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Communication

Facile Synthesis of AgAuPd/Graphene with High Performance for Hydrogen Generation from Formic Acid

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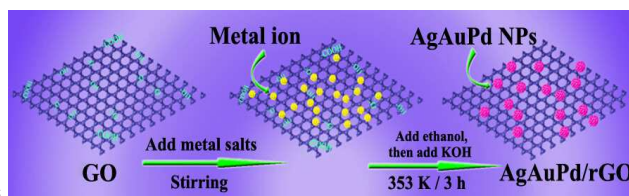
AgAuPd nanoparticles with small particle size, good dispersity and high degree of crystallinity on graphene are synthesized by a facile co-reduction route. The resultant AgAuPd/graphene exhibit 100% H₂ selectivity, 100% conversion and excellent catalytic activity toward the hydrogen generation from decomposition of formic acid without any additive at room temperature.

Hydrogen (H₂) is capable of providing highly stable, efficient and pollution-free power.^[1] Its potential applications in onboard automotive industry and stationary power generation are promising.^[2] However, H₂ generation from renewable sources and its secure storage remain as a big challenge in the H₂ energy based economy.^[3] Formic acid (FA, HCOOH), as a promising H₂ storage material with nontoxicity, high energy density, excellent stability, and possible regenerability by hydrogenation of carbon dioxide (CO₂), has attracted much research interest.^[4,5] H₂ can be generated by catalytic dehydrogenation of FA with the byproduct of CO₂.^[4] The undesirable dehydration of FA to generate carbon monoxide (CO) should be avoided.^[4,6]

Recently, many homogeneous and heterogeneous catalysts have been intensely investigated to increase the kinetic property of the dehydrogenation of FA at the mild reaction condition.^[4,7] For example, metal complex-based homogeneous catalysts have been reported to have high performance for the formic acid decomposition at near-ambient temperatures.^[4,8] Generally, heterogeneous nanocatalysts have the superiorities on controlling, retrieving, and recycling issues during or after reactions.^[6,9] Therefore, there is a strong desire to develop heterogeneous catalysts with high activity and selectivity for the formic acid decomposition under mild conditions.^[9,10] The performance of nanocatalyst is highly depended on its particle size, dispersion, crystallinity, support and etc.^[11, 12] Herein we report a facile, eco-friendly, one-pot method for the synthesis of the reduced graphene oxide (rGO) supported AgAuPd ultrafine nanoalloy (~3 nm) with good dispersion and crystallinity (AgAuPd/rGO) by simultaneous reduction using ethanol as the reduction agent. The prepared AgAuPd/rGO exhibits the 100% H₂ selectivity, and high activity toward H₂ generation from FA without any additive at 298 K.

Graphene oxide (GO) aqueous solution is firstly prepared using the modified Hummers' method as the graphene

precursor.^[13] AgAuPd/rGO is synthesized by coreduction of GO and the metal precursors of Ag, Au and Pd, as illustrated in Scheme 1. Typically, for preparation of Ag_{0.2}Au_{0.4}Pd_{0.4}/rGO, 5.0 mL of aqueous solution containing AgNO₃ (0.02 mmol), Na₂PdCl₄ (0.04 mmol) and HAuCl₄ (0.04 mmol) was added into the well dispersed GO aqueous solution (32.5 mg, 45 mL), and then 40 mL of ethanol was added into above solution. The PH of the solution was adjusted to be 9-10 by adding KOH (1.0 M) aqueous solution. The solution was refluxed in an water bath at 353 K for 3 h with stirring. After 3 h, the obtained product is washed with water for several times and re-dispersed in 10 mL of water for the catalytic H₂ generation from the FA aqueous solution at 298 K. Additionally, AgAuPd/rGO with different Ag: Au: Pd molar ratio, the physical mixture of Ag_{0.2}Au_{0.4}Pd_{0.4} and rGO, Pd/rGO and rGO were also synthesized through the same method mentioned above for comparison. Since pure graphene tends to aggregate due to its π - π stacking interactions,^[17a] various efforts have been made to avoid the aggration of graphene based catalysts, including electrostatic stabilization, chemical functionalization and adhering metal nanoparticles (NPs) on graphene sheets.^[17a-c] The present co-reduction method to prepare AgAuPd/rGO may has the priority to suppress the aggration of rGO because the *in situ* generated NPs can increase the interlayer spacing between rGO sheets.^[17d]



