



Facile fabrication of nickel nanostructures on a copper-based template via a galvanic replacement reaction in a deep eutectic solvent



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ARTICLE INFO

Article history:

Received 24 June 2016

Received in revised form 7 July 2016

Accepted 8 July 2016

Available online 09 July 2016

Keywords:

Copper

Nickel nanostructures

Nanoporous

Deep eutectic solvent

Galvanic replacement reaction

ABSTRACT

We describe an unusual galvanic replacement process for facile synthesis of nickel nanostructures by using Cu as a sacrificial template in a deep eutectic solvent (DES), ethaline. This replacement process occurred through a galvanic exchange of $[\text{NiCl}_4]^{2-}$ ions in ethaline at 353 K with an immersed Cu substrate, which acted as both reactive template and reductant. The mechanism for this replacement reaction and the morphology and topography evolution process of the nickel nanostructures were investigated. This facile preparation method performed in ethaline provides a novel way to fabricate nickel nanostructures with particulate or porous architecture on a copper-based template.

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1. Introduction

Galvanic replacement reactions have been shown to be capable of preparing metallic nanostructures, particularly for nanocrystals with hollow and core-shell nanoarchitectures [1–3]. In general, a sacrificial metal substrate can be treated as a reactive template with a suitable metal salt, whose redox potential should be higher than that of the template material [4,5]. Compared to electrodeposition and electroless processes, the galvanic replacement approach is easier to operate and control, since no additional substances, such as additives, reducing agents, complexants, buffers or accelerators are involved [6].

Conventional replacement reactions are mostly confined to aqueous solutions, where various aspects including speciation, reaction mechanism, kinetic control and resultant structure tuning have been extensively investigated [7–10]. Ionic liquids (ILs) have recently become attractive media for fabrication of metallic nanostructures by the galvanic replacement strategy [11–13]. ILs are generally aprotic with relatively high viscosity and provide a different chemical environment compared to molecule solutions. Unusual single-crystalline dendritic Au [11] and Au–Ag [12,13] nanostructures with high catalytic activity have been observed. Deep eutectic solvents (DESs) are mixtures of quaternary ammonium salts and hydrogen bond donors [14,15] and provide potential alternatives to conventional ILs. Porous silver films were self-assembled by simple galvanic replacement reactions from the choline chloride (ChCl)-based DES [16,17]. It was

found that by modulating reaction conditions, nanoporous Ag films with super hydrophobic properties could be obtained on a copper alloy substrate [18]. The intriguing solvent properties of DESs, such as polarity, surface tension, and highly ordered hydrogen bonding, potentially provide an environment for the generation of nanostructured materials [19–21]. Moreover, the capacity to tune redox properties in DESs [22] makes it possible to obtain galvanic exchange processes that are difficult to realize in aqueous solutions.

In this communication, we report that nickel nanostructures can be fabricated via galvanic replacement of a copper template in the DES ethaline. This is an unusual finding as nickel ($E^0 = -0.257$ V vs SHE) cannot normally be deposited onto copper ($E^0 = 0.34$ V vs SHE) [23] without chemical reducing agents. This is the first time that copper has been replaced with nickel by a galvanic replacement reaction. This study also investigates the reaction mechanism in ethaline.

2. Experimental

Choline chloride (ChCl, Aldrich, 98%), ethylene glycol (EG) (Aldrich, 99.5%), $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (Aldrich, 99.5%), and $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (Aldrich, 99.5%) were used as-received. Ethaline was prepared by mixing the components in the molar proportion of 1 ChCl:2 EG according to the method in [24].

