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Synthesis and Characterization of Fibrous Bimetallic CuPt Nanoparticles

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Abstract This paper reports a facile methode for the synthesis offibrous bimetallic CuPt Nanoparticles (CuPt NPs) using the liquid phase deposition methods deposited directly on an indium-tin oxide (ITO) substrate. The electron microscopy analysis result shows that CuPt NPs, constructed by networked-nanorod of diameter ca. 3.5 nm and length approximately 5.5 to 6.5 nm, exhibits aquasi sphericalmorphology and fibrous structure with diameter approximately 196±98 nm. The differences of individual element miscibility and the effect of lattice-mismatch between Pt and Cu isthe key factorfor the formation of fibrous structure. XPS analysis indicated that the fibrous bimetallic CuPt NPs feature metallic properties with highly reactive surface. This may increase the charge-transfer reactions in catalytic, electrochemistry and sensors application.

Keywords: fibrous structure, lattice-mismatch effect, CuPt

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1. Introduction

Bimetallic nanoparticles synthesis with large surface area, such as fibrous structure, has received considerable attention because of their ability to enhance electrical, magnetic, and catalytic properties [1, 2]. Platinum based bimetallic nanocrystal is amongs the metal nanoparticle that is used in a broad range of applications, such as catalysis [3], electrocatalysis [4], and sensing [5] due to its peculiar electrical and catalytic properties.Up to now, there are many Pt-based bimetallic nanostructures fabricated and performed an extraordinary catalytic properties in wide range of applications, particularly in acetone hydrogenation, electrocatalytic oxidation of methanol and the CO oxidation process. This paper report an effective approach to synthesize fibrous bimetallic CuPt nanoparticle that was prepared using liquid-phase deposition method. The nanoparticle is characterized by network nanorods forming highly porous structure. X-ray photoelectron spectroscopy analysis reveals that the structure exhibit active surface chemistry and potential to enhance catalytic performance.

