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ARTICLE TYPE

Au-Pd Alloy Catalyst with High Performance for Hydrogen Generation from Formic Acid-Formate Solution at Nearly 0 °C[†]

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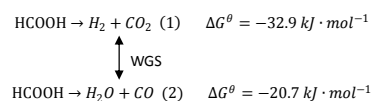
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By reduction of mixed noble metal precursors in aqueous phase at ice-water bath condition, well dispersed Au-Pd alloy nanoparticles supported on carbon black were facilely prepared. The catalyst exhibited high activity and selectivity at nearly 0 °C, with initial turnover frequency (TOF) up to 635 h⁻¹. At room temperature the initial TOF of the catalyst reaches 1075 h⁻¹, which was rather high compared with those reported in literature.

Efficient, safe and sustainable production and storage of energy is an important and challenging topic in recent years.¹ Hydrogen is considered as a clean and efficient energy carrier and has attracted increasing attention due to its wide application in proton exchange membrane fuel cells (PEMFCs).² However, controlled storage and release of hydrogen has been a major challenge that limits the development of hydrogen energy.³

Among various hydrogen storage strategies, chemical storage, where hydrogen is released by catalyzed decomposition of chemicals rich in hydrogen such as borohydrides, hydrazine and formic acid, is attractive because it is safer, more efficient and controllable compared to traditional hydrogen storage techniques.⁴⁻⁷ As a main byproduct of biomass process, formic acid is considered promising as hydrogen carrier because of its relatively high hydrogen content, non-toxicity and stability.⁴

Formic acid can be decomposed through two different pathways, dehydrogenation path (1), and dehydration path (2). The former path is essential to hydrogen release while the latter one produces CO, which can be toxic to the catalysts. The products of the two pathways can be interconnected at elevated temperature via water-gas shift (Scheme 1).



Scheme 1. Possible decomposition paths of formic acid

Selectivity of pathways can be achieved by adjusting catalysts, pH values and reaction temperature. Homogeneous catalysts such as metal (Fe, Ru, Ir, Rh, etc.) complexes with high activity and selectivity towards dehydrogenation of formic acid have been reported.⁸⁻¹⁴ Compared to homogeneous catalysts, heterogeneous catalysts could be easier to carry, separate and

recycle, and have been extensively studied. Heterogeneous catalysts for formic acid dehydrogenation are mainly focused on Au,¹⁵⁻¹⁹ Pd²⁰⁻²⁶ and Pt²⁷⁻²⁸ based catalysts. By controlling synthesis conditions, various catalysts have been synthesized and modified, for instance by addition of surfactant polymer,^{20,25} using different supports^{17,29} and formation of noble metals alloy with non-noble metals³⁰⁻³² and non-metals.³³ Bimetallic and trimetallic catalysts with different structures have been proved efficient in catalyzing dehydrogenation of formic acid.³⁴⁻⁴⁵

Au-Pd alloy has drawn great research interest since Xing et al successfully synthesized carbon supported Au-Pd alloy nanoparticles,^{34,35} and various metal alloy catalysts have been reported later. However, those catalysts either involve complex methods or toxic reagents in synthesis process or suffer great decrease in activity at low reaction temperature.

Herein, for the first time we report an effective catalyst for decomposition of formic acid to hydrogen at nearly 0 °C, with an initial TOF as high as 635 h⁻¹. At room temperature (25 °C) the catalyst exhibited an initial TOF of 1075 h⁻¹, which is higher than that of many reported formic acid dehydrogenation carried out at room temperature (Table S1).

The preparation of the catalyst was facile. By reduction of noble metal precursor in solution at ice-water bath condition, well dispersed Au-Pd alloy nanoparticles were obtained and were supported on carbon black (denoted as L-Au₆Pd₄, details see Supporting Information). The transmission electron microscopy (TEM) images of the as-prepared L-Au₆Pd₄ are shown in Figure 1a-c. The nanoparticles of Au-Pd alloy are well dispersed on the carbon black support with average particle size of around 2 nm. In comparison, if the reduction was performed at room temperature (this catalyst was denoted as R-Au₆Pd₄), TEM images of R-Au₆Pd₄ (Figure S1) show relatively severe aggregation of the metal particles. The size of some large aggregated particles could even reach 100 nm, and this would greatly compromise the activity of the catalyst. The energy dispersive X-ray spectrometry (EDS) proves the coexistence of both Au and Pd elements in each particle (Figure S2 and Table S3). The ratio of Au and Pd is roughly 6:4, which is consistent with the initial content of Au and Pd in the precursor. The element mapping by high-angle annular dark-field scanning TEM (HAADF-STEM) indicate that Au and Pd are evenly distributed in the metal nanoparticles (Figure 1c). The content of Au and Pd is also determined by inductively coupled plasma-atomic emission spectrometry (ICP-AES) (Table S3). The metal content

of L-Au₆Pd₄ catalyst is consistent with the result of EDS. This illustrates that reduction at low temperature is favorable to alloy formation and dispersion.

