

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

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Nowadays, searching for the effective hydrogen (H_2) storage/generation materials remains one of the most difficult challenges toward a fuel-cell-based H_2 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 H_2 storage and generation.^[2,3] Moreover, through the potential hydrogenation of waste carbon dioxide (CO_2) from industry, FA can be regenerated,^[2,4] and this makes the storage of H_2 in FA more attractive for a sustainable and reversible energy storage cycle.^[2,4]

FA can be catalytically decomposed to H_2 and CO_2 through a dehydrogenation pathway ($HCOOH(l) \rightarrow H_2(g) + CO_2(g)$, $\Delta G_{298K} = -35.0 \text{ kJ mol}^{-1}$).^[2] However, carbon monoxide (CO), which is a fatal poison to catalysts of fuel cells,^[5] can also be generated through a dehydration pathway ($HCOOH(l) \rightarrow H_2O(l) + CO(g)$, $\Delta G_{298K} = -14.9 \text{ kJ mol}^{-1}$).^[2] depending on the catalysts, pH values of the solutions, as well as the reaction temperatures.^[2,6] 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,7c] still need to be further promoted.^[6c-e,7,8] More importantly, all the reported heterogeneous catalysts up to now only consist of noble metals, including, for example, Pd, Au, Ag, and Pt,^[6c-e,7,8] which greatly hinders their large-scale practical applications because of their high costs and low reserves in the earth's crust.

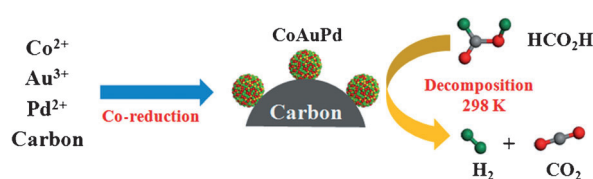
The first-row transition metals (FRTM) in nanoscale, such as cobalt (Co) nanoparticles (NPs), have been widely investigated as the catalytic materials in many important reactions

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 Co^0 in the protective nanoalloy structure makes its first application in FA dehydrogenation successful. More interestingly, the prepared CoAuPd/C with the lower consumption of noble metals exhibits the 100 % H_2 selectivity, highest activity, and excellent stability toward H_2 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 $Co_{0.30}Au_{0.35}Pd_{0.35}/C$, 5.0 mL of aqueous solution containing $CoCl_2$ (9.0 mM), Na_2PdCl_4 (10.5 mM), and $HAuCl_4$



Scheme 1. Preparation and application of CoAuPd/C nanocatalyst for FA decomposition at 298 K.

(10.5 mM) is mixed with 10.0 mL of aqueous solution containing the well-dispersed Vulcan XC-72 carbon (167.2 mg, $500 \text{ m}^2 \text{ g}^{-1}$).^[12] Then, the fresh $NaBH_4$ 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 $Co_{0.30}Au_{0.35}Pd_{0.35}/C$ is obtained and ready for the catalytic H_2 generation from FA aqueous solution at 298 K.

Figure 1 a shows the typical transmission electron microscopy (TEM) image of the as-prepared $Co_{0.30}Au_{0.35}Pd_{0.35}/C$. The NPs are well-dispersed on carbon with an average

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[**] This work is supported in part by the National Natural Science Foundation of China (grant number 51101070), the National Key Basic Research, Development Program (grant number 2010CB631001), the Program for New Century Excellent Talents in University of the Ministry of Education of China (grant number NCET-09-0431), the Jilin Province Science and Technology Development Program (grant number 201101061), and the Jilin University Fundamental Research Funds.

Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/anie.201301009>.

