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Cobalt@silver bimetallic nanoparticles: Solution based seedless surfactant assisted synthesis, optical properties, and morphology

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ABSTRACT

Simple solution based method was used for the synthesis of cobalt@silver bimetallic nanoclusters in presence of cetyltrimethylammonium bromide (CTAB) at room temperature. In a first step, monometallic cobalt nanoparticles (cobalt nucleus), was obtained which acted as a seed for the growth of silver shell in a second step under potential deposition. The optical images, UV–visible spectroscopic, transmission electron microscopic (TEM), scanning electron microscopic (SEM) data revealed that the formation of silver shell around the cobalt core and their thickness were strongly depends on the [Ag^+]. Surface resonance plasmon peak increasing with [Ag^+] and a red shift was observed. Number of the particles decreases with [Ag^+], indicating the number of the nucleation sites decreases, which in turn, provided the less sites to Ag^+ ions reduction. The reduction of Ag^+ ions occurred on the surface of Co^0 by under potential deposition. Growth of Ag^0 alone occurs on the surface of Co/Ag rather than forming more nucleation sites. The optical properties of as prepared Co@Ag nanocomposites are dominated by the metallic Ag. The absence of oxygen peak in the EDX spectra, confirmed the formation pure Co@Ag nanoparticles with no oxide, which might be due the strong capping actions of CTAB.

1. Introduction

Synthesis and structural evaluation of spherical, wires, rods, cubes, triangles, prisms, multi-branched, multi-pods transition metals mono-, bi-, and/or hollow-metallic nanoparticles by various methods (radiation, chemical, photochemical, seed growth, metal evaporation, thermal decomposition, and electro- chemical) with and without template(s) have been the subject of investigations from ca. three decades [1–15], and their potential applications in semiconductors, fields of optics, microelectronics, sensors, information storage, photography, catalyst production, super magnets, and determination of dyes, etc. are unlimited [16–20]. Park and Cheon reported the synthesis of Co-Pt nanoalloys (Co_{core} Pt_{shell}; smaller than 10 nm) via the redox transmetalation reactions between dicobalt octacarbonyl,$Co_2(CO)_8$, and Pt(hexafluoroacetylacetonate)$_2$ without the need for any additional reductants. They also suggested that the reaction proceeds selectively as long as the redox potential between the two metals was favorable [21]. Transmetallation is a type of organometallic reaction (redox-transmetalation and redox-transmetalation/ligand-exchange) The reaction is usually an irreversible process due to thermodynamic and kinetic reasons.

Xia et al. developed a simple and versatile route to the large-scale synthesis of various (triangular rings, prism-shaped boxes, cubic boxes, spherical capsules, and tubes) metal hollow nanostructure of Au-Ag alloys by using transmetallation reaction between AgNPs and an aqueous $HAuCl_4$ solution and pointed out that the SPR peaks have been readily shifted from 500 to 1200 nm by controlling the ratio between Ag^0 and $HAuCl_4$ [22,23]. Sastry et al. [24–26] and Cheng and Walker [27] been synthesized bimetallic nanoparticles (Au/Pt, Au/Ag, and Co/Au) by transmetallation reaction in an organic solvent and foam-based technique. The chemistry of nanosize- and colloidal-metal particles in terms of their physicochemical properties in solution has come a long way and their importance in semiconductors, superconductors, photography, catalyst production, supermagnets, etc. are unlimited. For stabilization of small particles, the use of polymers, ligands, solid matrix and surfactants has also been suggested. Although a number of stabilizers are available for the stabilization of nanosize particles in solution, these are associated with some demerits. In this content, surfactant aggregates, especially micelles, reverse micelles and macroemulsions, will get an edge over other stabilizers. Surfactants role in bulk solution and at interfaces is of great importance in surface chemistry. Surfactants properties have attracted growing attention for use in biological and chemical research applications. Henglein [1] in their pioneering review mentioned that the reactions on the surfaces of small particles are referred to as *microelectrode* due to the similarities with electrode reactions in electrochemistry.