Scheme 1 Schematic illustration for preparation of AgAuPd/rGO

The morphology of the as-prepared specimens, Ag_{0.2}Au_{0.4}Pd_{0.4}/rGO composite and Ag_{0.2}Au_{0.4}Pd_{0.4} NPs are characterized by transmission electron microscopy (TEM). It can be seen that the Ag_{0.2}Au_{0.4}Pd_{0.4} NPs supported on rGO are well dispersed with an average particle size of about 3.0nm (Fig. 1a and b), while the NPs without rGO are seriously aggregated (Fig. 1d), suggesting that rGO lead to the good dispersion of Ag_{0.2}Au_{0.4}Pd_{0.4} NPs on its surface. The high-resolution TEM (HRTEM) image reveals the crystalline

nature of the $\text{Ag}_{0.2}\text{Au}_{0.4}\text{Pd}_{0.4}$ NPs on rGO, and the lattice spacing is measured to be 0.231 nm (Fig. 1c), which is between those of the (111) planes of face-centered cubic (fcc) Au (0.235 nm, JCPDS file:65-8601), Ag (0.235 nm, JCPDS file:65-2871) and Pd (0.224 nm, JCPDS file:65-2867).^[14] And this reveals the formation of AgAuPd trimetallic alloy structure. Moreover, the X-ray diffraction (XRD) pattern of $\text{Ag}_{0.2}\text{Au}_{0.4}\text{Pd}_{0.4}/\text{rGO}$ composite (Fig. 1e) shows that, besides the peak of (002) plane of rGO,^[14c] all diffraction peaks can be assigned to (111), (200), (220) and (311) planes of a fcc structure located between fcc Ag, Au and Pd, which further proves that the $\text{Ag}_{0.2}\text{Au}_{0.4}\text{Pd}_{0.4}$ is formed as an alloy. The accurate molar ratio of Ag:Au:Pd is determined to be 0.17:0.34:0.49 by inductively coupled plasma-atomic emission spectrometry (ICP-AES), which is close to the appointed value. Based on the above analyses, $\text{Ag}_{0.2}\text{Au}_{0.4}\text{Pd}_{0.4}$ nanoalloy supported on rGO has been successfully synthesized by the present facile method.

