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Microwave-assisted optimization of platinum-nickel nanoalloys for catalytic water treatment

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ABSTRACT

Blending noble metal catalysts with inexpensive transition metals can reduce material cost in catalytic water treatment by improving the catalytic reactivity. An important challenge is, however, to synthesize a series of alloy nanoparticles with varied compositions so that the screening of catalytic reactivity can be performed rapidly for a contaminant of interest. Here, we report a facile approach for the rapid synthesis of bimetallic nanoalloys using cycle-controlled microwave-assisted polyol reduction, with an option of fixing the nanoalloys directly on graphene supports in a one-pot operation. Using Pt and Ni as the model noble and promoter metals, we show that Pt/Ni nanoparticles with diameters ranging from 2.8 to 4 nm can be readily synthesized within minutes. The surface Ni percentage of the nanoparticles are varied from 0 to 100%, which serves as a model system for nanoalloy screening. Using the model contaminant *p*-nitrophenol, we further show that the reactivity-composition relationship has a classic volcano shape as the Sabatier principle predicts. The highest reactivity is found with a surface Ni percentage of approximately 50%.

1. Introduction

Nanoparticles made of noble metals such as platinum (Pt), palladium (Pd), and gold (Au) have attracted increasing attention as catalysts for degrading organic and inorganic contaminants found in water and wastewater [1–7]. Compared to conventional treatment techniques, the use of catalysts can shorten treatment time, target recalcitrant compounds, and selectively transform wastes into valuable products. These attributes are particularly attractive as water reuse and resource recovery become increasingly incorporated into treatment practices [8,9]. An important challenge is, however, to reduce the high cost associated with the initial investment and subsequent replenishment of catalysts.

An effective strategy for reducing the cost of catalytic water treatment is to improve the reactivity of noble metal catalysts by blending them with promoter metals, forming bimetallic alloys. According to the classical Sabatier principle [10], an improved reactivity can be obtained by optimizing the reactant-catalyst interaction. For example, platinum is one of the best noble metals for catalyzing the degradation of environmental contaminants such as the reduction of *p*-nitrophenol (PNP) [1,11]. The reactivity of Pt can be further improved by blending with 3*d* transition metals such as copper (Cu) and nickel (Ni) [12–14], which are ineffective catalysts themselves. The improved reactivity after blending is attributable to the reduction of reactant-catalyst affinity through electronic (lowering the *d*-band center) and geometric (reducing bond distances) effects [15].

An important parameter that controls the reactivity of a bimetallic alloy catalyst is the blending ratio between the noble and transition metals, with the highest reactivity often found at an intermediate blending ratio (not necessarily 1:1). The relationship between reactivity and blending ratio is often revealed as a volcano curve with an apex indicating an optimized energy for reactant adsorption [16–20]. The compositional dependence of reactivity has been the basis of selecting effective catalysts for important reactions such as the oxygen reduction reaction [21,22], the methanol oxidation reaction [23,24], and the hydrolysis of ammonia borane [25,26]. In comparison, only limited efforts have been given to environmentally relevant reactions such as the PNP reduction. Stevenson, Henkelman, and colleagues investigated the reactivity of Pt/Cu alloy nanoparticles (aka. nanoalloys) at a 1:1 molar ratio; however, the ratio between Pt and Cu was not varied [14]. Pal and colleagues studied the reactivity of Pt/Ni nanoalloys with Pt:Ni ratios of 36:64, 20:80, and 4:96 [12,27]. However, the highest reactivity was found at the extreme ratio of 4:96 in their systems, inconsistent with the optimal intermediate blending ratios found for other reactions (Pt:Ni = 1:1 to 3:1) [24,28,29].

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To examine the compositional dependence of the catalytic reactivity of Pt nanoalloys in the PNP reduction, we synthesized Pt/Ni nanoparticles with varied surface compositions using a cycle-controlled microwave-assisted polyol reduction method. PNP is a Clean Water Act priority pollutant with an acceptable daily intake (ADI) of 0.32 mg per day over a month [30,31]. In comparison, the toxicity of reduced product *p*-aminophenol (PAP) is negligible with a ADI of 4.55 mg per day over a lifetime [32]. We selected Ni instead of Cu because Ni was expected to be more effective in weakening the adsorption energy of Pt with PNP [33,34], thereby providing a wider range for optimization. Through a quantitative volcano curve, we found the highest reactivity associated with a surface composition of near equimolar Pt and Ni. Furthermore, our synthesis method permitted the direct fixation of nanoalloys on microwave-absorbing supports such as graphene sheets, for the benefit of an extended service life. Our results suggest that blending noble metals with proper inexpensive promoters is a potentially feasible solution for reducing the cost of catalytic water treatment. The microwave-assisted method provides a facile and green approach [35,36] for nanoalloy synthesis so that the rapid optimization can be potentially performed for other targeted contaminants as well.

2. Experimental

All chemicals of reagent grade were purchased from Sigma Aldrich except otherwise specified. Deionized (DI) water was generated on site using a Millipore system.

