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Original Research Paper

Structural, electrical, and rheological properties of palladium/silver bimetallic nanoparticles prepared by conventional and ultrasonic-assisted reduction methods

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ABSTRACT

Polyvinylpyrrolidone stabilized Pd/Ag bimetallic nanoparticles (NPs) with average particle sizes of 9 and 6 nm were synthesized by simultaneous reduction in the presence and absence of ultrasound waves, respectively. The prepared NPs were characterized by six methods including X-ray diffraction (XRD), transmission electron microscopy (TEM), high resolution-TEM (HRTEM), UV–vis spectroscopy, scanning tunneling microscopy (STM), and energy dispersive X-ray (EDX) analysis. The rheological properties of Pd/Ag NPs in ethylene glycol as a base fluid with various mass fractions of NPs from 2% to 5% at different temperatures were studied experimentally and theoretically. The experimental results showed that viscosity of Pd/Ag NPs in ethylene glycol increases with increasing particle mass fraction and decreases with increasing temperature. A maximum of 31.58% increase in viscosity of ethylene glycol at 20 °C was observed when 5% Pd/Ag NPs was added. Measurement of the electrical conductivity of nanofluids of Pd/Ag bimetallic NPs in distilled water at different mass fractions and temperatures was performed. A 3841% increase in electrical conductivity of distilled water at 25 °C was observed when 1% Pd/Ag NPs was added. Both the rheological and electrical properties of Pd/Ag bimetallic NPs were measured in ethylene glycol and distilled water, respectively for the first time.

1. Introduction

Application of nanotechnology in several fields is driven by the use of a variety of nanostructures. The field of nanomaterials is a fast-growing area and has gained great attention by scientists and industry manufacturers because of its multi-functionality along with processing properties that can be tailored. In recent years, many studies have been carried out on noble metal nanoparticles (NPs) because they display fascinating properties which are different from the bulk materials [1–5]. Among the metallic NPs, bimetallic nanoclusters, in particular, have been demonstrated to be the most attractive ones for a variety of applications [6–9] with several important advantages over the monometallic ones. From not only the scientific but the technological point of view, bimetallic NPs have been investigated in many fields of science and industry. By combining two kinds of metals, some changes such as improving the catalytic quality [10], changing the surface plasmon band [11], and regulating the magnetic properties [12] of the parent metals may occur.

Several possible types of structures for bimetallic nanoclusters including core–shell [13–15], random alloy [16,17], crown-jewel [18,19], hollow structure [20,21], and dendritic structures [22] have been reported. In any of these cases, there is direct interaction between the metals. Bimetallic NPs may have unique features including (1) physical and chemical interactions among different atoms, (2) altered miscibility and interactions unique to nanometer dimensions, and (3) morphological variations [23].

Bimetallic palladium-based NPs show unique catalytic activity for hydrogenation of organic compounds. Singh et al. [24] used the Pd/Ni bimetallic NPs as a catalyst for hydrogen generation from decomposition of hydrous hydrazine. They found that the Pd/Ni bimetallic NPs compared with Pd or Ni monometallic NPs have higher H_2 selectivity in the reaction. Xiuli and coworkers [25] used Pd/Pt NPs as a catalyst in the hydrogenation of phenyl aldehydes. They also realized that Pd atoms in Pd/Pt NPs promote the activity of the catalytic hydrogenation mainly through geometric and

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electronic effects. Pd/Au bimetallic NPs were used as a catalyst in the hydrogenation of imidazolium based ionic liquids [26]. Recently, Smuleac et al. [27] synthesized Fe/Pd bimetallic NPs by a non-toxic green reducing agent, green tea extract, instead of the well-known sodium borohydride. They used the synthesized NPs for reductive degradation of chlorinated organic compounds.

Among the various kinds of Pd-based bimetallic NPs, Pd/Ag NPs show special properties. These NPs show catalytic activity for hydrogenation of cis,cis-1,3-cyclo octadiene and methyl acrylate [10,28], electrocatalytic reduction of benzyl chloride [29], electroless copper deposition [30], and catalytic reduction of N_2O [31].

A number of methods have been used to prepare the Pd/Ag bimetallic NPs including solvothermal method [32,33], UV irradiation [34,35], heterogeneous reaction [36], reduction of silver ions on the surface of palladium particles [30], reverses micelles [37], laser irradiation [38], γ-irradiation [28], microwave-polyol processes [39], and galvanic displacement reaction [40,41].

In addition to the above methods, colloidal bimetallic NPs have been prepared by sonochemical synthetic routes. Suslick and coworkers [42,43] were the first to demonstrate the exploitation of ultrasound to produce bimetallic NPs. They prepared Fe–Co alloys via the sonochemical decomposition of iron pentacarbonyl and cobalt tricarbonylnitrosyl. Mizukoshi and coworkers [44] reported a sonochemical synthesis of core–shell structured Pd/Au NPs in aqueous solutions. Bimetallic Pd/Cu NPs have been prepared by ultrasonic irradiation of Pd and Cu nitrate precursors using ethylene glycol (EG) and polyvinypyrrolidone (PVP) as reducing and stabilization agents, respectively by Nemamcha et al. [45]. Recently, Godínez-García and coworkers [46] synthesized Pd/Ag bimetallic NPs by high intensity ultrasound waves method. They used a mixture of 50% EG and 50% distilled water (DW) as a solvent.

