Electronic Supplementary Information

Highly efficient hydrogen generation from formic acid using reduced graphene oxide-supported AuPd nanoparticle catalyst

Xinchun Yang, Pradip Pachfule, Yao Chen, Nobuko Tsumori and Qiang Xu

National Institute of Advanced Industrial Science and Technology (AIST), Ikeda, Osaka, Japan. E-mail: q.xu@aist.go.jp, qxuchem@hotmail.com; Fax: +81-72-751-9628; Tel: +81-72-751-9562

Graduate School of Engineering, Kobe University, Nada Ku, Kobe, Hyogo, Japan

Toyama National College of Technology, 13, Hongo-machi, Toyama, 939-8630, Japan
Chemicals

Natural graphite (Alfa Aesar, 325 mesh, metals basis, 99.8%), sodium nitrate (NaNO₃, Kishida Chemicals Co. Ltd., 99%), sulfuric acid (H₂SO₄, Kishida Chemicals Co. Ltd., 98%), potassium permanganate (KMnO₄, Kishida Chemicals Co. Ltd., 99.3%), hydrogen peroxide (H₂O₂, Kishida Chemicals Co. Ltd., 30%) and hydrochloric acid (HCl, Wako Pure Chemical Industries, Ltd., 35-37%) were used to prepare graphite oxide.

Potassium teterchloropalladate (K₂PdCl₄, Wako Pure Chemical Industries, Ltd., >97%), gold chloride acid (HAuCl₄•4H₂O, Kishida Chemicals Co. Ltd., 99%), cobalt acetate (Co(CH₃COO)₂•4H₂O, Kishida Chemicals Co. Ltd., 99%), sodium borohydride (NaBH₄, Sigma-Aldrich, 99%), phosphoric acid (H₃PO₄, Tokyo Chemical Industry Co. Ltd., >89%) were used to prepare the reduced graphene oxide (rGO) supported AuPd nanoparticles.

Formic acid (FA, HCOOH, Merck Millipore, 98%) and sodium formate (SF, HCOONa, Sigma-Aldrich, 99.5%) were used for hydrogen release with the catalysts.

Preparation process of (Coₓ)ₓAuₚₚₓ+y/rGO catalysts

GO was synthesized by the modified Hummers’ method⁵¹ and then ultrasonicated in water to form a colloidal dispersion. A mixed solution (0.06 mmol) of K₂PdCl₄ and HAuCl₄ with or without Co(CH₃COO)₂ was added into the GO dispersion (0.1 wt%, 50 mL). After adding a fresh NaBH₄ solution (3.7 M, 0.5 mL), the resulted mixture was stirred for 2 h. Then, the CoₓAuₚₚₓ+y/rGO precipitation was separated by centrifugation. Subsequently, the precipitation was re-dispersed into 2.5 vol% H₃PO₄ (20 ml) under stirring for another 2 h. The rGO-supported AuPd nanoparticle catalyst was obtained by washing with water and centrifugation. The obtained catalyst was named as (Coₓ)ₓAuₚₚₓ+y/rGO, where (Co)ₓ represents the acid etching of Co, x represents the molar ratio of Co/(Au+Pd) and y is the molar ratio of Au/(Au+Pd).
Preparation process of the CO poisoned (Co₃)₆Au₀.₆Pd₀.₄/rGO catalyst

The obtained (Co₃)₆Au₀.₆Pd₀.₄/rGO catalyst was continuous stirred in a round-bottom flask (50 ml) under CO atmosphere for 1 hour. Then, the catalyst was used for the dehydrogenation of FA.

Characterization

The powder X-ray diffraction measurements were carried out using a Rigaku Ultima IV diffractometer with Cu-Kα radiation. The metal contents of the catalyst were analyzed using ICP-OES on Thermo Scientific iCAP6300. The TEM and HAADF-STEM images and EDX spectra were taken by Transmission electron microscope (TEM, TECNAI G² F20) with operating voltage at 200 kV equipped with energy-dispersive X-ray (EDX) detector. The N₂ adsorption/desorption isotherms were obtained at 77 K using automatic volumetric adsorption equipment (Belsorp-max). XPS spectra were recorded on a Shimadzu ESCA-3400 using an Mg Kα source. The generated gas from FA was analyzed by GC-8A (molecular sieve 5A, Ar as carrier gas) and GC-8A (Porapack N, He as carrier gas) analyzers (Shimadzu).