2.1. Synthesis of Pt nanoparticles and Pt/Ni nanoalloys

Stock solutions of platinum chloride ($PtCl_2$; 1.40 mM) and nickel chloride ($NiCl_2$; 1.43 mM) were prepared by dissolving 5.6 mg $PtCl_2$ and 5.1 mg $NiCl_2 \cdot 6H_2O$ in 15 mL diethyleneglycol (DEG), respectively, under vigorous stirring for 1 hour. Unsupported Pt/Ni nanoalloys were synthesized in 6 steps. First, 1 mL $PtCl_2$ and 1 mL $NiCl_2$ stock solutions were added to 5.5 mL DEG in a 20 mL scintillation vial and mixed by magnetic stirring for 15 minutes. Second, the vial was placed in a commercial microwave oven (R-209KK, Sharp Electronics Corp., Mahwan, New Jersey; 800 W, 2.45 GHz). Microwave radiation was administered in 1–8 cycles, each of which consisted of a 50-second "on" segment at the maximum power followed by a 30-second "off" segment. Third, the vial was taken out of the microwave oven and cooled in air to room temperature. Fourth, the reaction mixture was then centrifuged at 17,000 × *g* for 5 min to recover nanoalloys. The recovered nanoalloys were washed with 20 vol% acetone aqueous solution and then centrifuged for three times. Fifth, the cleaned nanoalloys were placed in a fume hood to evaporate residual water and acetone. The recovery efficiency of centrifugation and wash process was estimated at 75% using a known amount of Pt nanoparticles. Last, dried nanoalloys were dispersed in 7.5 mL DI water under sonication for 25 min. To make Pt nanoparticles, only the $PtCl_2$ solution was used in the first step.

2.2. Synthesis of graphene-supported Pt/Ni nanoalloys

Graphene oxide (GO) was prepared by the oxidative exfoliation of natural graphite (325 mesh, 96%, Alfa Aesar) according to the modified Hummers' method [37]. Briefly, 1 g graphite and 1 g sodium nitrate ($NaNO_3$) were added into 46 mL 98% sulfuric acid (H_2SO_4) in an ice bath under stirring. Six grams of potassium permanganate ($KMnO_4$) was slowly added to the mixture and stirred for 15 minutes. The mixture was then heated at 35 °C and stirred vigorously for 30 min into a thick paste. Ninety milliliters of DI water was slowly introduced to the mixture to sustain the reaction for another 40 minutes at 98 °C. Finally, 280 mL DI water was added to dilute the mixture and 5 mL 30% hydrogen peroxide (H_2O_2) was added to the mixture to terminate the reaction. GO was centrifuged and washed repeatedly with DI water to remove the remaining oxidizing reagents and salt products. The precipitate was freeze-dried (Labconco Freezone 4.5) into a powder for storage.

The stock solution of 290 mg L^{-1} GO was prepared by dispersing 15 mg GO powder in 52 mL DEG under sonication for 30 min. Graphene-supported Pt (G-Pt) nanoparticles and graphene-supported Pt/Ni (G-Pt/Ni) nanoalloys were synthesized following the 6-step procedure described for unsupported nanoalloys with the exception that DEG was replaced by the same volume of a stock solution of GO and DEG mixture.

2.3. Material characterization

Samples of supported and unsupported nanoalloys were characterized using a series of analytical techniques. Morphologies and sizes of nanoparticles and nanoalloys were examined using transmission electron microscopy (TEM; FEI Titan 80-300). High resolution TEM (HRTEM) images were taken to elucidate shape and crystallinity. Chemical composition was determined directly using energy-dispersive X-ray spectroscopy (EDX; Quantax 200) and X-ray fluorescence spectroscopy (XRF, Orbis Micro-XRF Analyzer) and indirectly using ion-coupled plasma optical emission spectroscopy (ICP-OES, Perkin Elmer Optima 2000) after acid digestion. For the XRF analysis, samples were drop-casted on silicon chips (University Wafer, Boston, Massachusetts) and dried in air. For the ICP-OES analysis, 1 mL aqueous solution was air-dried in a quartz vial, mixed with 1 mL aqua regia ($HCl:HNO_3 = 3:1$), heated to 80 °C, and digested for 4 h. The solution was diluted for 5 times and filtered through a 0.45 μm nylon membrane before introducing into the ICP-OES instrument. The yields of Pt and Ni were computed from the changes of Pt and Ni concentrations obtained from ICP-OES measurements before and after microwave irradiation. Molecular models of nanoalloys were created using CrystalMarker®.

2.4. Catalytic reduction of p-nitrophenol

To measure the catalytic reactivity of supported and unsupported nanoalloys, 1 mL aqueous solution was mixed with 32 mM sodium borohydride ($NaBH_4$) at a 1:1 volumetric ratio. To start the reduction reaction, 10 μL of 20 mM PNP was added into a 2 mL catalyst-$NaBH_4$ mixture in a standard UV/vis quartz cuvette. The progress of the reduction was monitored using a UV/vis

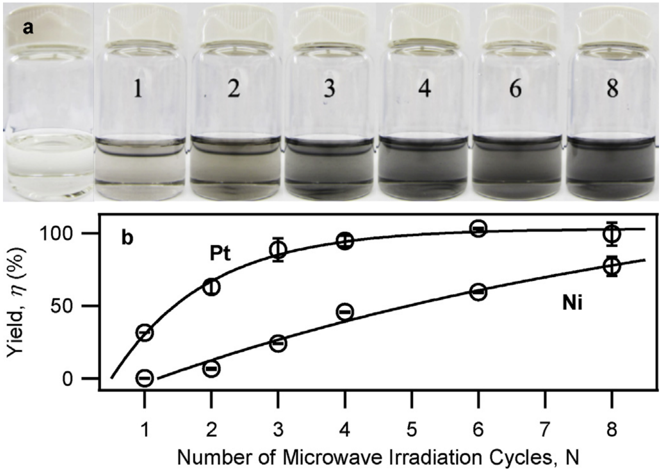

Fig. 1. Variation of Pt/Ni nanoalloy composition with the number of microwave irradiation cycles (1 cycle = 50 s on and then 30 s off). (a) Digital photographs of the synthesis solution before and after microwave irradiation (marked with the number of irradiation cycles). (b) Conversion of Pt and Ni from solution to particle measured by ICP-OES after acid digestion. The curves are exponential fits to show the trends of Pt and Ni yields.