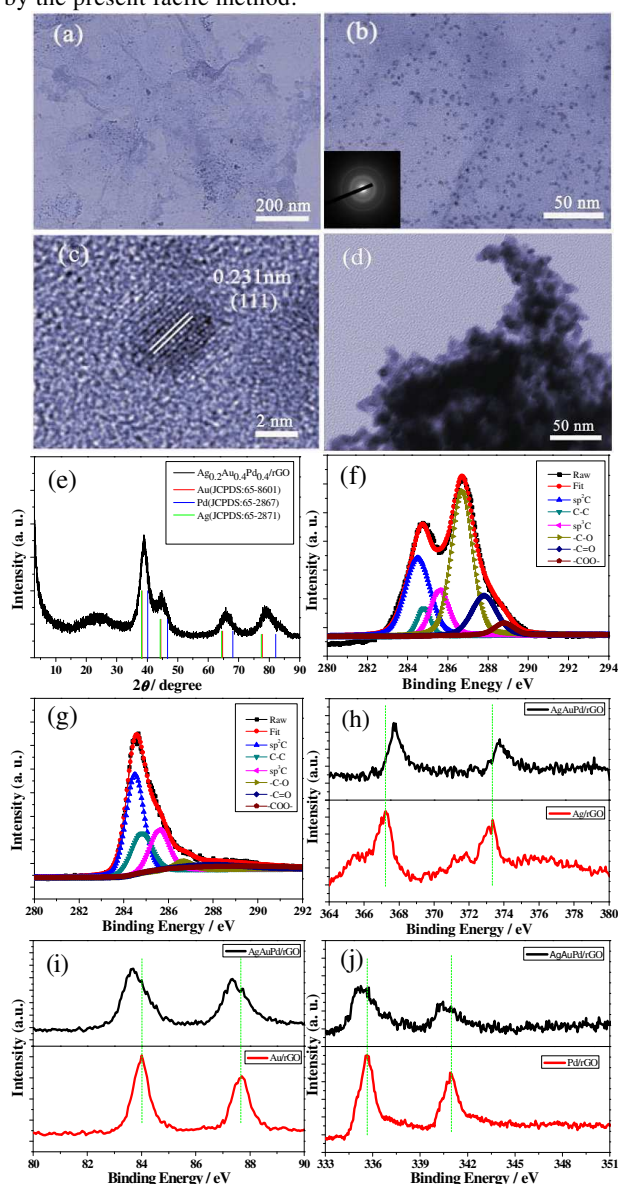


Fig. 1 TEM images with the (a) low, (b) middle, (c) high resolutions for $\text{Ag}_{0.2}\text{Au}_{0.4}\text{Pd}_{0.4}/\text{rGO}$ (Fig. 2b inset: the corresponding SAED pattern for

$\text{Ag}_{0.2}\text{Au}_{0.4}\text{Pd}_{0.4}/\text{rGO}$); (d) TEM images for free $\text{Ag}_{0.2}\text{Au}_{0.4}\text{Pd}_{0.4}$ NPs; (e) XRD pattern of $\text{Ag}_{0.2}\text{Au}_{0.4}\text{Pd}_{0.4}/\text{rGO}$ NPs; XPS spectra of C 1s in (f) GO and (g) $\text{Ag}_{0.2}\text{Au}_{0.4}\text{Pd}_{0.4}/\text{rGO}$; and XPS spectra of (h) Ag 3d for Ag/rGO and $\text{Ag}_{0.2}\text{Au}_{0.4}\text{Pd}_{0.4}/\text{rGO}$, (i) Au 4f for Au/rGO and $\text{Ag}_{0.2}\text{Au}_{0.4}\text{Pd}_{0.4}/\text{rGO}$, (j) Pd 3d for Pd/rGO and $\text{Ag}_{0.2}\text{Au}_{0.4}\text{Pd}_{0.4}/\text{rGO}$.

X-ray photoelectron spectroscopy (XPS) measurements are used to determine the compositions and chemical states of the $\text{Ag}_{0.2}\text{Au}_{0.4}\text{Pd}_{0.4}/\text{rGO}$ hybrid. The result for C 1s of the as-prepared GO (Fig. 1f) indicates that six different peaks centered at 284.5, 284.8, 285.6, 286.7, 287.8 and 288.8 eV are observed, corresponding to sp^2C , C-C, sp^3C , -C-O, -C=O and -COO groups, respectively.^[15,16] After reduction, the intensities of all the C 1s peaks binding to oxygen obviously decrease (Fig. 1g), revealing that most of the oxygen containing species are removed and the majority of the conjugated C networks are restored. This confirms the reduction of GO to rGO during the preparation of $\text{Ag}_{0.2}\text{Au}_{0.4}\text{Pd}_{0.4}/\text{rGO}$ hybrid, which is consistent with the Raman (Fig. S1) and ultraviolet visible (UV-Vis, Fig. S2) spectra. Additionally, the XPS results show that the binding energy for Ag 3d in $\text{Ag}_{0.2}\text{Au}_{0.4}\text{Pd}_{0.4}/\text{rGO}$ is located at the higher value relative to that in Ag/rGO (Fig. 1h); while binding energies for Au 4f and Pd 3d in $\text{Ag}_{0.2}\text{Au}_{0.4}\text{Pd}_{0.4}/\text{rGO}$ are shifted to the lower values compared with those in Au/rGO and Pd/rGO, respectively. These shifts demonstrate that some electrons are transferred from Ag to Au and Pd atoms in the $\text{Ag}_{0.2}\text{Au}_{0.4}\text{Pd}_{0.4}/\text{rGO}$ alloy structure. Such electron transfer in $\text{Ag}_{0.2}\text{Au}_{0.4}\text{Pd}_{0.4}/\text{rGO}$ has the potential to endow itself with the high activity to H_2 generation from FA at 298 K.

