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Synthesis of Ultrathin PdCu Alloy Nanosheets Used as Highly Efficient Electrocatalyst for Formic Acid Oxidation

Nailiang Yang, Zhicheng Zhang, Bo Chen, Ying Huang, Junze Chen, Zhuangchai Lai, Ye Chen, Melinda Sindoro, An-Liang Wang, Hongfei Cheng, Zhanxi Fan, Xiaozhi Liu, Bing Li, Yun Zong, Lin Gu, Hua Zhang*

Dr. N. Yang, Dr. Z. Zhang, Dr. B. Chen, Y. Huang, J. Chen, Z. Lai, Y. Chen, Dr. M. Sindoro, Dr. A.-L. Wang, H. Cheng, Dr. Z. Fan, Prof. H. Zhang
Center for Programmable Materials, School of Materials Science and Engineering,
Nanyang Technological University, 50 Nanyang Avenue, Singapore 639798,
Singapore

E-mail: h Zhang@ntu.edu.sg

Dr. B. Li, Dr. Y. Zong

Institute of Materials Research and Engineering

A*STAR (Agency for Science, Technology and Research)

2 Fusionopolis Way, Innovis #08-03, Singapore 138634, Singapore

X. Liu, Prof. L. Gu

Beijing National Laboratory for Condensed Matter Physics, Institute of Physics,
Chinese Academy of Sciences, Beijing 100190, China

School of Physical Sciences, University of Chinese Academy of Sciences, Beijing
100049, China

Prof. L. Gu

Collaborative Innovation Center of Quantum Matter, Beijing 100190, China

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Abstract: Inspired by the unique properties of ultrathin two-dimensional (2D) nanomaterials and excellent catalytic activities of noble metal nanostructures for renewable fuel cells, we report a facile method for the high-yield synthesis of ultrathin 2D PdCu alloy nanosheets under mild conditions. Impressively, the obtained PdCu

alloy nanosheet after treated with ethylenediamine can be used as a highly efficient electrocatalyst for the formic acid oxidation. Our study implicates that the rational design and controlled synthesis of ultrathin 2D noble metal alloy may open up new opportunities for enhancing catalytic activities of noble metal nanostructures.

Ultrathin two-dimensional (2D) nanomaterials have drawn increasing research attention since the report of graphene in 2004.^[1] Besides graphene, recently, other 2D nanomaterials, including transition metal dichalcogenides,^[2] layered double hydroxides,^[3] metal-organic frameworks,^[4] covalent-organic frameworks,^[5] black phosphorus,^[6] MXenes,^[7] and noble metals,^[8] have also been intensively explored. Impressively, these 2D nanomaterials with unique properties have shown various potential applications in electronics, optics, biomedicine, sensors, energy, *etc.*^[2e] In particular, ultrathin 2D nanostructures with relatively high surface area-to-volume ratio and high density of exposed atoms on their surface are very promising for catalysis reactions.^[9] For instance, the ultrathin Pd nanosheets showed much higher electrocatalytic activity compared to the tetrahedral and concave tetrahedral Pd nanomaterials as well as the commercial Pd catalyst in the formic acid oxidation (FAO).^[10]

As known, FAO is a key reaction in the direct formic acid fuel cell, which is a potential sustainable power source due to its clean and efficient energy supply.^[11] Previous reports have demonstrated that Pd-based electrocatalysts are good candidates for the FAO because they can provide high power density with remarkable anti-

poisoning capacity.^[11,12] However, the wide application of Pd-based electrocatalysts toward the FAO is limited by their high cost and low reserve in the Earth. To decrease the cost of Pd-based electrocatalysts and further increase their catalytic performance, alloying Pd with earth-abundant materials becomes a feasible, facile and effective strategy. Moreover, in the FAO, Cu is used to improve the catalytic performance and enhance the poisoning tolerance to intermediates, especially CO.^[13] Hence, PdCu alloy is expected to be a promising FAO catalyst with low cost and high efficiency. In this work, we develop a simple method to synthesize ultrathin PdCu alloy nanosheets with various Cu/Pd atomic ratios under mild experimental conditions. Meanwhile, the post-treatment of PdCu alloy nanosheets with ethylenediamine (EN) can dramatically enhance their electrocatalytic activity, exhibiting an excellent performance toward the FAO compared to the previously reported Pd-based catalysts measured under similar conditions.