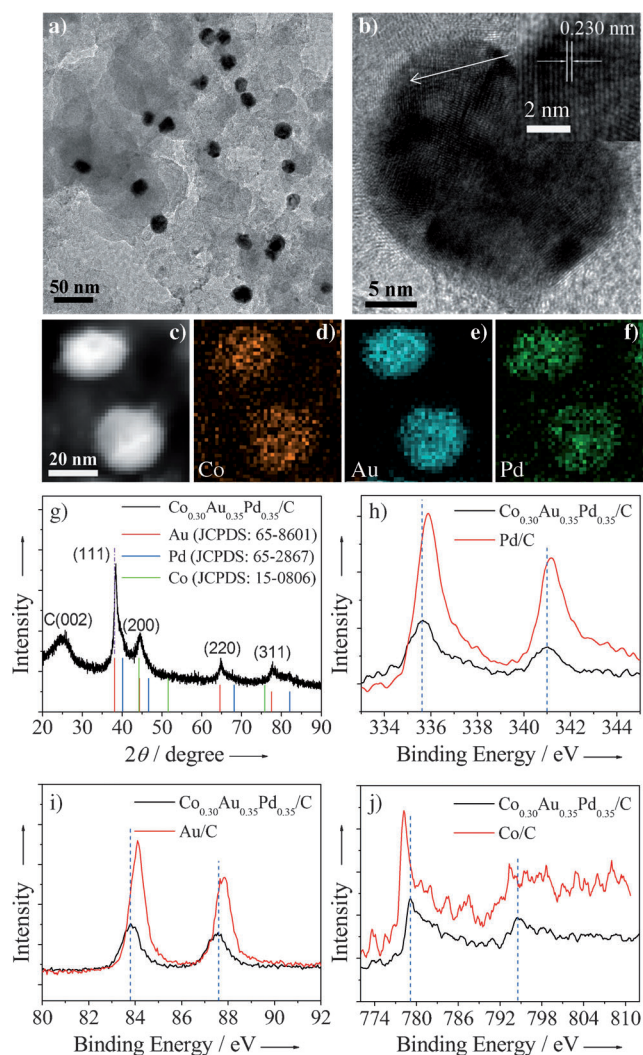


Figure 1. a) TEM, b) HRTEM, and c) HAADF-STEM images of $\text{Co}_{0.30}\text{Au}_{0.35}\text{Pd}_{0.35}/\text{C}$ and the corresponding elemental mappings for d) Co, e) Au, and f) Pd elements. g) XRD pattern of $\text{Co}_{0.30}\text{Au}_{0.35}\text{Pd}_{0.35}/\text{C}$. h) Pd 3d, i) Au 4f, and j) Co 2p XPS spectra for $\text{Co}_{0.30}\text{Au}_{0.35}\text{Pd}_{0.35}/\text{C}$, Pd/C, Au/C, and Co/C specimens.

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 $\text{Co}_{0.30}\text{Au}_{0.35}\text{Pd}_{0.35}$ NPs, and the lattice spacing is measured to be 0.230 nm (Figure 1 b), 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 1 c–f). The X-ray diffraction (XRD) pattern shows that the tri-metallic specimen has the fcc structure of metallic Au (Figure 1 g).^[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 $\text{Co}_{0.30}\text{Au}_{0.35}\text{Pd}_{0.35}$ 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 1 g), 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 $\text{Co}_{0.30}\text{Au}_{0.35}\text{Pd}_{0.35}$ 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 1 h,i) show that the binding energies for Pd 3d and Au 4f in $\text{Co}_{0.30}\text{Au}_{0.35}\text{Pd}_{0.35}/\text{C}$ 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 $\text{Co}_{0.30}\text{Au}_{0.35}\text{Pd}_{0.35}/\text{C}$ is shifted to higher value relative to those in Co/C (Figure 1 j). These shifts demonstrate that some electrons are transferred from Co to Pd and Au atoms in the alloy structure of $\text{Co}_{0.30}\text{Au}_{0.35}\text{Pd}_{0.35}$.^[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₍₁₁₁₎ (5.67 eV), Au₍₁₁₁₎ (5.54 eV), and Co₍₁₁₁₎ (5.44 eV).^[17] Such electron transfer in $\text{Co}_{0.30}\text{Au}_{0.35}\text{Pd}_{0.35}/\text{C}$ 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 $\text{Co}_{0.30}\text{Au}_{0.35}\text{Pd}_{0.35}/\text{C}$ 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 $\text{Co}_{0.30}\text{Au}_{0.35}\text{Pd}_{0.35}/\text{C}$ together with its mono-metallic (Pd/C, Au/C, and Co/C)^[12] and bi-metallic ($\text{Au}_{0.50}\text{Pd}_{0.50}/\text{C}$, $\text{Co}_{0.30}\text{Pd}_{0.70}/\text{C}$, and $\text{Co}_{0.30}\text{Au}_{0.70}/\text{C}$) counterparts^[12] for H₂ generation from FA decomposition at 298 K in ambient atmosphere are presented in Figure 2. Obviously, the as-prepared $\text{Co}_{0.30}\text{Au}_{0.35}\text{Pd}_{0.35}/\text{C}$ 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 $\text{Co}_{0.30}\text{Au}_{0.35}\text{Pd}_{0.35}/\text{C}$ 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 depended on the FA concentration. The generated gas over $\text{Co}_{0.30}\text{Au}_{0.35}\text{Pd}_{0.35}/\text{C}$ 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 $\text{Co}_{0.30}\text{Au}_{0.35}\text{Pd}_{0.35}/\text{C}$ catalyst, which is very important for fuel

