Materials science communication

Shape-controlled synthesis of gold–nickel bimetallic nanoparticles and their electrocatalytic properties

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HIGHLIGHTS

- Various shapes of Au–Ni nanoparticles were synthesized by changing halide anions.
- Clustered globular nanoparticles showed superior electrocatalytic activity.
- Portion of high indexed plane made difference in electrocatalytic activity.

GRAPHICAL ABSTRACT
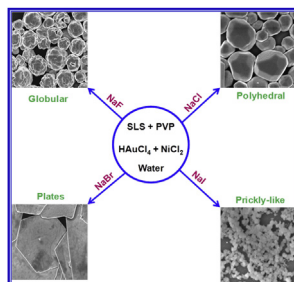
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ABSTRACT

Gold–nickel (Au–Ni) bimetallic nanoparticles in various forms of clustered globular, polyhedral, platelet and prickly nanoparticles were synthesized. The effect of sodium lauryl sulfate (SLS) and the halide anions on the shape of the Au–Ni nanoparticles were systematically investigated. By testing the electrocatalytic performances of differently shaped Au–Ni nanoparticles under methanol and ethanol oxidation conditions, the optimum shape for catalysis was suggested.

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There is growing interest in proton-exchange membrane (PEM) fuel cells due to their wide potential application in hand-held IT devices and transportations [1]. Platinum (Pt) and Pt-based bimetallic nanocrystal catalysts are the most popular and effective electrocatalysts for both the anode and the cathode of PEM fuel cells [1]. However, the slow kinetics of the cathode as well as the high cost and poor stability remain obstacles to their use in a wider range of applications [2,3]. Recent efforts have been focused on

alternative catalytic materials to improve the performance of fuel cells [4–6]. In this context, the composition-dependent anisotropy and surface structure of bimetallic nanocrystals have received considerable attention in recent years [7–9]. Complex nano-objects containing two or more different materials in the same nanoparticles not only combine the properties of individual constituents, but they also show unique properties which differ from those of ordinary monometallic counterparts [10–12]. The shape-controlled synthesis of bimetallic nanocrystals is fascinating because it enables for tailoring their catalytic activity, which often depends on the exposed facets [13–16]. Over the past few decades, many researchers have therefore attempted to synthesize mono-dispersed, well-defined Au–Ni nanoparticles with high selectivity [17–19]. Auten et al. reported the synthesis of Au–Ni spherical nanoparticles without the synthesis of other morphologies and the characterization of electrocatalytic properties [17]. Jiang et al. prepared Au–Ni bimetallic nanoparticles embedded in SiO_2 nanospheres. The Au–Ni@SiO_2 NPs showed higher catalytic activity than monometallic Au@SiO_2 and Ni@SiO_2 NPs [5]. Thus far, the systematic studies on the synthesis of Au–Ni nanoparticles with various morphologies have yet not been reported.

In this letter, we demonstrate the synthesis of Au–Ni nanoparticles in the various forms of clustered globular, polyhedral, platelet, and prickly nanoparticles (Scheme 1) for the first time. We also investigated their shape-dependent electrocatalytic properties with regard to the oxidation of methanol and ethanol to show feasibility toward the final application. We suggest the optimum morphology of Au–Ni nanoparticles as catalyst.

Basically, we utilized the hydrothermal process for the synthesis of Au–Ni bimetallic nanoparticles. Various shapes of Au–Ni bimetallic nanoparticles were easily realized by changing additives. In detail, the addition of different halide ions, i.e., F^-, Cl^-, Br^-, and I^- resulted in different shapes of nanoparticles such as globular, polyhedral, platelet, and prickly nanoparticles, respectively (Scheme 1). To tailor a crystal growth by controlling growth kinetics, inorganic/organic additives have been often introduced to the synthesis process. Studies have shown that additives such as Fe^{3+} [20], Ag^+ [21], Cu^{2+} [22], CTAB [23], and ligands [24,25] play

very important roles in controlling the nanoparticle morphology in different synthesis systems. In our results, halide ions are the key player governing the nanoparticle shape. The electro-negativity and ionic radii of different halide anions (F^-, Cl^-, Br^- and I^-) would affect the strength/number coordination of Au–Ni and halide ions [26–28]. Moreover, the affinity of halide ions to the gold surface scales as follows: $F^- < Cl^- < Br^- < I^-$ [26–28]. Ions with strong affinity can be tightly adsorbed on a certain crystallographic plane, suppressing the crystal growth, which explains that faceting becomes stronger with the affinity and that the strongest one, I^-, results in very small nanoparticles. As a consequence, replacement of F^- ions with an equimolar quantity of other halide anions (Cl^-, Br^-, and I^-) resulted in other morphologies of Au–Ni nanoparticles. Scheme 1 and Figs. 2–4 show that the products are predominantly made up of nanoparticles with polyhedral, platelet, and prickly shapes when the NaF is replaced with NaCl, NaBr, and NaI, respectively.