In a typical experiment, PdCu nanosheets were synthesized by the co-reduction of Pd(acac)₂ and Cu(acac)₂ (the molar ratio of Cu to Pd=0.34, i.e. Sample 3 shown below) with Mo(CO)₆ at 60 °C for 18 h (see Supporting Information for details). Transmission electron microscopy (TEM) images confirm that nanosheets (**Figure 1a** and Figure S1, Sample 3) with thickness of 2.8±0.3 nm, measured by atomic force microscopy (AFM) (Figure 1b and S2), were obtained. The composition of the obtained nanosheets was determined by the dark-field scanning TEM-energy dispersive X-ray spectroscopy (DF-STEM-EDS), revealing homogeneous distribution of Pd and Cu in the obtained nanosheets (Figure 1c).

In the high-resolution TEM (HRTEM) image of a typical nanosheet from Sample 3 (**Figure 2a**), the measured lattice distance of 0.23 nm can be attributed to the $1/3(422)$ fringes of face-centered cubic (*fcc*) structure.^[8,14] As a comparison, pure Pd nanosheets have also been synthesized by the same procedure without adding the Cu precursor, i.e., Cu(acac)₂. The morphology of synthesized Pd nanosheets (Figure S3) is similar with that of PdCu nanosheets (Figure 1a and Figure S1). The selected area electron diffraction (SAED) patterns of both PdCu (Sample 3) and Pd nanosheets were obtained (inset in Figure 2b). As shown in Figure 2b, compared to the peaks of Pd nanosheets (blue curve), a small shift of the corresponding peaks of PdCu nanosheets (red curve) to the larger radius of diffraction ring was observed, indicating the decreased crystal lattice spacing in PdCu nanosheets compared to the pure Pd nanosheets.

X-ray photoelectron spectroscopy (XPS) taken from Sample 3 further proved the formation of PdCu alloy (Figure 2c). Compared to the pure Pd nanosheet, the Pd 3d peaks of the PdCu alloy nanosheet shifted to lower binding energy. For the pure Pd nanosheet, the Pd 3d_{5/2} and Pd 3d_{3/2} peaks were centered at 335.6 and 340.9 eV, respectively, while for the PdCu alloy nanosheet, the position of Pd 3d_{5/2} and Pd 3d_{3/2} peaks shifted to 335.2 and 340.5 eV, respectively, owing to the smaller electron negativity of Cu than that of Pd,^[15] which induced the distinct change in the electronic structure of the alloy compared to the single metal.^[16] As a result, the modified electronic structure would affect the catalytic activity.^[17] Note that the Cu precursor cannot be reduced without Pd(acac)₂ under the same reaction condition. Therefore,

the formation of PdCu alloy could be explained by the noble metal-induced reduction mechanism.^[18] Based on this mechanism, Pd(II) was first reduced by Mo(CO)₆.^[19] The resulting Pd atoms then catalyzed the reduction of Cu(II), leading to the formation of small PdCu clusters.^[18] The PdCu nanosheets finally formed via a seed growth process.^[8a,19,20] As the reaction proceeded, more Cu atoms were embedded into the nanosheets, proven by the continuous shift of peaks to higher angle side in X-ray diffraction (XRD) patterns (Figure S4).

Importantly, our method can be used to synthesize a series of PdCu nanosheets with different Cu/Pd atomic ratios by changing the molar ratios of Cu to Pd precursors at reaction time of 18 h, i.e. Samples 1-5 shown in **Table 1**. In the synthesized samples, nanosheets were obtained in Samples 1-4, when the molar ratio of Cu to Pd precursors was less than 0.45 (**Figure 3a-d**). However, many nanoparticles appeared and adsorbed on the PdCu nanosheets (Sample 5), when the molar ratio of Cu to Pd precursors increased from 0.45 (Sample 4) to 0.59 (Sample 5) (Figure 3d-f). The XRD patterns showed the peaks of PdCu nanosheets shifted to the higher angle side when the proportion of Cu precursor was increased (Figure 3g), indicating the decrease of crystal lattice spacing. The atomic ratios of Cu to Pd in Samples 1-5, determined by the inductive coupled plasma optical emission spectrometry (ICP-OES), were 0.14, 0.24, 0.37, 0.45 and 0.56 (blue histograms in **Figure 4a**), consistent with the corresponding molar ratios of Cu to Pd precursors, i.e., 0.12, 0.23, 0.34, 0.45 and 0.59, respectively (Table 1).

