Journal of Physics and Chemistry of Solids 86 (2015) 155–161

Contents lists available at ScienceDirect

Journal of Physics and Chemistry of Solids

journal homepage: www.elsevier.com/locate/jpcs

Polyol mediated hexadecylamine capped silver allied nanobimetallic particles and their fluxional properties

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ARTICLE INFO

Article history:
Received 25 May 2015
Accepted 6 July 2015
Available online 9 July 2015

Keywords:
Alloys
Metals
Electron microscopy
X-ray diffraction
Optical properties

ABSTRACT

The syntheses of hexadecylamine seed mediated Ag/M (M=Co, Ni, Pd and Pt) allied nanobimetallic particles were successfully carried out by the successive reduction of ligand capped metal ions with polyols, resulting in concomitant precipitation of some high index faceted hybrid Ag/M bimetal nanoparticles. The optical measurements revealed the existence of surface plasmon band and peak broadening that causes diffusion processes of the metal sols to decrease making it possible to monitor the changes spectrophotometrically. The bimetallic nanoparticles were characterized by X-ray diffraction, X-ray photoelectron spectroscopy and electron microscopy techniques which confirm the formation of alloyed clusters.

1. Introduction

Bimetallic nanoparticles exhibit properties different from bulk materials with the same composition because of size confinement effects and their large volume fraction of interfaces. Bimetallic nanoparticles composed of two distinct metal elements are interesting as they possess unique physical and chemical properties due to their reduced size and tailored morphological structure [1,2]. This emerging class of materials can have a core/shell, heterostructure, intermetallic or an alloyed structure, and have applications in various fields including electronics, engineering, and catalysis [3,4].

There is a great enhancement in specific physical and chemical properties of bimetallic NPs due to synergistic effects. For example, nanostructured Ag materials have received considerable attention for many decades because of their widespread use in various fields such as optics, biology, and catalysis [5,6]. However, due to the limited reserves of Ag materials, it is expedient to reduce their usage. Incorporating heterometals (e.g. Fe, Co, Ni) into Ag NPs will reduce Ag usage, and also endow them bifunctional performance with possibilities of new properties [7].

Metallic nanoparticles of precise size can be easily synthesized by the "bottom-up" approach with surface-modification with organic functional groups. In the process, nanoparticles exhibit new optical properties which are not observed either in the individual molecules, or in the bulk metals. For example, the presence of a strong absorption band in the visible region arises as a result of the surface-plasmon-oscillation modes of the conduction electrons that are coupled through the surface to external electromagnetic fields [8]. Plasmon absorption bands arising due to the optical properties of palladium, platinum and silver nanoparticles in solution have become interesting to materials scientists. The size, shape and refractive index of the surrounding medium determines the color of metal nanoparticles [9]. Pt-nanoparticles with a secondary shell material such as Ag, Pd or Ni are interesting due to their specific catalytic activity and selectivity in hydrogenation and visible light induced hydrogen evolution [10,11].

Among several methods employed for the synthesis of bimetallic nanoparticles wet chemical co-precipitation is considered germane due to the fact that the products of precipitation reactions are generally sparingly soluble species formed under conditions of high supersaturation [12]. Nucleation is a key step of the precipitation process. The agglomeration of small particles precipitated from solution is unavoidable in the absence of a stabilizer because the thermodynamics favor the maximization of surface/volume ratio. The two approaches in stabilization include (a) steric repulsion between particles caused due to capping groups [13] and (b) electrostatic (van der Waals) repulsion resulting from the chemisorption of charged species at the surfaces [14]. The class of organically soluble stabilizers include: tetrahydrofuran (THF),

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http://dx.doi.org/10.1016/j.jpcs.2015.07.004
0022-3697/

mercaptosuccinic acid (MSA), 3-(aminopropyl) trimethoxysilane (3-APTMS), PVP-poly(vinylpyrrolidone) (PVP), dioctylsulfosuccinate sodium salt (AOT). The molecular structures of these compounds reveal the presence of hetero atoms and/or chelating ligands with lengthy alkyl chains and in certain cases steric hindrances which facilitate and control growth anisotropy.

Conventional methods for controlling metal–metal bond formation and crystal growth primarily use synthetic polymers. An example is the formation of cubic silver and palladium particles using poly(acrylate) or poly(vinylpyrrolidone) templates. Smaller multidentate ligands such as trisodium citrate can also be used to control crystal shape as well, for example, in the photo induced conversion of silver nanospheres to triangular prisms [15].

We report the use of hexadecylamine (HDA) as organic ligands in mediating the polyol reduction of metal salts precursors act as templates for moderate temperature reduction of metal salt precursors to initiate the nucleation and particle growth processes of formation of silver hybrid nanoparticles. The long chain hydrophobic aliphatic end of the hexadecylamine, functions in such a way that it can reproducibly fold into three-dimensional structures reminiscent of a surfactant molecule. This unique property can be exploited in synthesizing silver allied nanoparticles with fluxional morphological properties.

