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Factors that affect the stability, type and morphology of Pickering emulsion stabilized by silver nanoparticles/graphene oxide nanocomposites

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ABSTRACT

Silver nanoparticles/graphene oxide (AgNPs/GO) nanocomposites were easily fabricated by a green method without using any additional reductant and the prepared nanocomposites were then used to stabilize Pickering emulsions. The properties of the emulsions stabilized by the AgNPs/GO prepared with different AgNO3/GO mass ratios were investigated and the effects of the oil/water ratio, the AgNPs/GO concentration, and the pH on the stability, type and morphology of the emulsions were studied. In addition, the effects of adding different types and concentrations of electrolytes on the emulsion stability were studied. Adding electrolytes to the systems improved the stability of the Pickering emulsions due to the reduction in the particle zeta potentials. Polystyrene–AgNPs/GO composites were also prepared by Pickering emulsion polymerization and their catalytic performance for the reduction of4-nitrophenol was investigated.

1. Introduction

Graphene is a monolayer of carbon atoms arranged in a hexagonal lattice [1,2]. It has received considerable attention due to its unique two-dimensional (2D) structure and its excellent mechanical, electronic and optical properties [3–5]. Large amounts of graphene are easily produced via the reduction of graphene oxide (GO) which is obtained by the intense oxidation of graphite [6,7]. GO sheets are oxygenated graphene sheets that are covered with epoxy, hydroxyl, and carboxyl groups and they have large surface areas, so they have many potential applications, such as adsorption [8,9], separation of pollutants [10], and catalytic carriers for chemical reactions [11,12]. Their unique structures also offer opportunities to modify the GO and make functionalizedgraphene-based materials.

Recently,Ag-based catalysts have attracted much attention because of their relatively low cost and their broad applications in various reactions [13]. To prevent the aggregation of the nanoparticles, supports are often used to anchor and stabilize the metal nanoparticles. It has been found that GO is an ideal support material for growing and anchoring metal nanoparticles such as Au, Ag, Pd, Pt, and Ru nanoparticles (NPs) [14–17]. GO supported metal nanoparticles have excellent electrocatalytic and electrochemical properties.

Pickering emulsions or solid-stabilized emulsions are colloidal emulsions stabilized by solid particles instead of organic surfactants [18,19]. They have broad and important applications in the food [20], cosmetics [21], and pharmaceutical fields [22,23]. Solid particles have been shown to assemble at the fluid interface due to the reduction of the inter-facial energy of the system that occurs when a new interface is created between the particles and the liquid phases instead of at the liquid–liquid interface. The particles should be partly wetted by both phases for an effective stabilization of Pickering emulsions [24]. In general, the predominate hydrophilic or hydrophobic nature of the particles determines whether they tend to stabilize in oil-in-water (o/w) or water-in-oil (w/o) emulsions, respectively [25,26]. Multiple emulsions can be obtained by adding two types of particles with different hydrophobicities to oil and water mixtures. In some cases, multiple emulsions can form around a phase inversion of emulsions in a system containing only one particle type [27,28]. The differences in

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the wetting behavior of the particles are the reasons for the formation of multiple emulsions.

The preparation of Pickering emulsions have recently been studied by many researchers. Thompson et al. prepared oil-in-water Pickering emulsions with relatively narrow size distributions using a stirred cell membrane emulsification with poly (glycerol monomethacrylate) stabilized polystyrene (PS) particles as the sole emulsifier [29]. Shen and Resasco reported the preparation ofwater-in-oil andoil-in-water emulsions with variable fractions of emulsion volume when carbon nano tube-silica nanohybrids were used as stabilizers [30].

In addition, Pickering emulsions can be used as templates for the design and production of new functional hybrid materials with well-defined nanostructures [31]. Roberto et al. prepared "soft" nanocomposite clay armored polymer latexes by using Laponite clay XLS as a stabilizer in Pickering emulsion polymerization [32]. Sacanna and Philipse reported a novelsingle-step synthesis of monodispersedlatex-basedcore–shell colloids based on spontaneous Pickering emulsification [33]. Pickering emulsions polymerization is a versatile approach to prepare polymer/inorganic composites [34]. Gudarzi and Sharif used Pickering emulsion polymerization to fabricate PMMA/GO composites [35]. Since it was soap free, their new method paved the way for an environmentally benign process for the production of high quality polymer graphene nanocomposites.

There are two terms needed to introduce here in order to help the reader to understand this paper easily. The first term is Zeta potential, which is the potential difference between the dispersion medium and the stationary layer of fluid attached to the dispersed particle. The zeta potential of colloidal dispersions greatly affects the stability and aggregation of the dispersions [36]. The other one is DLVO theory, which is proposed for the stability of colloidal dispersions that invoked a fundamental instability driven by strong but short-ranged van der Waals attractions countered by the stabilizing influence of electrostatic repulsions [36].