In this paper, a new seedless method was developed to synthesize nano structured of Co@Ag, where silver solutions were added into a

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reaction mixture containing $NaBH_4$ and Co^{2+} ions solutions in presence of cetyltrimethylammonium bromide as a stabilizer. These methods give rise high quality core-shell nanomaterials in a single step reaction, and an in-depth mechanistic information about the growth of Co@Ag nanoculsters. To our best knowledge, such type of nanoparticles have not been reported previously. The chemical composition and the morphology of the as-synthesized nanomaterials were characterized by conventional physical, chemical, and spectroscopic methods.

2. Experimental

2.1. Materials and instruments

All reagents (cobalt nitrate, $Co(NO_3)_2$, BDH, 99%; sodium borohydride, $NaBH_4$, BDH, 99%; silver nitrate, $AgNO_3$, 99.9%, BDH; cetyltrimethylammonium bromide, Fluka, 99%; potassium permanganate, 99%, Fluka) were used as received without further purification. The glassware was washed with aqua regia (3:1 HCl and HNO_3), rinsed with double distilled (first time with alkaline $KMnO_4$) water, and drying prior to use. The resulting Co@Ag nanoparticles were characterized by using the following conventional techniques. Shimadzu UV–vis spectrophotometer; model UV-1800, Japan, transmission electron microscope (Hitachi 7600 with an accelerating voltage of 120 kV) were used to record the UV–visible spectra and determine the size, shape and the size distribution of resulting nanomaterials, respectively. Selected area electron diffraction (SADE) data were also recorded. XRD patterns were recorded using Ni-filtered Cu Kα radiation (λ = 1.54056 Å) Rigaku X-ray diffractometer operating at 40 kV and 150 mA at a scanning rate of 0.020 per step in the 2θ range of $100 \le 2\theta \le 800$. Surface image was characterized with SEM (JEOL JSM-6700F, JEOL Japan Electronics Co., Ltd., Tokyo, Japan). The infrared spectra were measured on a Fourier-transform infrared spectrophotometer (IRPrestige-21, IRAffinity-1, FTIR-8400S,Shimadzu Corporation Analytical and Measuring Instrument Division) by using KBr pellet technique. Elemental composition was determined with energy dispersive X-ray spectroscopy (EDX) by following on a TECHNAI-320 KV JAPAN, operating at 80 kV system equipped with energy dispersion X-ray spectroscopy. The samples for EDX, TEM, and SEM analysis were prepared by placing a drop of the as-synthesized nanomaterials onto a carbon-coated Cu grid (300 mesh), followed by a drying treatment at room temperature.

2.2. Synthesis of monometallic Co-, and Ag-NPs

Preliminary observations showed that the Co^{2+}-$NaBH_4$, and Ag^+-$NaBH_4$, redox reactions are very fast, and light pink and colorless reaction mixtures becomes gray and yellow turbid, respectively, with the mixing time of $NaBH_4$. Therefore, in order to obtain perfect transparent colored sols of cobalt and silver, all experiment are carried in presence of CTAB. Typically, in the first set of experiments, a solution of $NaBH_4$ (10.0 cm^3, 0.01 mol dm^{-3}) was added in the two separates reaction vessels containing an aqueous solution of Co^{2+} (5.0 cm^3; 0.01 mol dm^{-3}), and Ag^+ (5.0 cm^3; 0.01 mol dm^{-3}) with CTAB (5 cm^3; 0.01 mol dm^{-3}; total volume = 50 cm^3) under constant stirring at the room temperature. The molar ratio of $Co^{2+}/NaBH_4$ in the system was 2/1. As the reaction time increases, perfect transparent gray, and yellow-orange color appeared in the reaction vessels of Co^{2+}, and Ag^+, respectively, which indicates the onset of the evolution of the monometallic Co-, and Ag-nanoparticles, respectively [28,29]. The resulting cobalt and silver sols are stable for ca. 2 h and several months, respectively.