Catalysis activity determination

An aqueous suspension containing the as-prepared catalyst was placed in a two-neck round-bottom flask, which was placed in a water bath under ambient atmosphere. A gas burette filled with water was connected to the reaction flask to measure the volume of released gas. The reaction was started when the mixed aqueous solution of FA-SF was injected into the sealed flask to form a 4.5 mL of suspension. The molar ratio of AuPd/FA was fixed at 0.02 for all the catalytic reactions. The volume of the evolved gas was monitored by recording the displacement of water in the gas burette.
The turnover frequency (TOF) calculations

The TOF reported here is an apparent TOF value based on the number of (Au+Pd) atoms in catalyst, which is calculated from the equation as follows:

\[
TOF = \frac{P_0 V}{2RT n_{AuPd} t}
\]

where \( P_0 \) is the atmospheric pressure (101325 Pa), \( V \) is the final generated volume of (H\(_2\) + CO\(_2\)) gas, \( R \) is the universal gas constant (8.3145 m\(^3\) Pa mol\(^{-1}\) K\(^{-1}\)), \( T \) is the room temperature (298 K), \( n_{AuPd} \) is the total molar number of (Au + Pd) atoms in catalyst and \( t \) is the completion time of the reaction in hour.

Durability test

After the catalytic reaction, the catalyst was recollected by centrifugation, washed with water and recycled for durability. In each cycle 100 % FA is decomposed, corresponding to a TON value of 50 for each cycle.
Figure S1. XRD patterns of the products from the reaction between Co(CH₃COO)₂ and NaBH₄ (a) before and (b) after annealing (823 K, 3 h, Ar), and (c) JCPDS: 25-0102 (Co₃(BO₃)₂).
The reaction between Co(CH\textsubscript{3}COO)\textsubscript{2} and NaBH\textsubscript{4} in a molar ratio of 1:3.7 under an ambient condition for 2 h results in the formation of a black precipitation (Figure S2b), which exhibits very broad X-ray diffractions (XRD) (Figure S1a), characteristic of an amorphous phase. The sample crystallizes by annealing at 823 K for 3 h (Ar atmosphere), displaying the XRD peaks (Figure S1b) corresponding to Co\textsubscript{3}(BO\textsubscript{3})\textsubscript{2} phase (JCPDS: 25-0102, Figure S1c).\textsuperscript{52} The precipitation Co\textsubscript{3}(BO\textsubscript{3})\textsubscript{2} can be readily dissolved in H\textsubscript{3}PO\textsubscript{4} (Figure S2c). Thus, in our work, the cobalt was used as the sacrificial agent for the NNMSA.
Figure S3. XRD patterns of (a) Co$_2$Au$_{0.8}$Pd$_{0.4}$, (b) (Co$_3$)$_6$Au$_{0.6}$Pd$_{0.4}$, (c) Au$_{0.6}$Pd$_{0.4}$/rGO, (d) Co$_2$Au$_{0.8}$Pd$_{0.4}$/rGO, and (e) (Co$_3$)$_6$Au$_{0.6}$Pd$_{0.4}$/rGO.
Figure S4. TEM image of Au$_{0.6}$Pd$_{0.4}$/rGO.
Figure S5. (a) TEM and (b) HADDF-STEM images of Co$_3$Au$_{0.6}$Pd$_{0.4}$/rGO.
Figure S6. EDX patterns of (a) Co$_3$Au$_{0.6}$Pd$_{0.4}$/rGO and (b) (Co$_3$)$_x$Au$_{0.6}$Pd$_{0.4}$/rGO.
Figure S7. (a) HAADF-STEM image of Co$_2$Au$_{0.8}$Pd$_{0.4}$/rGO and (b) the corresponding EDX-line scan along the red line in (a).
Figure S8. (a) HAADF-STEM image of (Co0.6)Au0.4/Pd0.6/rGO and (b) the corresponding EDX-line scan along the red line in (a).
Figure S9. Volume of the generated gas (CO$_2$+H$_2$) versus time for the dehydrogenation of FA over the (Co$_x$)$_x$Au$_{0.6}$Pd$_{0.4}$/rGO catalyst at 323 K ($n_{\text{AuPd}}/n_{\text{FA}}=0.02$, $n_{\text{SF}}/n_{\text{FA}}=2.5$).
Figure 10. Volume of the generated gas (CO$_2$+H$_2$) versus time for the dehydrogenation of FA over the (Co$_3$)$_2$Au$_{0.6}$Pd$_{0.4}$/rGO catalyst with different loadings of metals (a) $n_{\text{AuPd}} = 0.04$ mmol, (b) $n_{\text{AuPd}} = 0.05$ mmol and (c) $n_{\text{AuPd}} = 0.06$ mmol and the same GO amount at 323 K ($n_{\text{GF}}/n_{\text{FA}} = 2.5$, FA = 3 mmol), showing TOF values of 4338, 4300, and 4840 h$^{-1}$, respectively.
Figure S11. Gas chromatograms (GC) of the released gas (under Ar atmosphere) from the decomposition of FA in the FA/SF system ($n_{SF}/n_{FA}=2.5$) over the (Co$_3$)E@Au$_{0.6}$Pd$_{0.4}$/rGO catalyst at 323 K with (a) CO, air and H$_2$ and (b) CO$_2$ as reference gas, indicative of the absence of CO and presence of CO$_2$ and H$_2$ in the released gas.
Figure S12. Volume of the generated gas (CO₂+H₂) versus time for the dehydrogenation of FA with different $n_{SF}/n_{FA}$ molar ratios over the (Co₃)₅Au₀.₆Pd₀.₄/GO catalyst at 323 K ($n_{AuPd}/n_{FA}$ = 0.02).
Figure S13. Volume of the generated gas (CO$_2$+H$_2$) versus time for the dehydrogenation of FA over the (Co$_3$)$_{1-x}$Au$_x$Pd$_{1-y}$/rGO catalysts at 323 K ($n_{AuPd}/n_{FA} = 0.02$, $n_{SF}/n_{FA} = 2.5$).
Figure S14. Volumes of the generated gas (CO$_2$+H$_2$) versus time for the dehydrogenation of FA over the support-free (a) (Co$_3$)$_e$Au$_{0.8}$Pd$_{0.4}$ and (b) Au$_{0.8}$Pd$_{0.4}$ catalysts at 323 K ($n_{AuPd}/n_{FA} = 0.02$, $n_{SF}/n_{FA} = 2.5$).
Figure S15. (a) Volume of the generated gas (CO₂ + H₂) versus time, (b) Arrhenius plot and TOF values for the dehydrogenation of FA over the (Co₃)₆Au₉Pd₆/rGO catalyst at different temperatures (nₐuₚd/nₚa = 0.02, nₛf/nₚa = 2.5).
Figure S16. XRD pattern of the (Co$_3$)$_2$Au$_{0.6}$Pd$_{0.4}$/rGO catalyst after 5 catalytic cycles ($n_{\text{AuPd}}/n_{\text{FA}} = 0.02$, $n_{\text{SF}}/n_{\text{FA}} = 2.5$, 323 K).
Figure S17. (a) TEM image and (b) size histogram of AuPd NPs of the (Co$_3$)$_6$Au$_{0.6}$Pd$_{0.4}$/rGO catalyst after 5 cycles for dehydrogenation of FA ($n_{\text{AuPd}}/n_{\text{FA}} = 0.02$, $n_{\text{SF}}/n_{\text{FA}} = 2.5$, 323 K).
Figure S18. Volume of the generated gas (CO$_2$ + H$_2$) versus time for the dehydrogenation of FA over the CO poisoned (Co$_3$)$_{6}$Au$_{0.6}$Pd$_{0.4}$/rGO catalyst, prepared by exposing the catalyst to CO atmosphere, at 323 K ($n_{\text{AuPd}}/n_{\text{FA}} = 0.02$, $n_{\text{SF}}/n_{\text{FA}} = 2.5$).
Table S1 Catalytic activities for dehydrogenation of formic acid catalysed by related heterogeneous catalysts.