The first aim of the present work is to prepare Pd/Ag bimetallic NPs from aqueous solutions of silver nitrate and palladium nitrate dihydrate by simultaneous reduction method in the presence and absence of ultrasound (US) waves. The sodium borohydride ($NaBH_4$) and PVP were used as reducing and stabilizer agents, respectively. The second goal is to prepare the nanofluids of Pd/Ag NPs in DW and EG.

Many investigators have studied the various characteristics of fluid flow and heat transfer behavior of nanofluids [47–51]. The viscosity of nanofluids is critical to product performance in many industrial applications and process efficiency. For example, the viscosity of nanofluids is essential for establishing an adequate pumping power as well as the convective heat transfer coefficient. In the actual thermal measurement, the nanofluids are expected to be used under the flow conditions; hence, the rheological properties of nanofluids would affect their heat transfer performance [52,53]. The third goal is the measurement of the rheological properties of Pd/Ag NPs-EG nanofluids at different temperatures and mass fractions.

Although the thermal conductivity and viscosity of the nanofluids have been measured widely [41–45], very few studies concerning the electrical conductivity of nanofluids have been done. The electrical conductivity of the nanofluids may give information on the state of dispersion and stability. In this context, the present work was undertaken to explore the electrical transport property of Pd/Ag bimetallic NPs in DW. Towards this purpose, the forth goal of this work, the effect of particle mass fraction and temperature on the electrical conductivity of the Pd/Ag bimetallic NPs-DW nanofluids was analyzed and presented.

To the best of our knowledge, this research is the first work which reports the electrical conductivity of suspensions of Pd/Ag bimetallic NPs in DW and the rheological behavior of Pd/Ag-EG nanofluid as functions of both temperature and mass fraction of NPs.

2. Experimental section

2.1. Materials

The starting materials used in this work were silver nitrate ($AgNO_3$), palladium nitrate dihydrate ($Pd(NO_3)_2{\cdot}2H_2O$), $NaBH_4$, and PVP (M_w = 2000 g/mol). All chemicals were used as received without further purification. All the solutions were prepared by DW.

2.2. Synthesis procedure

A typical synthesis of the Pd/Ag bimetallic NPs was carried out as follows. The total concentration of metal ions was kept constant 5×10^{-5} M. In brief, 5×10^{-4} mol $AgNO_3$, 5×10^{-4} mol $Pd(NO_3)_2{\cdot}2H_2O$, and 0.02 g PVP were dissolved in 100 ml DW under vigorous stirring. PVP protects the NPs from agglomerating. Then, 1.6×10^{-3} mol $NaBH_4$ was added. The reaction mixture was sonicated for 60 min with a sonicator (Sonicator-4000) operating at 20 kHz. The power transferred to the solution was 33 W cm^{-2} measured by means of calorimetric method. The reaction temperature was controlled to 30 ± 1 °C with the help of condensation water surrounding the reactor cell. During the reduction reaction, the solution color changed from colorless to black with dark colloidal particles. The fresh samples were centrifuged, washed with DW three times, and dried in the vacuum oven overnight. A similar procedure was done for the Pd and Ag NPs. Control experiments were also carried out in the absence of US waves. The NPs were dispersed in DW and EG to prepare the nanofluids using intensive ultrasonic vibration for 15 min. The stability of a suspension is defined in terms of the change in one or more physical or physicochemical properties over given time period. The nanofluids in DW were fairly stable for a couple of days without visually observable sedimentation. The nanofluids in EG were found to be very stable for several months.

2.3. Characterization techniques

The powder phases were determined by means of a Bruker/D8 Advanced diffractometer in the 2θ ranging from 20° to 80° by step of 0.04° with graphite monochromatic Cu Kα radiation (λ = 1.541 Å).

The TEM analyses of the samples were obtained using a LEO 912 AB instrument. The electron beam accelerating voltage was 120 kV. The UV–vis absorbance spectra were obtained for the samples using an Agilent photodiode-array Model 8453 was equipped with glass of 1 cm path length. The spectra were recorded at room temperature in air within the range of 200–800 nm.

The HRTEM analyses were carried out using FEIT ecnai F20 Field emission by the use of an accelerating voltage of 200 kV. The STM images (200 × 200 nm and 30 × 30 nm) were provided by STM SS1 with Pt/Ir STM tip, 1.7 nA constant current, and 0.23 V voltage. The EDX analysis was carried out using the type Inca 400 (Oxford Instruments). The electrical conductivity of suspensions of Ag NPs, Pd NPs, and Pd/Ag bimetallic NPs in DW was measured using an EDT instrument BA 380.

The viscosity of the nanofluids of Pd/Ag NPs in EG was measured using a Brookfield Viscometer (LV DV-II + Pro EXTRA) with a small sample adaptor. The water jacket was connected to a circulating cooling water bath (BL 7100, Major Science) to control the water temperature. The repeatability of viscometer is ±0.2%.

The zeta potential of the Pd/Ag bimetallic NPs NPs in DW was measured using the Zetasizer from Malvern instrument.