Considering their unique electronic structure and morphology, the ultrathin PdCu alloy nanosheets could be used as active catalysts for the electro-oxidation of small organic molecules or hydrogenation reactions.^[10,12,21] As a proof-of-concept application, the electrocatalytic FAO using PdCu alloy nanosheets was investigated. As shown in Figure S5, PdCu nanosheets (Sample 3) exhibited low electrocatalytic activity (blue curve), since the capping agent, oleic acid, blocked the catalytically active sites on their surface.^[22] Therefore, a ligand exchange experiment was designed, in which EN was used to replace the oleic acid on PdCu nanosheets, since amine was reported as a ligand to successfully replace the oleic acid on Fe₃O₄ nanoparticles.^[23] Fourier transform infrared spectroscopy (FT-IR) confirmed the oleic acid on PdCu alloy nanosheets (Sample 3) has been changed to EN, since the vibration peak of O=C-O group disappeared, while the typical peaks of -NH₂ in EN appeared after ligand exchange (Figure S6). Furthermore, TEM confirmed that the morphologies of the EN-treated PdCu alloy nanosheets were still maintained including Sample 3 (Figure S7). However, the Cu/Pd atomic ratios in the EN-treated PdCu alloy nanosheets decreased from 0.14, 0.24, 0.37, 0.45 and 0.56 (blue histograms in Figure 4a) to 0.09, 0.12, 0.15, 0.19 and 0.24, respectively (red histograms in Figure 4a, Table 1). The decrease of Cu/Pd atomic ratio might be due to the strong interaction between Cu and EN,^[24] resulting in partially etching Cu atoms in the alloy nanosheets. Since EN is an electron donor, the surface of EN-treated PdCu alloy nanosheets became electron rich,^[25] which is beneficial for the absorption of electron-deficient

reactants,^[25] such as formic acid in FAO. As a result, the catalytic performance of EN-treated PdCu alloy nanosheets could be enhanced.

In order to calculate the electrochemically active surface area (ECSA) of EN-treated PdCu alloy nanosheets, cyclic voltammogram (CV) measurements were conducted in 0.5 M H₂SO₄ aqueous solution (Figure S8a). The ECSAs can be normalized to the mass of alloy (PdCu) or the mass of Pd. As shown in Figure 4b and Table 1, the EN-treated Samples 3 and 4 have the highest ECSAs, i.e. 126.2 ± 12.5 m²/g_{PdCu} and 139.8 ± 14.9 m²/g_{Pd}, respectively. The obtained ECSAs of our EN-treated Samples 1-5 (Table 1) are much higher than those of the commercial Pd black and other Pd-based catalysts measured under the similar conditions (Table S1), but less than those of Pd nanoparticles composited with DNA-graphene or 5,10,15,20-tetrakis(4-hydroxyphenyl) porphyrins (THPP), i.e. Pd-DNA-graphene or Pd/THPP, respectively, because of the higher specific surface areas of the aforementioned Pd composites.^[26]

Mass activities in electrocatalytic FAO were recorded by CV measurements in aqueous solution containing 0.5 M H₂SO₄ and 0.25 M HCOOH. Figures 4c and 4d show the typical CV curves (EN-treated Sample 3 and commercial Pd black) and the calculated mass activities of PdCu alloy nanosheets (EN-treated Samples 1-5), respectively. The mass activities can be normalized to the mass of alloy (PdCu) or the mass of Pd. As shown in Figure 4d and Table 1, the EN-treated Samples 3 and 4 have the highest mass activities, i.e. 1493.5 ± 38.0 mA/mg_{PdCu} and 1655.7 ± 74.6 mA/mg_{Pd}, respectively. Importantly, there is only a little difference (<1.7%) between the

catalytic activities of EN-treated Samples 3 and 4 (Table 1). Impressively, the mass activities of EN-treated PdCu alloy nanosheets are higher than those of commercial Pd black and other Pd-based catalysts measured under similar conditions (Table S1, Figure S9), except for that of Pd/THPP (Table S1), because the π -conjugated THPP matrix can improve both the charge and mass transfer between the Pd/THPP and solution.^[26b]

As mentioned above, Sample 3 with Cu/Pd atomic ratio of 0.15 and Sample 4 with Cu/Pd atomic ratio of 0.19 after EN treatment showed the highest catalytic activities in FAO. These optimum ratios are similar to those of PdCu nanotripods (Cu/Pd=0.15) for FAO,^[11] or PdCu nanoparticles (Cu/Pd=0.18) for methanol oxidation.^[17] In the PdCu alloy catalyzed FAO, Pd is the active catalyst, and the presence of Cu can facilitate the adsorption and oxidation of intermediates, especially CO.^[11,16,24,27] Therefore, the improved catalytic performance in FAO was obtained.