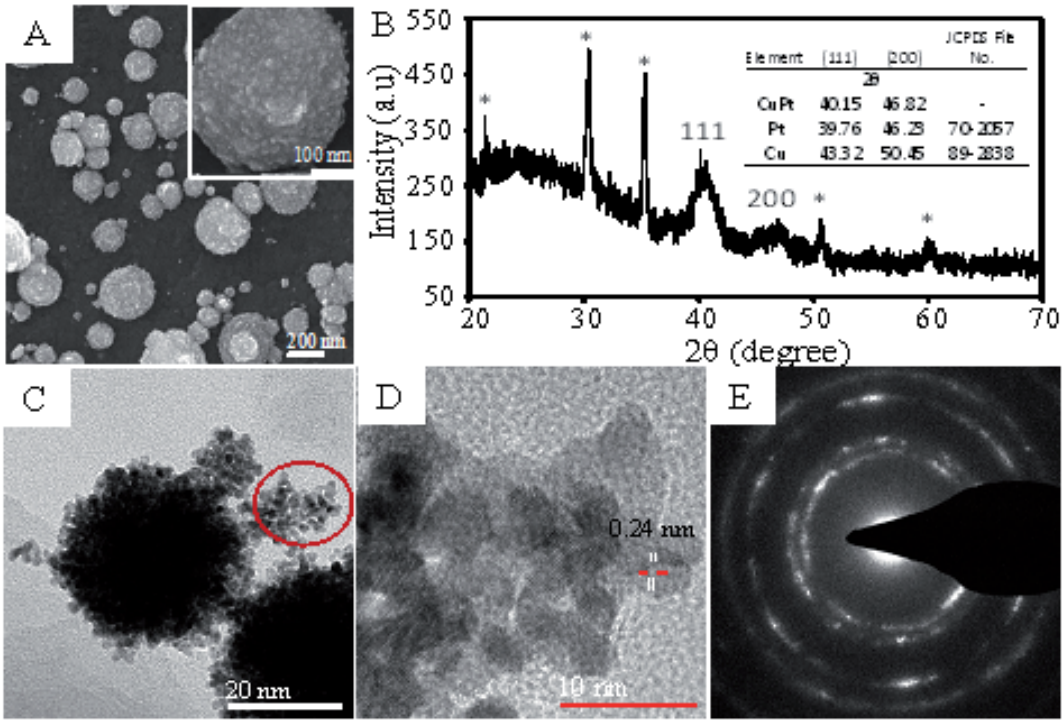

Figure 1: (A) FESEM image of fibrous bimetallic CuPt NPs. The inset in A is the high-resolution of the CuPt NPs. (B) XRD spectrum of fibrous bimetallic CuPt NPs. (C) Low resolution and (D) high-resolution TEM images of fibrous bimetallic CuPt FNPs, (E) SAED diffraction pattern from the nanostructure.

2. Experimental Section

Potassium hexachloroplatinate (K_2PtCl_6), Copper(II)Sulfate ($CuSO_4$) anhydrous, Sodium dodecyl sulfate (SDS) and Formic acid were all from Fluka. All chemicals were used as received. ITO substrate (sheet resistance of 9–22 Ω per square was purchased from a VinKarola instrument, USA) was cleaned by consecutive ultrasonication in acetone and ethanol for 30 min, respectively prior to the growth process.

The bimetallic CuPt NPs deposited on the ITO substrate were prepared following our recently reported method [6], by simply immersing the clean substrate into a 15 mL aqueous solution that contained 1 mM K_2PtCl_6, 0.2 mM $CuSO_4$anhydrous, 10 mM SDS and 10 mM formic acid and continuously stirred at 400 rpm during the reaction. The growth temperature and time was set to 40 ^{0}C and 4 h, respectively. Then the sample was removed from the growth solution and rinsed with a copious amount of deionized water. The final product was dried with a flow of nitrogen gas.

The morphology of bimetallic CuPt NPs was characterized by field emission scanning electron microscope (FESEM) Hitachi S-4800 operated at an accelerating voltage of 2 kV and high-resolution transmission electron microscopy(HRTEM) FEI Tecnai G2 F20 operated at accelerating voltage of 200 kV and 10-6 Pa with X-twin objectives lens. The atomic composition, structural properties and chemical state of bimetallic CuPt NPs was analyzed by energy-dispersive X-ray mapping (EDX-mapping), X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) analysis. EDX apparatus is equipped with X-maxN 80T detector. Moreover, XRD apparatus is equipped with XRD BRUKER D8

Advance system with CuKα irradiation (λ = 1.541Å) and XPS apparatus is equipped with operated at a scan rate of 10 °/min and Ulvac-PHI XPS *Quantera* II, with Al Kα – 1486.6 eV mono-chromated scanning X-ray source, respectively.

3. Results and Discussion

The thin layer of CuPt NPs with fuzzy gray color was observed on the ITO substrate after a growth process for 4 h in the growth solution containing K_2PtCl_6, $CuSO_4$ anhydrous, SDS and formic acid. The typicalFESEM analysis result of the sample is illustrated on Fig.1a. An uneven distribution of CuPt NPs nanoparticles was formed that covers nearly 65% of the ITO substrate.The nanoparticle exhibited quasi spherical shape with anextremely rough surfaces and diameter of approximately 196±98nm.

To obtain the information of bimetallic CuPt NPs phase, XRD analysis was carried out to CuPt NPs sample. the sample was characterized by XRD. Fig. 1b reveals two prominent peaks, i.e. at 2θ = 40.15^o and 46.82^{o}corresponds to the Pt crystal plane (111) and (200) respectively, but slightly shifted. When observed the others peaks are belongs to by the ITO substrate. To clarify the formation of bimetallic CuPt NPs, the present XRD result is compared to individual Ag and Pt (the inset table in Fig.1b). The formation of bimetallic CuPtNPs could be signed by the two prominent peaks of bimetallic CuPt NPs are fell in between those of the two pure metal elements where slightly higher angle compared to the individual Pt, i.e. 0.39 ^{o} to 0.59 ^{o} and lower angle compared to the individual Cu, i.e. 3.17^o to 3.63^o. This condition indicate that the intermetallic compound was formed upon introduction of Cu ions into the Pt host lattice [7].

