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A single pot synthesis of crystalline and porous Ni–Pt sponges

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ABSTRACT

NiPt sponges were prepared by PVP–$NaBH_4$ reduction of Ni and Pt precursor salts under low temperature (100 °C) followed by prolonged aging at room temperature for 2 months. Powder X-ray diffraction (PXRD) patterns suggested the presence of face-centered cubic (FCC) structure of NiPt particles. Compared with the standard diffraction data of pure Ni and Pt, the main peaks of NiPt particles shifted towards higher 2θ value. The X-ray photoelectron spectroscopy (XPS) signals of NiPt alloy suggested the equal proportion of Ni° and Pt° on the surface which is a characteristic of 1:1 NiPt-based bimetallics. Scanning electron microscopic (SEM) images of spongy-like NiPt alloy on a silicon wafer substrate showed interconnection of porous “tunnels” that are constructed with small pores of a pore size around 200 nm.

1. Introduction

The synthesis of nanostructured functional materials with controlled structure and morphology is critical for scientific and technological applications [1]. The interest in nanoscale materials arise from the possibility of manipulating them in multiple dimensions [2] and used as functional materials within the integrated systems [3]. They incorporate functional properties enabling low-cost fabrication of revolutionary high-value, high-performance applications in a broad range of industries from life and physical sciences to information technology and communications [4–6]. Nanocrystalline alloys and magnetic materials exhibit a comprehensive overview of this fast-moving field such as MRI for medical diagnosis, high-density magnetic recording, controlled drug delivery, biological targeting or separation, and catalysis [7–13]. In recent years, there has been an increased interest in coating surfaces of magnetic nanoparticles with a thin-shell material for various electronic and biomedical applications [3,14].

Although recent advances in synthesizing metal nanostructures with controlled morphologies are found in the literature [15,16], there are no reports of spongy bimetallic alloys. Bimetallic systems often offer advantages over single-metal systems e.g. metal alloy nanoparticles can show enhanced catalytic and selectivity properties relative to their single-metal components [17,18] and both optical [19] and magnetic [20] properties can be fine-tuned by adjusting the metal ratios in alloy nanoparticles. The technologically relevant Co–Pt and Fe–Pt systems are important targets since hollow nanospheres of these alloy systems could find widespread use in magnetic, catalytic, and biomedical applications [21]. Here, we report, to the best of our knowledge, the first e.g. of spongy Ni–Pt alloy system synthesized through a novel and potentially applicable to the other bimetallic systems.

2. Experimental

In a typical synthesis, $Ni(C_2H_3O_2)_2{\cdot}4H_2O$ (4.3 mg) and poly(vinyl pyrrolidone) (PVP, MW 40,000, 100 mg) were dissolved in 50 mL of deionised H_2O (18.2 MΩ), sonicated for 30 min, and purged with N_2 followed by dropwise addition of a freshly prepared $NaBH_4$ solution (10 mg in 20 mL of H_2O) with stirring. 10 min after the addition of $NaBH_4$, K_2PtCl_6 (16.4 mg in 20 mL H_2O) was added dropwise with stirring at 100 °C. The solution was stirred for 24 h in inert atmosphere (N_2) and aged for 2 months. The yellow colour of the initial reaction solution changed into black after 2 months prolonged aging (Fig. 1). The fine aged powder was collected by centrifugation, washed several times with H_2O and ethanol, and dried under vacuum. The reaction of formation is summarized in the following redox reactions:

(1) Before addition of K_2PtCl_6, the solution of $Ni(C_2H_3O_2)_2{\cdot}4H_2O$ ionises in presence of $NaBH_4$ and PVP:

$$Ni(CH_3COO)_2 \leftrightarrow Ni^{2+} + 2(CH_3COO)^-$$

(2) The aqueous solution of K_2PtCl_6 ionises to form $[Pt^{4+}Cl_6]^{2-}$:

$$K_2PtCl_6 \leftrightarrow 2K^+ + [PtCl_6]^{2-}$$

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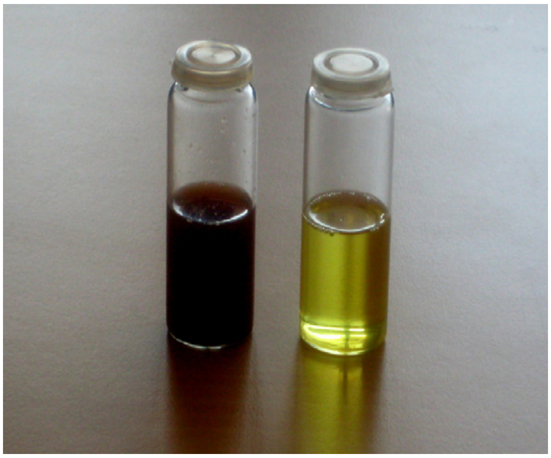

Fig. 1. The reaction solution before and after the NiPt sponges formation.