Cyclic voltammetric (CV) experiments were conducted in an open system in a conventional three-electrode cell made of glass using a CHI 760D electrochemical working station. A 2 mm diameter Pt working electrode, a Pt counter electrode and a 1 mm diameter Ag wire (10 mm in length) reference electrode were used. Galvanic replacement

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experiments were performed in vials with 20 mL 0.10 M $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ containing ethaline at 353 K. Samples and solvents at different stages of the reaction were taken for characterization. The as-prepared samples were rinsed with anhydrous alcohol followed by distilled water, air dried and analyzed directly by scanning electron microscopy (SEM, HITACHI S-3400N), X-ray diffraction spectroscopy (XRD, SHIMADZU X-ray 6000 with Cu-K α), X-ray photoelectron spectroscopy (XPS, PHI 5000 Versa-Probe), and atomic force microscopy (AFM, Dimension 3100). UV–VIS spectra of the resultant solutions were determined at room temperature by diluting samples to a concentration of 0.1 mM and measuring in a 1 cm path length quartz cuvette with a Varian Cary 50 UV–VIS spectrophotometer. The nanoporous copper (NPC) templates used were prepared as reported previously [25] and the resultant samples were characterized by transmission electron microscopy (TEM, JEOL JEM-2010F).

3. Results and discussion

Cyclic voltammograms (CVs) for the redox behavior of copper and nickel on a Pt electrode from ethaline containing 0.10 M $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and 0.10 M $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, respectively, at 353 K are presented in Fig. 1a. Two well-defined redox couples ($\text{Cu}^{\text{II}}/\text{Cu}^{\text{I}}$ and $\text{Cu}^{\text{I}}/\text{Cu}^{\text{0}}$) can be observed, which have been studied previously at room temperature [22]. For nickel, a single $\text{Ni}^{\text{II}}/\text{Ni}^{\text{0}}$ redox couple is obtained. It is notable that the redox potential for $\text{Cu}^{\text{I}}/\text{Cu}^{\text{0}}$ (–0.350 V) in ethaline is ca. 200 mV more negative than that of $\text{Ni}^{\text{II}}/\text{Ni}^{\text{0}}$ (–0.154 V), determined by the average of onset potentials (E_{ca} , E_{oa}) and (E_{cb} , E_{ob}) respectively [20]. This result

indicates that a galvanic replacement reaction of copper with nickel is thermodynamically feasible in ethaline at 353 K. To confirm this, a copper substrate was immersed in ethaline with 0.10 M $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ for 5 h at 353 K and a thin, well-adhering film with a silvery metallic-like deposit was obtained (Fig. 1b). SEM analysis shows that the flat copper surface was transformed to a rougher surface filled with nanoparticles (ca. 33.4 ± 1.2 nm) and cracks after reaction with the Ni^{II} species.

The X-ray diffraction (XRD) pattern for the resultant deposit is shown in Fig. 1c. The corresponding diffraction peaks centered at 43.6° , 50.6° and 74.3° are located between standard Cu (JCPDS Card No. 04-0836) and Ni (JCPDS Card No. 65-0380). Although it is difficult to assign the peaks unequivocally to Cu/Ni as they have very similar lattice parameters [8], the shift of the diffraction peaks towards those for Ni after the replacement reaction can be attributed to the partial replacement of Cu atoms with Ni atoms, which causes a decrease in the lattice parameters [26].

In addition, the surface chemical states of the deposit were further revealed by XPS, as shown in Fig. 1d. Peaks in the full XPS spectrum correspond to Cu, Ni, O, and C. Detection of O is most likely due to a surface reaction of the freshly deposited products, and the presence of C comes mainly from the solvent residue. Curve fitting of the $\text{Cu } 2\text{p}$ and $\text{Ni } 2\text{p}$ XPS signals (inserts in Fig. 1d) give single metallic copper (932.7 and 952.4 eV) with different nickel species. The principal doublet peaks at 852.6 and 869.9 eV correspond to metallic nickel. The peaks at 855.8 and 873.6 eV can be assigned to Ni^{II} species such as NiO. It is clear that the $\text{Ni } 2\text{p}$ spectrum shows a complex structure with intense satellite peaks of ca. 6 eV higher binding energy (BE) adjacent to the $\text{Ni } 2\text{P}_{3/2}$