2. Experimental

The seed mediated or successive reduction method deployed was modified from literature method and used to prepare monodispersed Ag/M nanohybrids at optimum concentration of metal precursors under controlled temperature conditions [16,17]. The reaction mechanism for the formation of bimetallic nanoparticles via the anisotropic nucleation and growth mechanism is shown in Scheme 1.

2.1. Materials

All inorganic salts, solvents and chemical reagents used were analytical grade, and were purchased from Sigma-Aldrich Corporation, UK. They are as follow: *n*-hexadecylamine (HDA), tri-*n*-octylphosphine (TOP), silver nitrate, nickel (II) acetate, cobalt (II) acetate, palladium (II) chloride, platinum (IV) chloride, glycerol (GLY), diethylene glycol (DEG), methanol (99.5% *w*/*w*) and toluene.

2.2. Synthesis of allied Ag/M nanoparticles

Fractal monodispersed bimetallic AgM (M = Co, Ni, Ru, Pd, Pt) nanostructured particles were prepared by the seed growth or successive addition method [11,12]. Briefly, 24.92–25.81 mmol, 90% *w*/*w* HDA (capping agent) was measured into a round bottom flask containing a magnetic stirrer and it was gradually heated to melt. 5.0 mL tri-*n*-octylphosphine (TOP) was added as dispersing solvent; 5.0 mL diethylene glycol (DEG) or glycerol as the reducing agent. The mixture was stirred and gradually heated at the rate of 2.0 °C/min to 200 °C followed by the injection of 0.56 mmol Co $(CO_2CH_3)_2 \cdot 4H_2O$ dispersed in 5.0 mL dioctylether. A rapid color change to brown was observed. The resultant mixture was left to allow for the growth of Co nanoparticles which also acted as a seed for the next reaction. Then, 0.41–0.85 mmol $AgNO_3$ similarly dispersed in 5.0 mL TOP was injected into the colloidal mixture, followed by hot injection of 5.0 mL aliquot of diethylene glycol. The reaction continued for 2 h with continuous stirring. After the hot injection of silver nitrate solution, a shiny brown colored Ag/Co sol was obtained. While hot, the Ag/Co sol was copiously washed with methanol several times, and centrifuged at 4400 rpm for 10–15 min. to remove excess unreacted stabilizer. The Ag/Co sol was later redispersed in toluene.

The procedure was subsequently repeated for other metal precursors 0.44 mmol $Ni(CO_2CH_3)_2 \cdot 4H_2O$; 0.33 mmol $PdCl_2$; 0.16 mmol $PtCl_4$; 0.30–0.62 mmol $AgNO_3$ were used to co-precipitate Ag/Ni, Ag/Pd and Ag/Pt HDA capped bimetallic nanoparticles respectively.

2.3. Isolation of Ag/M nanoparticles

The centrifuged sols obtained after decantation was redispersed in toluene and cleaned in ultrasonic bath at 50 °C for 60 min before further characterization.

2.4. Characterization

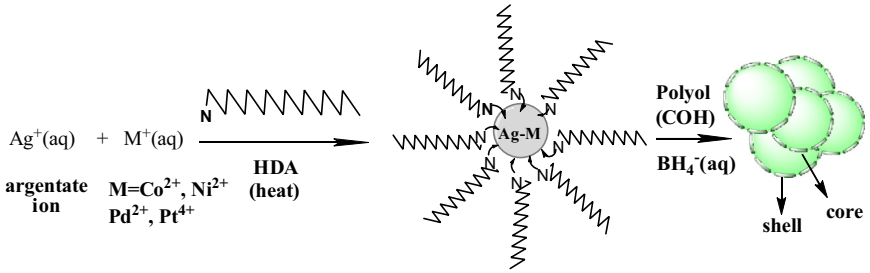
2.4.1. Optical characterization

A Varian Cary 50 Conc UV–vis spectrophotometer was used to carry out the optical measurements and the samples were placed in silica cuvettes (1 cm path length), using toluene as a reference solvent. A Perkin-Elmer LS 55 Luminescence spectrometer was used to measure the photoluminescence of the particles. The samples were placed in a quartz cuvette (1 cm path length).

2.4.2. Structural characterization

The crystalline phase was identified by X-ray diffraction (XRD), employing a scanning rate of 0.05° min^{-1} in a 2θ range from 20° to 80°, using a Bruker AXS D8 diffractometer equipped with nickel filtered Cu Kα radiation ($\lambda = 1.5406$ Å) at 40 kV, 40 mA and at room temperature. The morphology and particle sizes of the samples were characterized by a JEOL 1010 TEM with an accelerating voltage of 100 kV, Megaview III camera, and Soft Imaging Systems iTEM software. The detail morphological and structural features were investigated using HRTEM images with a JEOL 2010 TEM operated at an accelerating voltage of 200 kV.

The survey of surface property and high resolution spectra of nanoparticles were collected using XPS PHI 5000 Versaprobe-Scanning ESCA Microprobe, with 100 μm 25 W 15 kV Al monochromatic X-ray beams.



Scheme 1. Anisotropic reduction and nucleation processes of Ag/M nanohybrid leading to core–shell structure.