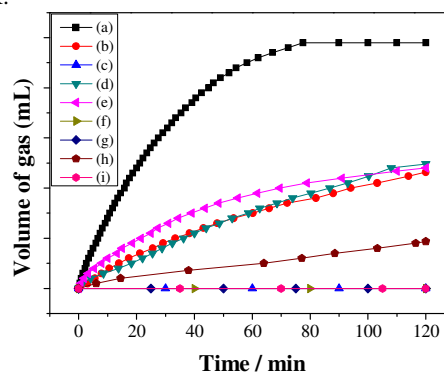


Fig. 2 Gas generation by the decomposition of FA (1 M, 5 mL) vs. time in the presence of (a) $\text{Ag}_{0.2}\text{Au}_{0.4}\text{Pd}_{0.4}/\text{rGO}$ hybrid, (b) the physical mixture of $\text{Ag}_{0.2}\text{Au}_{0.4}\text{Pd}_{0.4}$ and rGO, (c) $\text{Ag}_{0.33}\text{Au}_{0.67}/\text{rGO}$, (d) $\text{Ag}_{0.33}\text{Pd}_{0.67}/\text{rGO}$, (e) $\text{Au}_{0.5}\text{Pd}_{0.5}/\text{rGO}$, (f) Ag/rGO, (g) Au/rGO, (h) Pd/rGO, (i) rGO at 298 K under ambient atmosphere. ($n_{\text{metal}}/n_{\text{FA}} = 0.02$)

Fig. 2 shows the catalytic activities of $\text{Ag}_{0.2}\text{Au}_{0.4}\text{Pd}_{0.4}/\text{rGO}$ hybrid, the physical mixture of $\text{Ag}_{0.2}\text{Au}_{0.4}\text{Pd}_{0.4}$ and rGO, bimetallic ($\text{Ag}_{0.33}\text{Au}_{0.67}/\text{rGO}$, $\text{Ag}_{0.33}\text{Pd}_{0.67}/\text{rGO}$ and $\text{Au}_{0.5}\text{Pd}_{0.5}/\text{rGO}$), mono-metallic (Ag/rGO, Au/rGO and Pd/rGO) counterparts and rGO for H_2 generation from FA decomposition at 298 K under ambient atmosphere. Obviously, the as-prepared $\text{Ag}_{0.2}\text{Au}_{0.4}\text{Pd}_{0.4}/\text{rGO}$ hybrid exhibits the highest activity, with which 245 mL of gas can be released within 77.5 min without any additive at 298 K, corresponding to a conversion of 100%. Furthermore, the initial TOF over the $\text{Ag}_{0.2}\text{Au}_{0.4}\text{Pd}_{0.4}/\text{rGO}$ composite is

measured to be 73.6 mol H₂ mol catalyst⁻¹ h⁻¹ at 298 K during the first 20 min, which is faster than most of the additive free heterogeneous catalysts ever reported at the room temperature. (Table S1)^[6, 10h, 21, 23b, 23c, 24, 25] In contrast, the physical mixture (Ag_{0.2}Au_{0.4}Pd_{0.4} and rGO) shows much lower activity, with which 110 mL of gas is obtained within 120 min. Over bimetallic Ag_{0.33}Pd_{0.67}/rGO and Au_{0.5}Pd_{0.5}/rGO catalysts, 124 and 120 mL gas can be released within 120 min, respectively, while Ag_{0.33}Au_{0.67}/rGO has no activity. With monometallic Pd/rGO, only 47 mL of gas can be generated within 120 min, whereas Au/rGO and Ag/rGO shows no activity. In addition, no gas is generated from FA in the case of only rGO, suggesting that rGO serve as a support for the growth of Ag_{0.2}Au_{0.4}Pd_{0.4}/rGO NPs, rather than catalysts for this reaction. Therefore, the enhanced catalytic performance of Ag_{0.2}Au_{0.4}Pd_{0.4}/rGO may be attributed to its special composition and surface electronic state in the alloy structure as well as the small particle size and well dispersion due to the support of rGO. The generated gas over Ag_{0.2}Au_{0.4}Pd_{0.4}/rGO is identified by mass spectrometry (MS, Fig. S3) and gas chromatography (GC, Fig. S4) to be H₂ and CO₂ with the H₂: CO₂ molar ration of 1.0: 1.0, and no CO has been detected (Fig. S5, detection limit for CO: 10 ppm). This indicates the as-synthesized Ag_{0.2}Au_{0.4}Pd_{0.4}/rGO catalyst can catalyze FA aqueous solution decomposition into CO-free H₂, which is very important for fuel cell applications. To further determine the effect of the metal composition in system of AgAuPd/rGO on the catalytic performance, the molar ration of Ag: Au: Pd has been varied by several values. Setting the molar content of Ag as a constant of 0.2, Ag_{0.2}Au_{0.8-x}Pd_x/rGO system (x=0, 0.2, 0.4, 0.6, 0.8) reaches its highest activity when the molar ratio of Au: Pd is 1:1, namely, x is 0.4 (Figure S6). And then, setting the molar ratio of Au: Pd as 1:1, Ag_{1-2y}Au_yPd_y/rGO (y= 0.5, 0.4, 0.3, 0.25, 0.2, and 0) shows the best performance when the Ag molar content is 0.2, namely, y is 0.4 (Figure S7). As a result, once the ratio of Ag: Au: Pd is changed from 0.2: 0.4: 0.4, the resultant AgAuPd/rGO shows the decreased catalytic performance, and can not lead to the full conversion of FA within 120 min.

