

Structural control and catalytic application of alloy nanoparticles

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Bimetallic nanoalloys have great potential as novel catalysts because their chemical properties can be modified by changing the composition and elemental distribution within the lattice as well as their sizes and morphologies. It is widely accepted that the catalytic properties of bimetallic NPs can be controlled by elemental composition through modification of the electronic structure. One can further expect that the catalytic activity of bimetallic NPs with a given composition will be affected by the mixing mode of each constituent element.

CuPd NPs stabilized by polymers and solid supports have been extensively studied as catalysts. Interestingly, the CuPd NPs with ordered body-centered-cubic (B2) structure, the most stable phase for $\text{Cu}_x\text{Pd}_{100-x}$ ($50 < x < 70$), show unique chemical and catalytic properties as compared with NPs possessing other structures. We attempted in the present study to synthesize B2-type CuPd NAs by annealing precursor CuPd NPs at a low temperature under hydrogen.¹

Ammonia (NH_3) is a main component in chemical fertilizers and recently has been noted as an energy carrier for alkaline fuel cells. At the same time, over-manuring with synthetic fertilizers causes an increase in the concentration of nitrate ion (NO_3^-) and its derivatives in ground water. Here, we performed the reduction of NO_3^- into NH_3 with photocatalytically generated hydrogen over CuPd nanoalloy as an environmentally benign process. Photocatalytic hydrogen evolution and nitrate reduction were simultaneously examined over CuPd nanoalloys deposited on TiO_2 (CuPd/TiO_2). The efficiency of hydrogen evolution over CuPd/TiO_2 was better than that over Pd nanoparticle deposited on TiO_2 . As for nitrate reduction, ammonia was selectively produced with hydrogen generated photocatalytically over CuPd nanoalloys deposited on TiO_2 (CuPd/TiO_2). The efficiency of hydrogen evolution over CuPd/TiO_2 was higher than that over Pd/TiO_2 . Ammonia was selectively (78%) produced with hydrogen in the reduction of nitrate generated photocatalytically over CuPd/TiO_2 . (Fig. 1)² The highly selective production of ammonia is ascribed to continuous generation of nascent hydrogen atoms on the surface of the CuPd nanoalloy, where Cu and Pd atoms are homogeneously mixed.

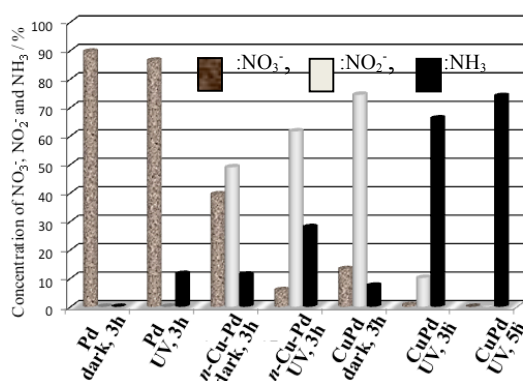


Fig. 1. Concentrations of NO_3^- , NO_2^- , NH_3 and N_2 relative to the initial NO_3^- concentration after reaction in a $470 \mu\text{M}$ NO_3^- aqueous solution including 10 vol% methanol.

[1] M. Yamauchi, T. Tsukuda, Dalton Trans., 40, 4842-4845 (2011).

[2] M. Yamauchi, R. Abe, T. Tsukuda, K. Kato, M. Takata, *J. Am. Chem. Soc.*, 133, 1150-1152 (2011).