(3) Redox process:

$$Ni^{2+} + 2e^{-} \rightarrow Ni^{0}(s)$$

$$[Pt^{4+}Cl_6]^{2-} \rightarrow Pt^{0}(s) + 3Cl_2 + 2e^{-}$$

$$Ni^{2+} + [Pt^{4+}Cl_6]^{2-} \rightarrow Ni^{0}(s) + Pt^{0}(s) + 3Cl_2$$

The synthesis of Ni–Pt alloy composites with and without the use of NaOH, a stabilizing agent PVP and hydrazine was reported [22] by Lee and co-workers. In the absence of NaOH, Ni–Pt alloy contained a lower Ni content where the stoichiometry was not 1:1. Chen and Hsieh [23] noted that Ni nanoparticles could only be obtained under alkaline pH conditions. Furthermore the addition of NaOH during the reduction of H_2PtCl_6 by ethylene glycol also favored the formation of smaller particles possibly through an enhancement effect on the rate of reduction [24]. Thus the addition of NaOH maintains the pH of the reaction environment for the facile reduction of Ni^{2+} ions and controls the size of the bimetallic nanoparticles formation. Chen and Hsieh stated that the reduction of Ni ions to Ni nanoparticles was not feasible at room temperature even after stirring for 24 h. However, under the experimental conditions employed in the current study, the co-reduction of Ni^{2+} and $[PtCl_4]^{2-}$ ions using PVP was able to proceed at reasonable temperature and aging for 2 months to result in the fine PtNi sponges. The only disadvantage being the prolonged time taken for the particle formation.

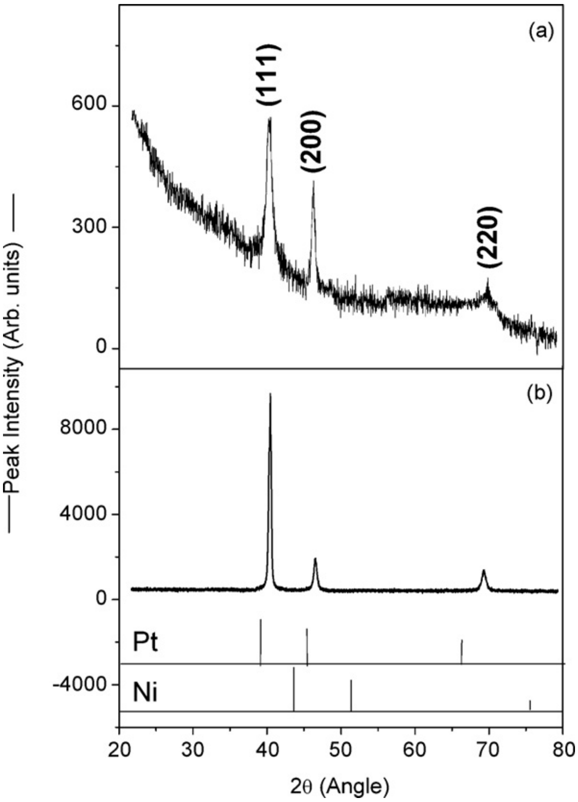

Fig. 2. XRD patterns of NiPt sponges obtained after 2 months of prolonged storage in presence of N_2 (a) as prepared and (b) heated at 250 °C.

3. Results and discussion

The XRD patterns of the as prepared NiPt alloy and that dried at 250 °C for 2 h are shown in Fig. 2(a) and (b). All of the NiPt particles have signatures of the face-centered cubic (FCC) structure and no peaks due to pure Ni, NiO or $Ni(OH)_2$ were observed. Compared with the standard diffraction data of pure Ni and Pt, the main peaks (1 1 1), (2 0 0) and (2 2 0) of NiPt alloy are clearly shifted towards higher 2θ value. This higher-angle shift in the peak position indicates a decrease in the lattice constant caused by replaced Pt with Ni atoms. Moreover, the lattice parameters of the alloy are smaller than those of Pt and the ratio of the decrease is proportional to the Ni content, reflecting the incorporation of equivalent number of Ni, which has a smaller atomic radius into an alloy. It is very important to investigate the electronic states of the surface of the alloys. The Pt 4f spectra of Ni–Pt alloys are shown in Fig. 3(a) and (b). The Pt $4f_{7/2}$ and $4f_{5/2}$ spectra were observed at 70.8 and 75.15 eV, respec-

