous catalyst [4–7], energy as a component in Li batteries [8], electronic [9], optical sensors [10], and environmental applications [11,12] due to their size- and shape-dependent optical, electrical, electronic and antibacterial properties. Therefore, a number of protocols have been proposed for synthesis silver nanoparticles in both polar (e.g. water) [13–15] and nonpolar organic solvents [16–18] for a widely usage in the several productions. However, due to the metal precursor ($AgNO_3$), most of the previous protocols were preferably performed in either water or

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water-misible solvents. In the aqueous solvents, AgNPs are generally synthesized via the chemical reduction of silver ions with a reducing agent and control size and shape by an additional stabilizer [19–21]. Due to the synthesis protocol, the applications of those AgNPs was limited to the industrial and commercial products using water-based solvent. If the AgNPs were successfully synthesized and well-dispersed in organic solvents, it will open-up a new window of applications in polymers, coating materials and textiles which might require organic solvents as a media. However, to synthesize silver nanoparticles in organic solvents, a synthesis protocol is complicated and should be well-designed. For a practical usage of AgNPs, the transferring protocol of AgNPs is a potential alternative way to transfer AgNPs in aqueous solution to organic solvents [22–24]. Many authors reported the transferring process of silver nanoparticles into an organic phase by hydrophobization of the particle surface using various ligands such as alkylamines [25,26], ionic surfactants [27,28], amide coupling agents [29], etc. Such phase transfer procedures are very useful as aqueous phase synthesis of silver nanoparticles is relatively simple, inexpensive, and more reproducible, and furthermore, shape and size can be easily controlled using suitable stabilizers. However, there is a few severe limitations of the transferring process as (i) amount of transferring agents should be carefully optimized as they can be possibly from double layers around the particle, (ii) only small size of the particles might possibly be transferred and (iii) surface of the particle are dirty with the covered transferring agent molecules.

To overcome these limitations, the carrier system has been proposed to transfer the AgNPs to organic solvents. The system uses a carrier material as a transferring agent instead of using the surfactants. However, the type of carrier material should be well-considered as it should provide the functional groups to stabilize AgNPs, no loss on the properties of AgNPs, inert to any chemical reaction. From the literature overviews, the graphene oxide (GO) has emerged as a material that is often used to support and stabilize AgNPs for the preparation of novel nanocomposites for catalyst [30], antibacterial [31], SERS substrate [32], and sensors [33]. GO is not only providing strong interactions with the AgNPs but also enhances the properties of AgNPs [34]. According to the electronic charge of AgNP and oxygen rich functional groups on the GO, the generated AgNPs could be stabilized on the GO sheet and these functional group can be modified in order to increase hydrophobicity for transferring them into non-polar solvents. Therefore, GO might be considered as a good carrier material to transfer the AgNPs to organic media. Until now, no data exists to concern the phase transfer of AgNPs into organic solvents using GO as a carrier. Furthermore, this might be the first to report the phase transfer of the composite GO/AgNPs to be well dispersed in organic media. If the transferring protocol of the GO/AgNP composites is successfully developed, this will open up the new applications of the composites in electronics, polymers, coating etc.

In this work, we developed a simple, non-toxic, cost-effective, quick and environmentally friendly synthesis approach to fabricate graphene oxide based composite with silver nanoparticle (GO/AgNP) and the powerful protocol to modify them to form stable suspensions which can be well-dispersed in several organic solvents. Scheme 1 shows the overall protocol to transfer AgNPs into organic solvents using GO as a carrier. This proposed protocol provides several advantages such as (i) this protocol might not be affected from the uniformity of the AgNPs, (ii) the composite GO/AgNP can be stored in solid form and re-dispersed by sonication before using, (iii) the stability of AgNPs deposited on GO is very high (not oxidized to silver oxide), and (iv) it provides an appropriate color (gray metallic) instead of yellow which suitable in some commercial products.

The existence of AgNPs on GO nanosheets was examined by several techniques such as UV–Vis spectroscopy, XRD, TGA, and TEM. Furthermore, the stability of AgNPs decorated on GO was evaluated by the bath sonication. A hydrophobicity of the composites was increased using a primary amine with long hydrocarbon chain, oleylamine (OAm), to modify the surface of the GO/AgNP composites. The dispersion behavior and the stability of the modified GO/AgNPs in six organic solvents (e.g. toluene, *n*-butanol, iso-butyl acetate, ethyl acetate, acetonitrile, and ethylene glycol) were also investigated.

2. Experimental

2.1. Chemicals and materials

2 mg/mL of graphene oxide nanocolloids (GO) and oleylamine (OAm) were purchased from Sigma-Aldrich company. Ethanol (EtOH), ethyl acetate (EtOAc), and acetonitrile (ACN) were obtained from Merck (Thailand), while dimethylformamide (DMF), toluene (TOL) and ethylene glycol (EG) were purchased from Carlo Erba. Isobutyl acetate (*i*-BuOAc) and n-butanol (*n*-BuOH) were purchased from BDH chemicals and RCI Labscan Limited (Thailand), respectively. Silver nitrate ($AgNO_3$) was obtained from Aencore chemical company. All reagents and solvents were in analytical grade and were used without further purification. All glassware and magnetic bars were cleaned with detergent and followed by deionized (DI) water.

2.2. Preparation of GO/AgNP composites

The stock solution of 1500 ppm $AgNO_3$ was prepared by dissolving 0.075 g of $AgNO_3$ in 50 mL of DI water. 200 ppm of graphene oxide (GO) suspension was prepared by mixing 2.5 mL of GO suspension in 22.5 mL of DI water. The synthesis of GO/AgNP composites was performed by mixing 25 mL of the prepared 200 ppm GO with 25 mL of the stock solution of $AgNO_3$ and then immediately poured in 100 mL of DMF. The mixed solution was stirred and heated in sand bath with controlled temperature at 130–150 °C for 2 h. The reaction was incubated under ambient conditions until it cool down to the room temperature. The obtained GO/AgNP suspensions were then centrifuged at 5000 rpm for 20 min and then washed the colloids of GO/AgNPs by DI water for several times in order to remove the excess silver ions (Ag^+) and DMF. The obtained GO/AgNP composites were dried at 60 °C for 3 h. The existence of silver nanoparticles (AgNPs) on GO were characterized by UV–Vis spectroscopy, transmission electron microscopy, X-ray diffraction and thermal gravitation analysis.

2.3. Preparation of GO-OAm and GO/AgNPs-OAm

Oleylamine was used as a phase transferring agent to transfer GO into organic solvents. To transfer GO into organic solvents, the dried suspension of 200 ppm GO was modified by adding the oleylamine. The modified GO-OAm was then dispersed in organic solvents by sonication process. The various amounts of OAm was performed in order to determine the optimized condition for transferring GO in organic solvents. After obtaining the optimized amount of OAm, the appropriate amount of OAm was added to 2 mg of the GO/AgNP composites. The mixture was sonicated by bath sonication for 2 min to generate GO/AgNPs-OAm. To examine the dispersion behavior, the GO/AgNPs-OAm was dispersed in 5 mL of organic solvents; TOL, *n*-BuOH, *i*-BuOAc, EtOAc, ACN and EG with bath sonication (Elmasonic Model: P30H) for 1 h, the GO/AgNPs-OAm was well suspended in organic solvents affording the formation of uniformed dispersed gray colloids.