<table>
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<th>Catalyst</th>
<th>Solvent/medium</th>
<th>Temp. (K)</th>
<th>CO evolution</th>
<th>TOF (h&lt;sup&gt;-1&lt;/sup&gt;)</th>
<th>Ref.</th>
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<td>(Co&lt;sub&gt;3&lt;/sub&gt;)Au&lt;sub&gt;0.6&lt;/sub&gt;Pd&lt;sub&gt;0.4&lt;/sub&gt;/rGO</td>
<td>Aqueous/HCOONa</td>
<td>323</td>
<td>No</td>
<td>4840</td>
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<tr>
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<td>No</td>
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<tr>
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<td>No</td>
<td>2882</td>
<td>S4</td>
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<tr>
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<td>No</td>
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Table S2 TOFs for the dehydrogenation of FA over (Co<sub>3</sub>)Au<sub>0.6</sub>Pd<sub>0.4</sub>/rGO for the cycles of durability test (n<sub>AlPd</sub>/n<sub>FA</sub> = 0.02, n<sub>SF</sub>/n<sub>FA</sub> = 2.5, 323 K).

<table>
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<tr>
<th>Cycles</th>
<th>TOF / h&lt;sup&gt;-1&lt;/sup&gt;</th>
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<td>2nd</td>
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References