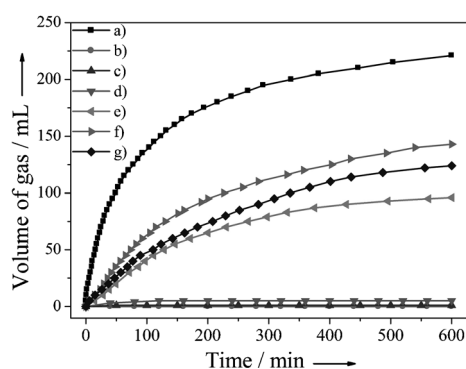


Figure 2. Gas generation by decomposition of FA (0.5 M, 10 mL) versus time in the presence of a) $\text{Co}_{0.30}\text{Au}_{0.35}\text{Pd}_{0.35}/\text{C}$, b) Co/C , c) Au/C , d) $\text{Co}_{0.30}\text{Au}_{0.70}/\text{C}$, e) Pd/C , f) $\text{Co}_{0.30}\text{Pd}_{0.70}/\text{C}$, and g) $\text{Au}_{0.50}\text{Pd}_{0.50}/\text{C}$ ($n_{\text{metal}}/n_{\text{FA}} = 0.02$) at 298 K in ambient atmosphere.

cell applications.^[5,18] The initial turnover frequency [TOF, Eq. (S1)] over $\text{Co}_{0.30}\text{Au}_{0.35}\text{Pd}_{0.35}/\text{C}$ is measured to be 80 h^{-1} at 298 K. To the best of our knowledge, this initial TOF value is the highest value ever reported for FA decomposition using a heterogeneous catalyst without any additive at room temperature,^[6e] and is even comparable to most of those with additives or at elevated temperatures.^[7a–c,g,i] Furthermore, the decomposition of FA can be almost completed within 600 minutes [91 % of conversion, Eq. (S2), Figure 2a]. The initial rate of H_2 generation [Eq. (S3)] is determined to be $7.9 \text{ L H}_2 \text{ h}^{-1} \text{ g}_{\text{metal}}^{-1}$, corresponding to a theoretical power density of $10.7 \text{ Wh}^{-1} \text{ g}_{\text{metal}}^{-1}$ for energy generation.^[6e,7a,e] Therefore, 0.5–2.0 g of the present catalyst would be sufficient to supply H_2 for the small PEM fuel cell devices (0.5–2.0 Wh).^[6e,7a,e]

From Figure 2, it is obvious that Pd atoms are the crucial active sites in all the prepared catalysts. Namely, without Pd addition, Co/C , Au/C , and $\text{Co}_{0.30}\text{Au}_{0.70}/\text{C}$ show no activity at all (Figure 2b–d). On the contrary, with Pd addition, the activities of Pd/C , $\text{Co}_{0.30}\text{Pd}_{0.70}/\text{C}$, $\text{Au}_{0.50}\text{Pd}_{0.50}/\text{C}$, and $\text{Co}_{0.30}\text{Au}_{0.35}\text{Pd}_{0.35}/\text{C}$ have been enhanced obviously (Figure 2a,e–g), in which the bi-metallic $\text{Co}_{0.30}\text{Pd}_{0.70}/\text{C}$ and $\text{Au}_{0.50}\text{Pd}_{0.50}/\text{C}$ are more active than the mono-metallic Pd/C but far inferior to the tri-metallic $\text{Co}_{0.30}\text{Au}_{0.35}\text{Pd}_{0.35}/\text{C}$. Additionally, the present molar ratio of $\text{Co}:\text{Au}:\text{Pd}$ (0.30:0.35:0.35) in the CoAuPd/C system is found to be the most active one for FA decomposition (Figures S10 and S11).

Considering that the NPs of the prepared mono- and bi-metallic catalysts have the similar shapes but smaller sizes compared with tri-metallic $\text{Co}_{0.30}\text{Au}_{0.35}\text{Pd}_{0.35}/\text{C}$ (Figure S12), the enhanced catalytic performance of $\text{Co}_{0.30}\text{Au}_{0.35}\text{Pd}_{0.35}/\text{C}$ may be attributed to its special composition and surface electronic state (Figure 1h–j) in the alloy structure.^[19] And this has been further supported by the fact that the physical mixture of Pd/C , Au/C and Co/C (molar ratio of $\text{Co}:\text{Au}:\text{Pd}$ is 0.30:0.35:0.35) for the same reaction exhibits much lower activity (Figure S13) than that of $\text{Co}_{0.30}\text{Au}_{0.35}\text{Pd}_{0.35}/\text{C}$. More detailed experimental and theoretical studies on the mechanism of $\text{Co}_{0.30}\text{Au}_{0.35}\text{Pd}_{0.35}/\text{C}$ catalyzed FA dehydrogenation are still underway.

In summary, the $\text{Co}_{0.30}\text{Au}_{0.35}\text{Pd}_{0.35}$ nanoalloy supported on carbon has been successfully applied as a stable and low-cost catalyst for CO-free H_2 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 % ever reported 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 H_2 from FA to meet the requirement of practical application of FA as a H_2 storage/generation material.

Received: February 4, 2013

Published online: March 19, 2013

Keywords: formic acid · heterogeneous catalysis · hydrogen storage · nanoalloys · non-noble metals

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