To investigate time evolution of the clustered globular nanoparticles formed by NaF, FE-SEM images were taken at different growth times (Fig. 1). Reactions less than 3 h resulted in 100 ~ 500 nm-sized Au–Ni clustered globular nanoparticles with a relatively low population. A broad size distribution over the entire growth stage was observed and the population increased with the reaction time, indicating that homogeneous nucleation continuously occurred. Through the observation of time-dependent growth of Au–Ni nanoparticles, the clustered globular particles were not formed by aggregation but by the presence of scattered nucleation sites on the surface [29–33]. The botryoidal growth during all of the growth stages indicates that heterogeneous nucleation in short range is thermodynamically preferred, which is probably an effect of the NaF molecules as a shape controller. The size increased up to 6 h and then decreased. Moreover, chasms between the constituents and smaller nanoparticles were observed after a reaction time of 12 h (Fig. 1d). This observation is valid for all shapes. For all shapes, dissolution occurred, leading to microstructural changes after a reaction time of 12 h regardless of the anion species (Figs. 2–4). The optimum reaction time should be less than 12 h.

The results of the XRD analysis are shown in Fig. 5. Since no hexagonal Ni formation in the Au–Ni system has been reported, cubic-phase nickel was expected to form [17–19,34,35]. However, the diffraction peaks of the clustered globular nanoparticles exhibited hexagonal-phase nickel (JCPDS 00-004-0850) present with cubic-phase gold (JCPDS 04-0784). The hexagonal-phase nickel is metastable and can only be obtained under certain conditions [36,37]. Hexagonal-phase Ni has wholly different magnetic properties due to the much larger bond distance, which is expected to affect the catalytic properties [36]. The main peak of the cubic-phase nickel is located at 44.508° (JCPDS 00-004-0850), which is too close to the Au (200) peak to be distinguished. From the fact that a Ni (200) peak at 51.847° was not detected, we can conclude that the no cubic-phase nickel was synthesized or at least negligible. The XRD data indicated that no nickel oxides were detected, consistent with the energy-dispersive X-ray spectroscopy measurements (Fig. S1). The XRD analysis of the other shapes revealed that the polyhedral, platelet and prickly nanoparticles consisted of the hexagonal-phase nickel and cubic-phase gold, identical to the globular nanoparticles. Although an unknown phase was found in the polyhedral nanoparticles (Fig. 2b), further analysis of the phase was omitted because the emergence of the unknown phase had an adverse effect on the catalytic properties.

The effects of PVP and SLS were also investigated. While globular shapes of nanoparticles were formed with PVP and SLS (Fig. S2a and b), ill-defined spheres with a diameter less than ~50 nm were observed in the absence of SLS (Fig S2c) or PVP
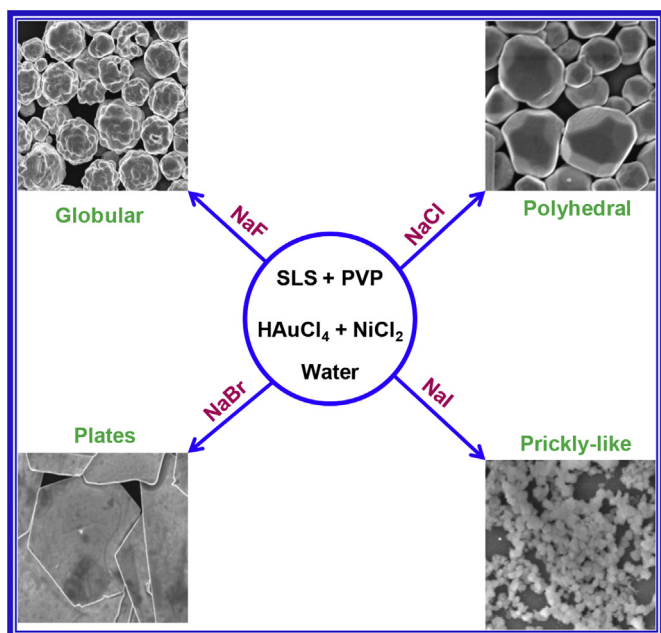
Scheme 1. Summary of Au–Ni nanostructures controlled by halide anions.