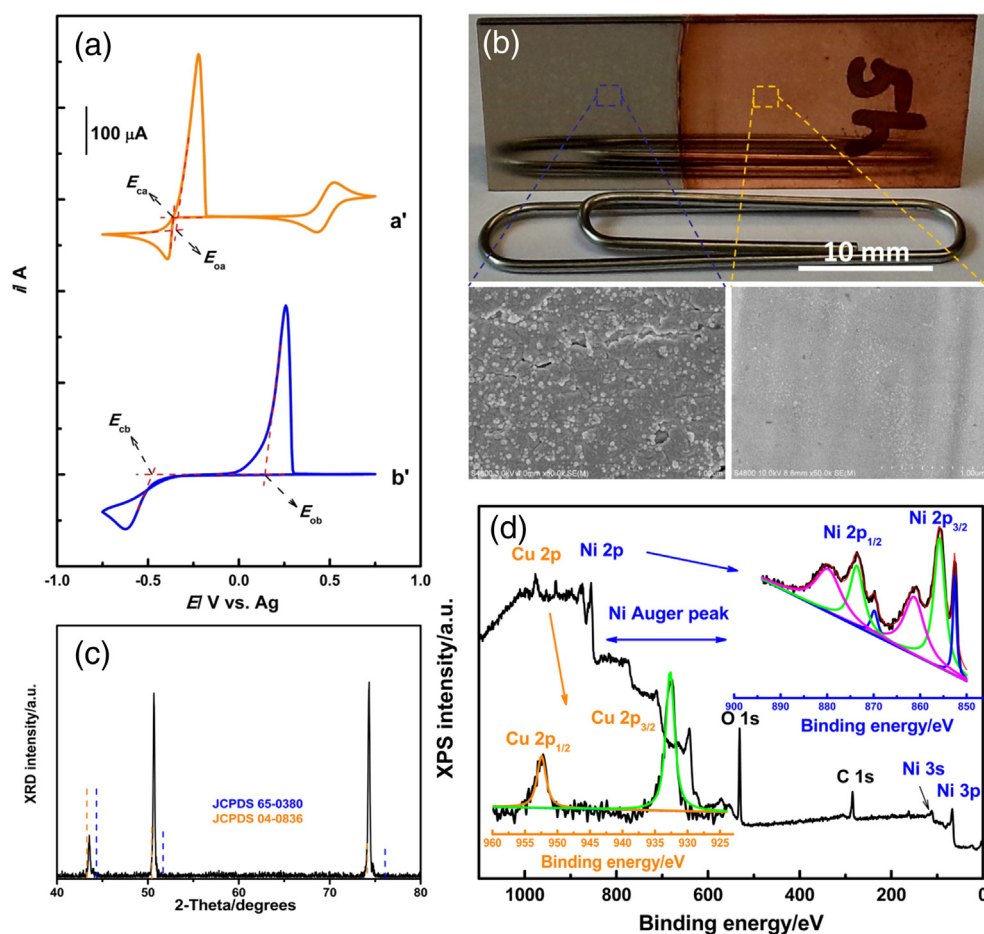


Fig. 1. (a) CVs of 0.10 M $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (a') and 0.10 M $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (b') in ethaline recorded at Pt electrode, respectively. Scan rate: 10 mV/s. Temperature: 353 K. (b) Photographic image for Cu foil before and after replacement for 5 h in 0.10 M $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ /ethaline at 353 K, and corresponding SEM analysis. (c) XRD pattern of the prepared Ni/Cu sample: The standard patterns of pure Ni (blue, JCPDS 65-0380) and Cu (orange, JCPDS 04-0836) are attached for comparison. (d) XPS survey spectra of the Ni loaded Cu foil, and the corresponding $\text{Cu } 2\text{p}$ and $\text{Ni } 2\text{p}$ XPS spectra analysis. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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