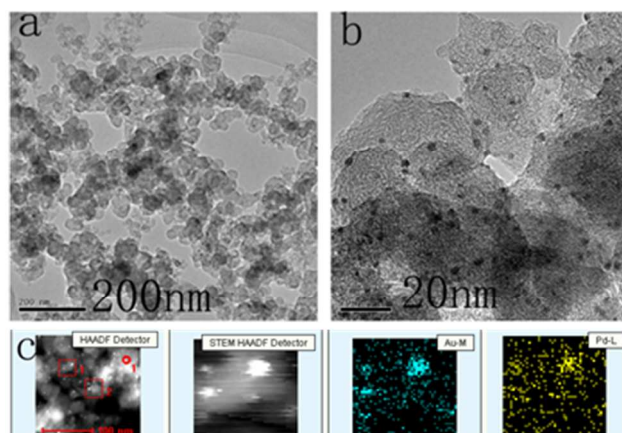


Figure 1. TEM images of L-Au₆Pd₄ (a, b) and element mapping (c).

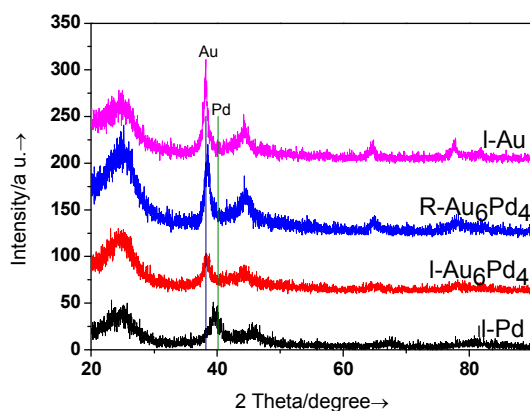


Figure 2. XRD patterns of L-Au₆Pd₄, R-Au₆Pd₄, L-Au and L-Pd.

The X-ray diffraction (XRD) patterns (Figure 2) of R-Au₆Pd₄ and L-Au₆Pd₄ show that the nanoparticles have the fcc structure of metallic Au. The coexistence of Pd and Au in fcc phase confirms the formation of Au-Pd alloy, which can be explained by Hume-Rothery rule, as the relative difference of the atom radii of Au (0.144 nm) and Pd (0.138 nm) is 4.2% (lower than 15%). Thus Pd can be incorporated into Au lattice to form fcc structure.³⁰ The characteristic peak of Au in R-Au₆Pd₄ is sharper than that of L-Au₆Pd₄, indicating larger particle size according to the Scherrer equation. As shown in Figure 2, the characteristic peak of Au in L-Au₆Pd₄ is widened and slightly shifted to higher degrees, which indicates a contradiction in Au lattice resulting from the formation of Au-Pd alloy.

The activity of L-Au₆Pd₄ for H₂ generation at nearly 0 °C (under ice-water bath condition) is shown in Figure 3. Total volume of reforming gas generated with L-Au₆Pd₄ within 2 h was 235 ml and the initial TOF reached 635 h⁻¹. At room temperature, 315 ml gas was generated within 2 h with the initial TOF of 1075

h⁻¹. When R-Au₆Pd₄ was applied to catalyze formic acid dehydrogenation at nearly 0 °C, only 150 ml gas was generated (Figure S3).

The higher activity of L-Au₆Pd₄ could be ascribed to smaller particle size and better alloy structure resulting from the low reduction temperature. Low temperature efficiently controls the nucleation and aggregation of noble metal nanoparticles,^{46, 47} which leads to larger surface area available for reactant. The lower reduction temperature also provides steady reduction speed, resulting in better dispersion and uniform particle size. In addition, the metal content of the catalyst and concentration of precursor are relatively low, contributing to smaller particle and higher dispersion as well. The activation energy is calculated to be 21.98 kJ•mol⁻¹, lower than activation energy reported in some earlier research (Table S2).