To evaluate how the structure of bimetallic CuPt NPs, high-resolution TEM analysis was carried out (Fig.1D). As shown in the Fig.1D, large number of nanorod overlapping constructed CuPt NPs structure. The length and diameter nanorod are approximately 5.5 to 6.5 nm and 3.5 nm respectively. As have been mentioned previously, the current reaction is modification of our previous approuch for synthesis of Pt fibrous cubes. Changing of nanoparticle morphology from the fibrous cubes (PtNCs) to quasi sphericalCuPt NPs was due to the introduction of the Cu^{2+} ion into the growth solution. The differences of individual element miscibility and the effect of lattice-mismatch, between Pt and Cu which is as high as 8.2%, is assume the key factor for the modificationof the morphology. With a fibrous morphology, the CuPt NPs may provide a high active surface area for enhanced surface reaction and may accelerate the diffusion of reactant and product onto the surface in catalytic application process.

High-resolution TEM image for single nanorod (Fig.1d) revealed that nanoparticle is single crystal as evidenced by the lattice fringes across the full extent of nanorod particle. The d-spacing value of approximately 0.24 nm. The comparison between d-spacing value of PtNCs (111) faceted and CuPt NPs reveals that the nature of crystal has grown along the [111] direction. The crystallinity of CuPt NPs has been also revealed by Selected-area electron diffraction (SAED) pattern (Fig 1E). Due to the some of nanorods structure overlapping difraction, it caused the polycrystalline detected, practically the structure is monocrystalline.

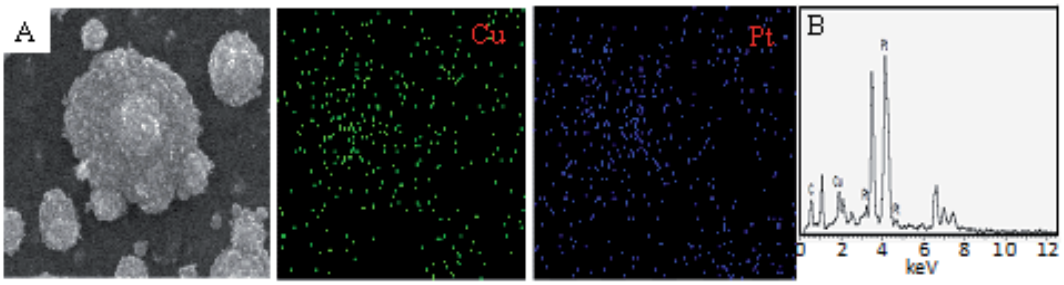

Figure 2: EDX mapping (A) and spectrum (B) of Bimetallic CuPt NPs.

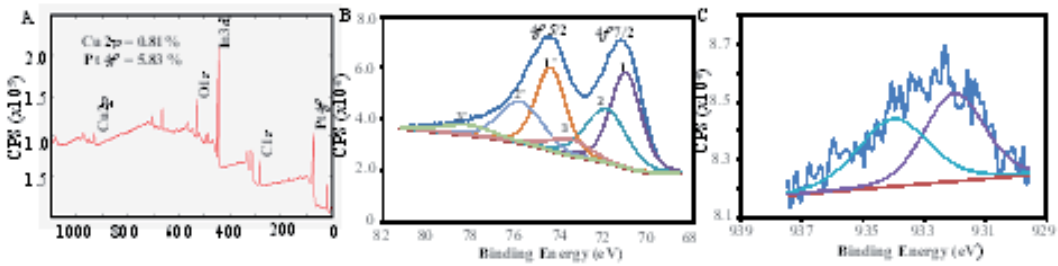

Figure 3: (A) Wide-spectrum scan of bimetallic CuPt NPs. High-resolution spectra for Cu 2*p* (B), and Pt 4*f* (C).