In order to demonstrate the advantages of ethanol as the reducing agent, we use similar method to synthesize Ag_{0.2}Au_{0.4}Pd_{0.4}/rGO NPs with NaBH₄ as the reducing agent, and the reducing temperature is 353 K and 298 K respectively. As shown in Fig. S8, the NPs reducing at 353 K have a larger average size of about 6.19 nm with severe aggregation, and the dispersion is very poor. The NPs reducing at 298 K have a mean size of about 3.40 nm with good dispersion, which is similar to the Ag_{0.2}Au_{0.4}Pd_{0.4} NPs with ethanol reducing at 353 K. The corresponding SAED patterns (Fig. 2b inset, Fig. S8b inset, Fig. S8d inset) of the three specimens reveal that all of them are crystallized. However, as seen from their XRD patterns (Fig. S9), Ag_{0.2}Au_{0.4}Pd_{0.4} reduced by ethanol at 353 K shows the best crystallinity, and that reduced by NaBH₄ at 298 K has the lowest crystallinity. The accurate molar ratios of Ag: Au: Pd in Ag_{0.2}Au_{0.4}Pd_{0.4}/rGO reduced by NaBH₄ at 353 K and 298 K (determined by ICP-AES) are 0.20:0.32:0.48 and 0.20:0.33:0.47, respectively, which are near to that in Ag_{0.2}Au_{0.4}Pd_{0.4}/rGO reduced by ethanol at 353 K. Moreover,

the XPS spectra of Ag, Au, and Pd in the three specimens show the similar electronic states with no obvious peak shift (Fig. S11). The catalytic activities of the three specimens for hydrogen generation from FA at 298 K are presented in Fig. S10 for comparison. It can be seen that, within 90 min, only 150 mL of gas can be generated over Ag_{0.2}Au_{0.4}Pd_{0.4}/rGO reduced by NaBH₄ at 353 K, and no gas was obtained with catalyst reduced by NaBH₄ at 298 K. Therefore, it can be concluded that the small particle size, good dispersity and high degree of crystallinity due to the present synthetic method result in the excellent catalytic performance of Ag_{0.2}Au_{0.4}Pd_{0.4}/rGO.

In summary, Ag_{0.2}Au_{0.4}Pd_{0.4} NPs decorated on rGO with small particle size, good dispersity and high degree of crystallinity are successfully synthesized by co-reduction of GO and the metal precursors using ethanol as the reduction agent at 353 K. The resultant Ag_{0.2}Au_{0.4}Pd_{0.4}/rGO composite shows 100% conversion, 100% H₂ selectivity, and excellent activity for dehydrogenation of FA in aqueous solution without any additive at room temperature. This improvement in the catalytic performance of the Ag_{0.2}Au_{0.4}Pd_{0.4}/rGO composite may strongly encourage the practical application of FA as a promising H₂ storage material.

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Notes and references

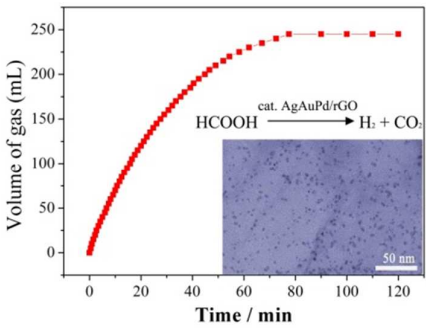
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† Electronic Supplementary Information (ESI) available: experimental procedures; Raman, UV-Vis, XPS, TEM, MS and GC, XRD data; TOF and conversion data; and the results of H₂ generation from FA. See DOI: 10.1039/b000000x/

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Well dispersed and ultrafine AgAuPd nanoalloy supported on rGO shows excellent catalytic performance toward hydrogen generation from formic acid decomposition.