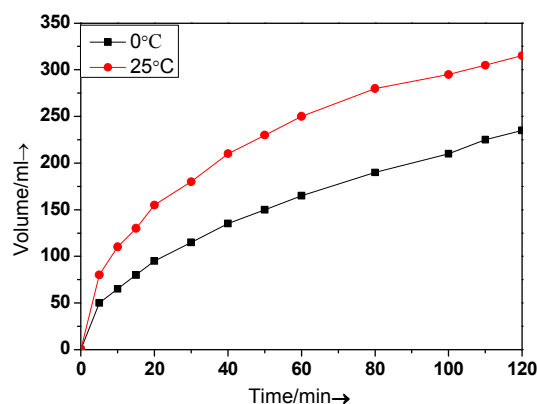


Figure 3. H₂ generation with L-Au₆Pd₄ at nearly 0 °C and room temperature from FA/SF (1.1M FA, 4.0M SF).

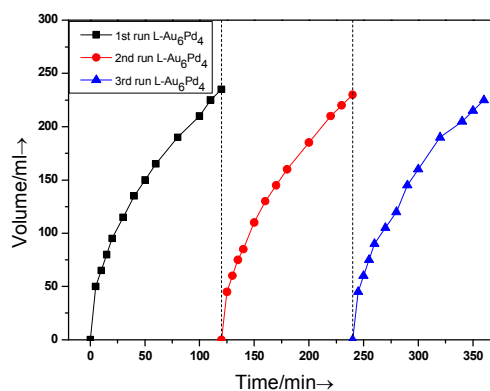


Figure 4. H₂ generation with L-Au₆Pd₄ at sequential runs at nearly 0 °C from FA/SF (1.1M FA, 4.0M SF)

After catalytic reaction the catalyst was recycled and dried for recycling test. As can be seen in Figure 4, recycled catalyst (r-L-Au₆Pd₄) showed similar activity as the as-prepared catalyst (with 230 ml gas generated within 2 h). Considering the loss of catalyst in recycling process, the catalyst remained equal activity towards hydrogen generation after recycling, indicating that the

structure of L-Au₆Pd₄ catalyst is stable during the reaction.

The results of gas chromatography (GC) showed that the concentration of CO in the reforming gas was about 100 ppm (Figure S8 and S9), around the CO limit of hydrogen proton exchange membrane fuel cells.⁴⁸

The electronic and synergistic effect was studied by X-ray Photoelectron Spectroscopy (XPS). The results of XPS showed that the binding energies for Au 4f in L-Au₆Pd₄ (85.08 eV for 4f_{7/2}, 88.63 eV for 4f_{5/2}) were shifted to lower values compared with those in L-Au (83.9 eV for 4f_{7/2}, 87.7 eV for 4f_{5/2}).⁴⁹ The peak shift indicated transfer of electron between Au and Pd. This confirms the formation of Au-Pd alloy and this was consistent with the results of HAADF-STEM and XRD.

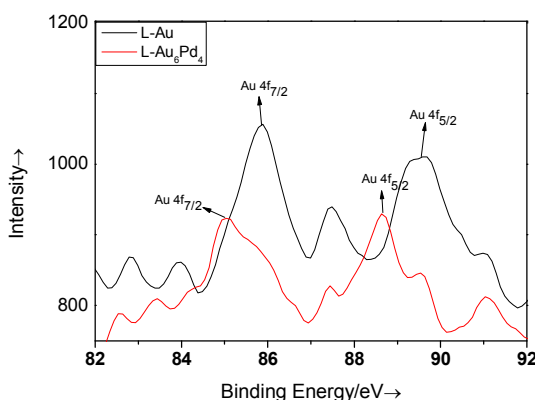


Figure 5. Au 4f XPS spectra for L-Au₆Pd₄ and L-Au

Gas volume generated with catalysts synthesized with different Au and Pd ratios (Figure S5) demonstrated that the content of Pd was crucial to the activity. Without alloying with Au the activity of pure Pd decrease greatly. Meanwhile, pure Au/C catalyst showed no activity towards dehydrogenation of formic acid. As shown in Figure S5, when the ratio of Au and Pd was 6:4, the catalyst exhibited the best performance.

In summary, well dispersed Au-Pd alloy nanoparticles supported on carbon black was successfully synthesized and exhibited high activity and selectivity towards dehydrogenation of formic acid at nearly 0 °C, with initial TOF of 635 h⁻¹. The initial TOF at room temperature reached 1075 h⁻¹. The low temperature activity of the catalyst is important for the application of proton exchange membrane fuel cell in cold areas. The catalyst can be easily recycled and exhibited excellent stability.

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Notes and references

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