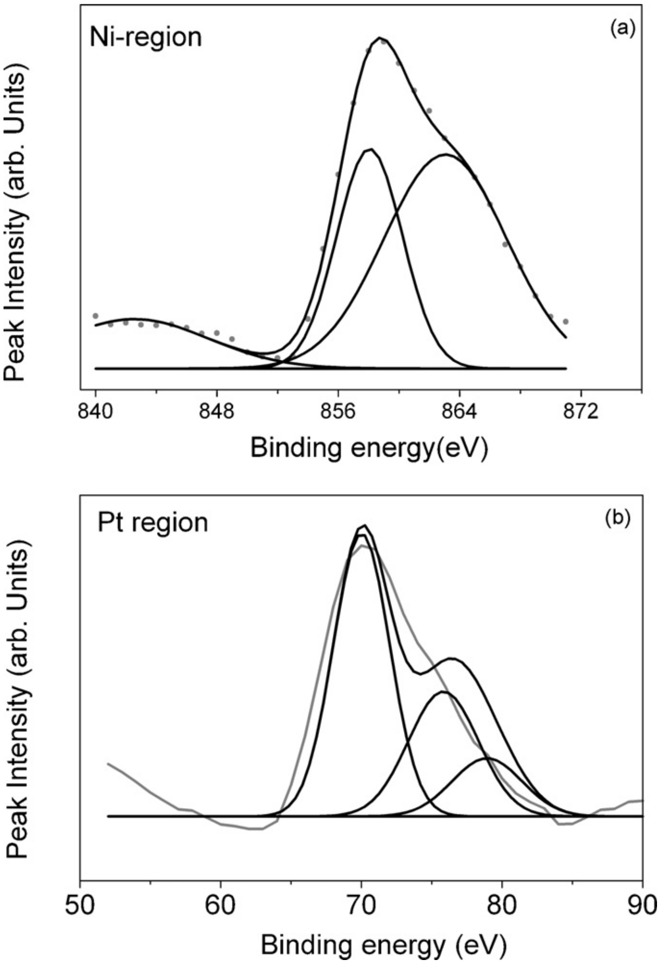

Fig. 3. X-ray photoelectron spectroscopy of the NiPt alloy in (a) Ni region and (b) Pt region.

