An Efficient CoAuPd/C Catalyst for Hydrogen Generation from Formic Acid at Room Temperature**

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Nowadays, searching for the effective hydrogen (H₂) storage/generation materials remains one of the most difficult challenges toward a fuel-cell-based H₂ economy as a long-term solution for secure energy in future.[1] Formic acid (FA, HCOOH), a major product of biomass processing with high-energy density, nontoxicity, and excellent stability at room temperature, has recently attracted tremendous research interests for H₂ storage and generation.[2] Moreover, through the potential hydrogenation of waste carbon dioxide (CO₂) from industry, FA can be regenerated,[2,4] and this makes the storage of H₂ in FA more attractive for a sustainable and reversible energy storage cycle.[2,4]

FA can be catalytically decomposed to H₂ and CO₂ through a dehydrogenation pathway (HCOOH(l) → H₂(g) + CO₂(g), ΔG²⁹⁸K = −35.0 kJ mol⁻¹).[2] However, carbon monoxide (CO), which is a fatal poison to catalysts of fuel cells,[5] can also be generated through a dehydration pathway (HCOOH(l) → H₂O(l) + CO(g), ΔG²⁹⁸K = −14.9 kJ mol⁻¹),[2] depending on the catalysts, pH values of the solutions, as well as the reaction temperatures.[2,4] Recently, much progress has been made on the heterogeneous catalysis for the selective dehydrogenation of FA.[6c–e,7] However, the thermodynamic and kinetic properties of FA dehydrogenation, especially without any extra additive,[6c,7] still need to be further promoted.[6c–e,7] More importantly, all the reported heterogeneous catalysts up to now consist of noble metals, including, for example, Pd, Au, Ag, and Pt,[6c–e,7] which greatly hinders their large-scale practical applications because of their high costs and low reserves in the earth’s crust.

The first-row transition metals (FRTM) in nanoscale, such as cobalt (Co) nanoparticles (NPs), have been widely investigated as the catalytic materials in many important reactions because of their potential activities and relatively low costs.[9] Whereas, for FA dehydrogenation, nano-FRTM are easily etched by acidic FA solution. Hence, there is no report on application of nanocatalyst that includes FRTM for FA dehydrogenation.[6c–e,7,8]

When FRTM are alloyed with noble metals, their stabilities under acidic condition can be enhanced, which depends on the degree of alloying, metallic composition, and particle size of the material.[10] Moreover, the incorporation of FRTM into the noble metals with the alloy structure may not only lead to the enhancement of the catalytic performance, but also reduce the consumption of the noble metals.[11] In this sense, a novel strategy to improve the activities and lower the costs of solid catalysts for FA dehydrogenation is to design the polymetallic nanomaterials containing FRTM and noble metals within the stable alloy structures.

Herein, we report the facile synthesis of the CoAuPd nanoalloy based on a non-noble metal and supported on carbon (CoAuPd/C) at room temperature (298 K). The elevated stability of Co⁰ in the protective nanoalloy structure makes it’s first application in FA dehydrogenation successful. More interestingly, the prepared CoAuPd/C with the lower consumption of noble metals exhibits the 100% H₂ selectivity, highest activity, and excellent stability toward H₂ generation from FA without any additive at 298 K. As shown in Scheme 1, CoAuPd/C is synthesized through a surfactant-free co-reduction method.[12] Typically, for preparation of Co₅₃₀Au₀₃₅Pd₀₃₅/C, 5.0 mL of aqueous solution containing CoCl₂ (9.0 mm), Na₂PdCl₄ (10.5 mm), and HAuCl₄ (10.5 mm) is mixed with 10.0 mL of aqueous solution containing the well-dispersed Vulcan XC-72 carbon (167.2 mg, 500 m² g⁻¹).[13] Then, the fresh NaBH₄ aqueous solution (5.0 mL, 300.0 mm) is added to the above mixture under magnetic stirring in argon (Ar) atmosphere. After 2 h, the product of Co₅₃₀Au₀₃₅Pd₀₃₅/C is obtained and ready for the catalytic H₂ generation from FA aqueous solution at 298 K.