In this work, silver nanoparticles/graphene oxide (AgNPs/GO) nanocomposites were easily fabricated by a green method without using any additional reductant. The prepared nanocomposites were then used to stabilize Pickering emulsions and the behavior of the Pickering emulsions stabilized by AgNPs/GO was analyzed in detail. The effects of different conditions on the properties of the Pickering emulsions stabilized by AgNPs/GO were investigated. In addition, the effect of adding different electrolytes to improve the emulsion stability by controlling the extent of particle flocculation was investigated. Furthermore, PS microspheres with AgNPs/GO on the surface were prepared by Pickering emulsion polymerization and their catalytic performance for the reduction of 4-nitrophenol(4-NP) was investigated.

2. Experimental

2.1. Materials

Graphite was obtained from Qingdao Graphite Processing Factory. Potassium permanganate, sodium nitrate, concentrated sulfuric acid, 30% hydrogen peroxide, hydrochloric acid, sodium hydroxide, sodium chloride, magnesium chloride hexahydrate, silver nitrate, sodium borohydride and the organic reagents were all purchased from Tianjin Chemical Technology Co. All chemicals were analytical grade and used as received.

2.2. Preparation of GO

GO was prepared from purified natural graphite by a modified Hummers method [37]. Experimental details are given in the literature [38].

2.3. Preparation of silver nanoparticles/GO nanocomposites (AgNPs/GO)

An $AgNO_3$ aqueous solution (15 mL, 0.4 mg/mL) was mixed with various amounts of an aqueous GO suspension (8 mg/mL). The mixture was stirred for 15 min at 84 °C, during which time the Ag nanoparticles were deposited on the surface of the GO sheets to form AgNPs/GO.

2.4. Preparation of Pickering emulsions stabilized by different concentrations of AgNPs/GO

First, AgNPs/GO prepared from different $AgNO_3$/GO mass ratios was used to prepare Pickering emulsions. Then the $AgNO_3$/GO mass ratio was fixed at 0.375, and other experimental conditions such as the oil/water ratio, the AgNPs/GO concentration, and the pH were varied in order to investigate their effects on the emulsion stability. To investigate the effect of the electrolyte on the emulsion stability, salts of different valences and concentrations were added to the aqueous dispersions. An aqueous dispersion of GO was mixed with an organic solvent and sonicated with an ultrasonic dipping probe close to the surface to form the Pickering emulsions. For example, for the benzyl chloride–water emulsion with an oil/water ratio of 1/1, 6 mL of benzyl chloride was added to 6 mL of 0.5 mg/mL aqueous $AgNO_3$/GO suspension in a vial. The mixture was sonicated at 160 W for 3 min and allowed to stand before characterization.

2.5. Preparation of the PS-AgNPs/GO composites and their catalytic reduction of4-nitrophenol

First, 10 mL of an aqueous dispersion of AgNPs/GO (0.72 mg/mL) was mixed with 1 mL of styrene (St) and 10 mg of azobisisobutyronitrile (AIBN) in a flask. After sonication for 3 min, the flask was purged under vacuum and then flushed with nitrogen. The polymerization of St was conducted at 70 °C for 18 h with stirring.

The prepared PS–AgNPs/GO composites were deposited on a stainless steel wire mesh (mesh count: 300) and collected, and then they were used to catalyze the reduction of 4-NP. First, 5 mL of aqueous 4-NP solution (1.54×10^{-3} M) was mixed with 1 mL of freshly prepared aqueous $NaBH_4$ solution (0.88 M) and a deep yellow solution was formed. Then, a moderate amount of the catalyst was added to the solution and when the solution became colorless it indicated that the reaction was finished. The reaction progress was monitored by UV–vis spectroscopy at 400 nm (the characteristic peak of 4-NP). After the reaction was finished, the supernatant was removed. New reactants were then added to the residue of the catalyst that settled on the bottom of the flask to begin another cycle of reaction and treatment.

2.6. Characterization

The morphologies of the AgNPs/GO and PS–AgNPs/GO composites were characterized using transmission electron microscopy (TEM, Philips Tecnai G2 F20) at 200 kV. Ultraviolet–visible (UV–vis) absorption spectra were recorded with aTU-1901 UV–vis spectrophotometer. X- ray powder diffraction (XRD) analysis was conducted on a BDX3300X-ray diffractometer at a scanning rate of 4°/min over the 2θ range of 10° – 90°, employing CuKα radiation (λ = 0.15418 nm). X-ray photoelectron spectroscopy (XPS) was conducted on an X-ray photoelectron spectrometer (PHI1600 ESCA System, PERKIN ELMER, USA). The zeta potentials of the AgNPs/GO dispersions at different pH values and salt concentrations were measured using a Malvern Zetasizer Nano ZS at 25 °C. The photographs of the emulsions stabilized by AgNPs/GO were recorded with a digital camera (COOLPIX S620, Nikon,