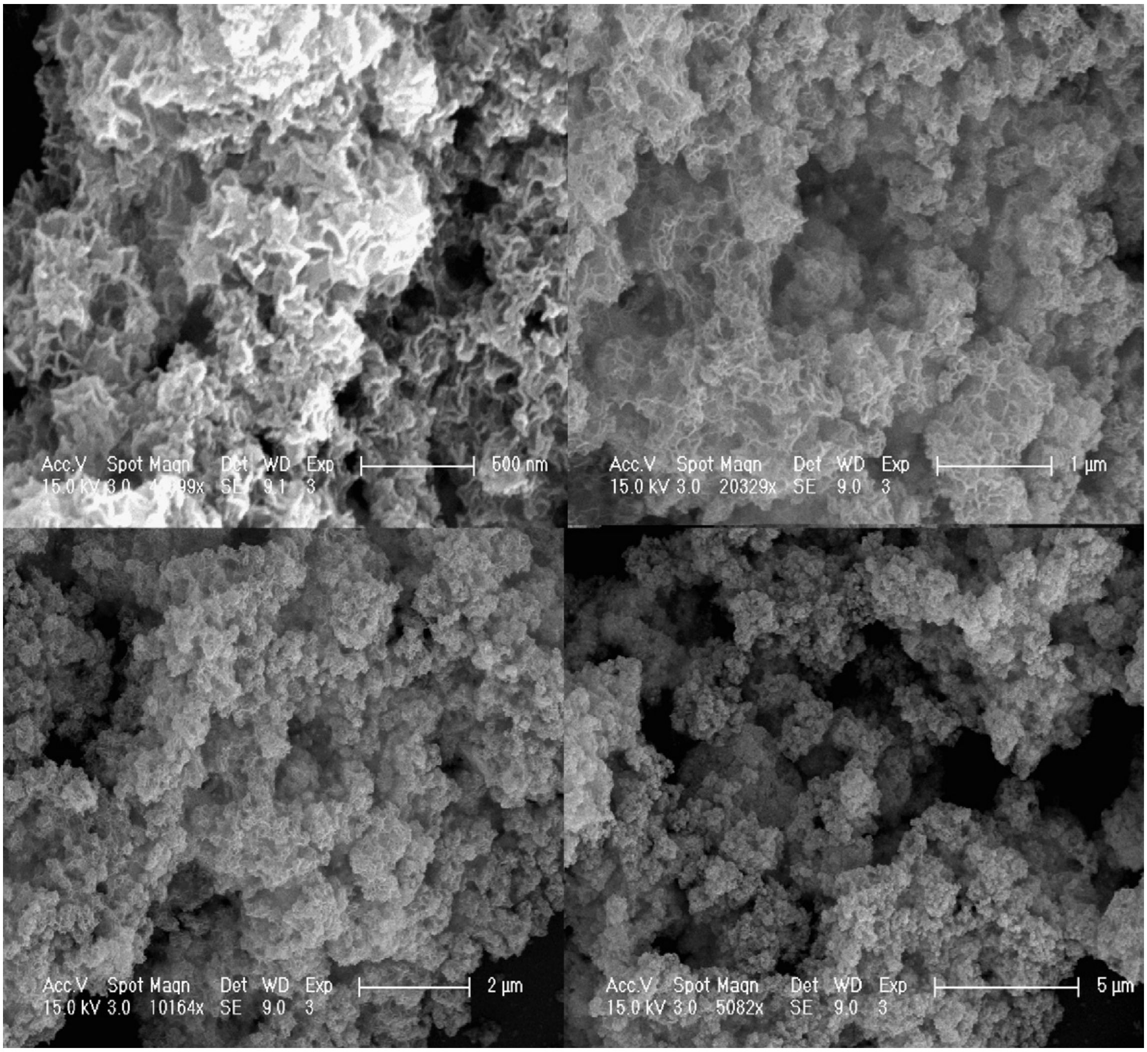

Fig. 4. SEM images of spongy NiPt alloy synthesized after 2 months of prolonged storage in presence of N_2.

tively. These values of Pt 4f peaks were very close to those of 70.9 and 75.2 eV for bulk Pt metal [25,26]. The results suggest that Pt is present in the zerovalent state, though the binding energies of Pt (II, IV) compounds are similar. The Ni 2p spectra are shown in Fig. 3(b). Actually, the existence of a second Ni species (e.g. NiO (853.8 eV), $Ni(OH)_2$ (855.6 eV) and NiOOH (857.3 eV)) cannot be excluded, because the spectra are poorly resolved. However, the position of the peak top is located at the binding energy of 852 eV corresponding to zerovalent Ni [25,26]. It is important to note that in these alloys Ni is found to be in the zerovalent metallic state, even though it is well known that bulk Ni is easily oxidized in the atmosphere. The Ni 2p spectrum was interpreted by the presence of a high binding energy satellite peak (~858.84 eV) adjacent to the main peaks [27–29]. Taking the satellite peak into account, the Ni $2p_{3/2}$ peak could be deconvoluted into two peaks at 858.1 and 863.31 eV associated well with the Ni°. From the intensities of the deconvoluted X-ray photoelectron spectroscopy (XPS) signal of Ni, it is obvious that the proportion of Ni° on the surface of the nanoparticles was quite the same suggesting a characteristic of 1:1 (Ni:Pt) based bimetallics [22].

The scanning electron microscopic (SEM) images of PVP and $NaBH_4$ derived NiPt alloy presents a spongy-like porous structure (Fig. 4) on a silicon wafer substrate. The porous surface structure here can be clearly divided into two levels of sub-structures. The first level of structure is composed of interconnected porous “tunnels” that are constructed with small pores of a pore size around 200 nm. On the other hand, as the second level of the structure, the interconnection of these porous “tunnels” forms a larger porous structure with irregular pores.

4. Conclusion

This communication is simply based on the preparation of fine NiPt nanosponges. The material has been characterized by XRD, XPS and SEM analysis. The presence of 1:1 Ni and Pt makes this powder composition very important for different materials, electronics and medical applications. This method of preparation could be a general method of preparation for the other metal–metal alloy nanoparticles.

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