Figure 1a shows the typical transmission electron microscopy (TEM) image of the as-prepared Co₅₃₀Au₀₃₅Pd₀₃₅/C. The NPs are well-dispersed on carbon with an average particle size of 5–6 nm.
particle size of about 20 nm. The corresponding energy-dispersive X-ray (EDX) spectrum displays all the existences of Co, Au, and Pd elements (see Figure S1 in the Supporting Information). And the molar ratio of Co:Au:Pd is determined to be 0.292:0.357:0.351 by inductively coupled plasma-atomic emission spectrometry (ICP-AES), which agrees very well with the appointed value. The high-resolution TEM (HRTEM) image reveals the crystalline nature of the Co0.30Au0.35Pd0.35 NPs, and the lattice spacing is measured to be 0.230 nm (Figure 1b), which is similar to that of the (111) plane of face-centered cubic (fcc) Au (0.235 nm, JCPDS file: 65-8601).[13] The elemental mappings corresponded to a high-angle annular dark-field scanning TEM (HAADF-STEM) image indicating that Co, Au, and Pd are homogeneously distributed in each particle (Figure 1c–f). The X-ray diffraction (XRD) pattern shows that the tri-metallic specimen has the fcc structure of metallic Au (Figure 1g). [13] Moreover, this fcc structure is stable even after heat treatment at 573 K in Ar (Figure S2). The coexistence of Co, Au, and Pd elements in the pure fcc phase confirms the formation of a Co0.30Au0.35Pd0.35 nanoalloy. This can explain that, according to the Hume–Rothery rule,[14] the relative differences of the atomic radii of Au (0.144 nm)[15] to Co (0.125 nm)[15] and Pd (0.138 nm)[15] are (13.2% and 4.2%, respectively) both lower than 15%, Co and Pd atoms can thus be incorporated into the Au lattice to form an fcc alloy structure. Compared with fcc Au, the diffraction peaks of the present fcc phase are slightly shifted to higher angles (Figure 1g), indicating a little decrease in the symmetry of the crystal lattice of Au after addition of Co and Pd, and this is consistent with the HRTEM result. Based on the above experimental and theoretical analyses, a Co0.30Au0.35Pd0.35 nanoalloy supported on carbon has been successfully synthesized through the present facile co-reduction method at 298 K.

Additionally, the X-ray photoelectron spectroscopy (XPS) results (Figure 1h,i) show that the binding energies for Pd 3d and Au 4f in Co0.30Au0.35Pd0.35/C are both shifted to the lower values compared with those in Pd/C and Au/C, respectively. Whereas the binding energy for Co 2p in Co0.30Au0.35Pd0.35/C is shifted to higher energy relative to those in Co/C (Figure 1j). These shifts demonstrate that some electrons are transferred from Co to Pd and Au atoms in the alloy structure of Co0.30Au0.35Pd0.35.[16] It can be easily understood that, once Co atoms are closely interacting with Pd and Au, for instance, in the present alloy structure, electrons can be transferred from atoms of Co to Pd and Au to equilibrate the Fermi level because of the difference of the work functions of Pd (5.67 eV), Au (5.54 eV), and Co (5.44 eV).[17] Such electron transfer in Co0.30Au0.35Pd0.35/C has the potential to endow itself with the high activity to H2 generation from FA at 298 K. Fortunately, this assumption has been confirmed immediately. Moreover, the as-prepared Co0.30Au0.35Pd0.35/C has good physical and chemical stabilities in FA solution (see Figures S3 and S4),[12] which makes possible its application for H2 generation from FA solution. The catalytic activities of Co0.30Au0.35Pd0.35/C together with its mono-metallic (Pd/C, Au/C, and Co/C)[12] and bi-metallic (Au0.50Pd0.50/C, Co0.30Pd0.70/C, and Co0.30Au0.70/C) counterparts[12] for H2 generation from FA decomposition at 298 K in ambient atmosphere are presented in Figure 2. Obviously, the as-prepared Co0.30Au0.35Pd0.35/C exhibits a much better activity than those of mono- and bi-metallic catalysts synthesized by the same method.[12] It should be noted that the decreasing rate in the H2 generation curve over Co0.30Au0.35Pd0.35/C is due to the reducing FA concentration during the reaction process but not the deactivation of the catalyst (Figure S5).[12] Moreover, the reaction rate has a near linear dependency on the FA concentration with a slope of 0.75 (Figure S6),[12] which further confirms that the reaction rate is strongly dependent on the FA concentration. The generated gas over Co0.30Au0.35Pd0.35/C is identified by mass spectrometry (MS, Figure S7) and gas chromatograph (GC, Figure S8) to be H2 and CO2 with the H2 :CO2 molar ratio of 1.0:1.0, and no CO has been detected (detection limit: about 10 ppm, Figure S9). This indicates that CO-free H2 can be released from FA aqueous solution over the present Co0.30Au0.35Pd0.35/C catalyst, which is very important for fuel...
Figure 2. Gas generation by decomposition of FA (0.5 mL, 10 mL versus time in the presence of a) Co0.30Au0.35Pd0.35/C, b) Co/C, c) Au/C, d) Co0.30Au0.70/C, e) Pd/C, f) Co0.30Pd0.70/C, and g) Au0.50Pd0.50/C (n_{metal} / n_{carbon} = 0.02) at 298 K in ambient atmosphere.

In summary, the Co0.30Au0.35Pd0.35 nanoalloy supported on carbon has been successfully applied as a stable and low-cost catalyst for CO-free H2 generation from FA aqueous solution at 298 K. The initial TOF and final conversion for the decomposition of FA can reach the highest values of 80 h⁻¹ and 91% even without any extra additive at room temperature. This improvement on the catalytic performance of the nanocatalyst based on a non-noble metal might lead to a new approach to further develop cost-effective and highly efficient solid catalysts for the generation of H2 from FA to meet the requirement of practical application of FA as a H2 storage/generation material.

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[12] See the Supporting Information.