2.3. Synthesis of $Co_{core}Ag_{shell}$ nano-composites

The bimetallic nanoparticles,$Co_{core}Ag_{shell}$ nano-composite, were synthesized as follows: In the second set of experiments, to fabricate the core/shell composite, the different [Ag^+] (from 0.5 to 3.0×10^{-3} mol dm^{-3}) were added in the resulting sky blue color cobalt sols having [CoNPs] = 1.6×10^{-3} mol dm^{-3}. The solution reacted for 2 h under stirring at room temperature. The color change from gray, dark brown to dark yellow black indicated the formation of Co/Ag NPs. The resulting materials were separated by centrifugation at 10,000 rpm for 20 min, washed several times with water, and dried in air. The pH of the working reaction mixture was measured at beginning as well as end of the reaction, and was found to be constant, ca. 5.8 for the entire reaction period.

3. Results and discussion

3.1. TEM images

The morphologies of the as-prepared nanomaterials were examined with TEM method. First, Co-NPs and Ag-NPs were prepared for comparison. The morphology of these nanomaterials are shown in Fig. 1, which shows that the as-prepared Co-NPs and Ag-NPs have an irregular aggregated needle-shaped crystalline platelets morphology (length ca. 50 nm, width ca. 10 nm; Fig. 1A), and poly dispersed irregular shaped with dimensions 140 nm to 220 nm (Fig. 1B), respectively. The turbostratic morphology is characteristic of the α-hydroxides CoNPs [30]. To determine the morphology of bimetallic Ag/Co nanoparticles, TEM images of the three samples containing different molar ratio of Co^{2+}/Ag^+ were recorded. These results are summarized in Fig. 2 for $Co^{2+}/Ag^+ = 2.5$ (A), 1.1 (B) and 0.76(C). Inspection of Fig. 2 clearly suggests that the [Ag^+] has significant impact on the morphology of as-synthesized Co@Ag nanoparticles. The adsorption of Ag-NPs onto the needle-sheet shaped Co-NPs (Fig.2A), formation of $Co_{core}Ag_{shell}$ nanoparticles (Fig. 2B) and aggregation of small particles with large particles

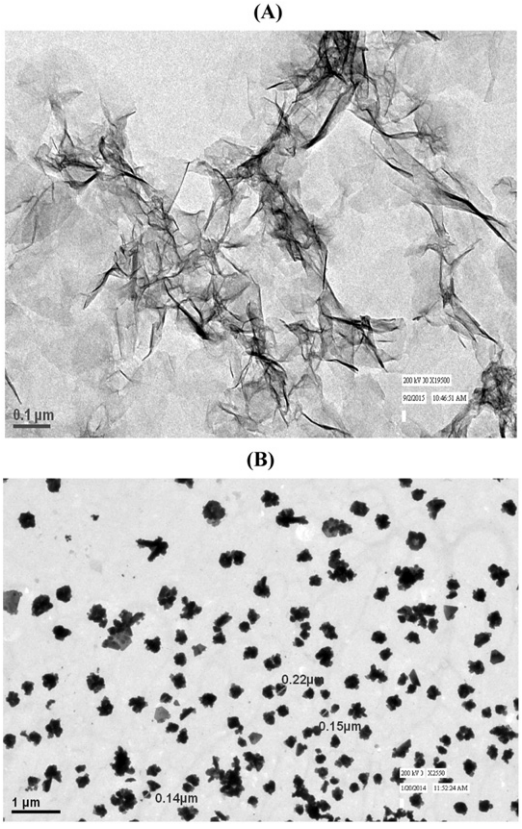

Fig. 1. TEM images of monometallic Co-NPs (A), and Ag-NPs (B). *Reaction conditions*: [CTAB] = 8.0×10^{-4} mol dm^{-3}, [Co^{2+}] = 1.6×10^{-3} mol dm^{-3}, [Ag^+] = 10.0×10^{-4} mol dm^{-3} and [$NaBH_4$] = 3.3×10^{-3} mol dm^{-3} and 2.0×10^{-4} mol dm^{-3} for Co-NPs and Ag-NPs, respectively.