To further confirm the formation of bimetallic CuPt NPs and the element distribution in bimetallic CuPtNPs, Energy-Dispersive X-ray mapping analysis was carried out. The result is shown in Fig.2. Fig.2 reveals, the CuPtNPs is clearly constructed by the Cu and Pt element which are homogeneously distributed on CuPt NPs structure. The atomic composition analysis shows that Cu concentrations are much lower compared to Pt, namely 1:5.4. As also observed from the analysis result, carbon elements was detected in the fibrous bimetallic CuPt NPs structure. It is simply analyzed that it come from the surfactant source.

XPS analysis was employed to know the chemical state and the surface composition of the CuPt NPs. The result is shown in Fig. 3. Gaussian–Lorentzian (G–L) mixed function (70% Gaussian and 30% Lorentzian components) with Shirley-type background as the peak line shape was used in the curve fitting process. Based on survey scan analysis (Fig.3.a), we found that the molar ratio of Cu and Pt is approximately as high as 1:7.2 on the surface. This ratio is slightly different from the bulk elemental analysis using EDX mapping, i.e. as high as 1:5.4. Nevertheless Pt element is still predominant. Fig. 3b and c show the typical high resolution spectra for Cu (2*p*) and Pt (4*f*) core level states.On the typical high resolution spectra Pt4*f*, there are three pairs of overlapping GL Curves on Pt 4*f*7/2, it means, Pt has three oxidation states of Pt, namely Pt (0) at 71.05 eV (curve 1), Pt^{2+} at 71.97 (curve 2) and and Pt^{4+} at 73.61 (curve 3) eV (Fig. 3B). It reveals that the Pt has been reduced from Pt^{4+} to Pt^{2+} and Pt 0 species in intermetallic compound. The Metallic state of Pt in CuPt NPs shows a negative shift if it is compared to the pure Pt, i.e. 71.3 eV [8]. It may be caused by the perturbed electronic interaction between Pt and Cu atomic orbit and in turn to its alloy formation. The evidentiary of bimetallic formation also can be seen with the presence of Pt (0) is the predominant species, as high as 52.45%.

Meanwhile on the typical high resolution spectra Cu 2*p* show two pairs of overlapping GL Curves. Based on curve fitting on Cu*p*3/2, it infers that Cu has two oxidation state, i.e. at 932.01 eV and 934.0 eV binding energy respectively. It means, Cu is composed by two oxidation states, namely Cu (0) and Cu^{2+}species respectively. If we see the relative intensities of avery oxidation state, the intensity of Cu (0) species is higher then Cu^{2+} species, i.e. 51.10%. The comparison of Cu (0) binding energy (current result) and pure Cu was also occured. A negative shift of binding energy is appeared when metallic state of Cu is compared to the system of pure Cu (932.63 eV) [9]. It can be understood that Cu has electron donating property and it has a possibility to donate the electron to the half filled of Pt *f*-orbital in the formation of bimetal nanoparticle. Considering that metallic state of Cu and Pt have high intensity in the compound and shows negative energy shifting, it indicates the CuPt NPs is conformed completely formed.

4. Summary

In this experiment, CuPt NPs were synthesized directly on an indium tin oxide (ITO) substrate by Liquid phase deposition methods. The FESEM and HRTEM analysisshows that a fibrous bimetallic CuPt NPs nanoparticles was formed and cover nearly 65% of the ITO substrate.The nanoparticle is constructed by large number of nanorods overlapping. Through the molar ratio of Cu^{2+} to Pt^{4+} ion in growth solution preparation as high as 1:5, the geometry of nanoparticle could be efficiently adjusted, the average diameter of the nanoparticle is approximately 196±98 nm.The differences of individual element miscibility and the effect of lattice-mismatch between Pt and Cu isthe key factor for the formation of fibrous morphology. XPS analysis revealed that the higher percentage of Cu (0) and Pt (0) species established, indicates that the CuPt NPs surface is chemically reactive and may be considered as a potential in nanocatalyst.

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