The high catalytic activity of our EN-treated ultrathin PdCu alloy nanosheets can be attributed to the following aspects: (1) the ultrathin morphology of PdCu alloy nanosheets providing high ECSA, (2) the electronic structure of PdCu alloy nanosheets enhancing the catalytic activity compared to Pd,^[16,17] (3) the synergistic effect between Pd and Cu leading to the high catalytic activity^[11,17,27a-d] and (4) the EN-treatment on PdCu alloy nanosheets removing the inert oleic acid and simultaneously enhancing their catalytic activity.

In summary, ultrathin PdCu alloy nanosheets have been successfully synthesized via a facile wet chemical method under normal pressure, relatively low temperature

(60 °C) and without the toxic carbon monoxide (CO) gas. The obtained PdCu alloy nanosheets were characterized by XPS, XRD, SAED, EDS and ICP-OES. The excellent catalytic activity of our EN-treated PdCu nanosheets toward the FAO can be attributed to their ultrathin morphology, unique electronic structure, synergistic effect between Pd and Cu and post-treatment with EN. This work provides a new strategy to synthesize highly active alloy catalysts for various applications.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

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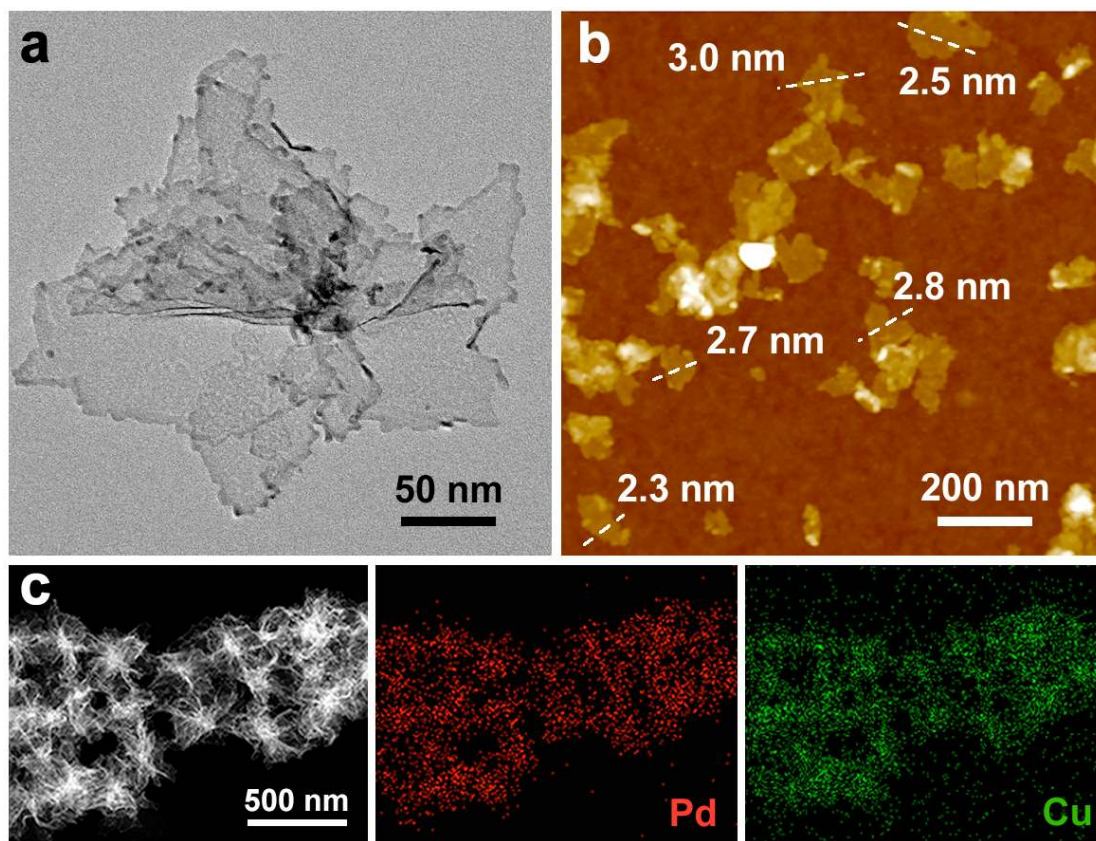


Figure 1. (a) TEM image, (b) AFM image, and (c) DF-STEM-EDS elemental mapping of the synthesized ultrathin PdCu alloy nanosheets (Sample 3).

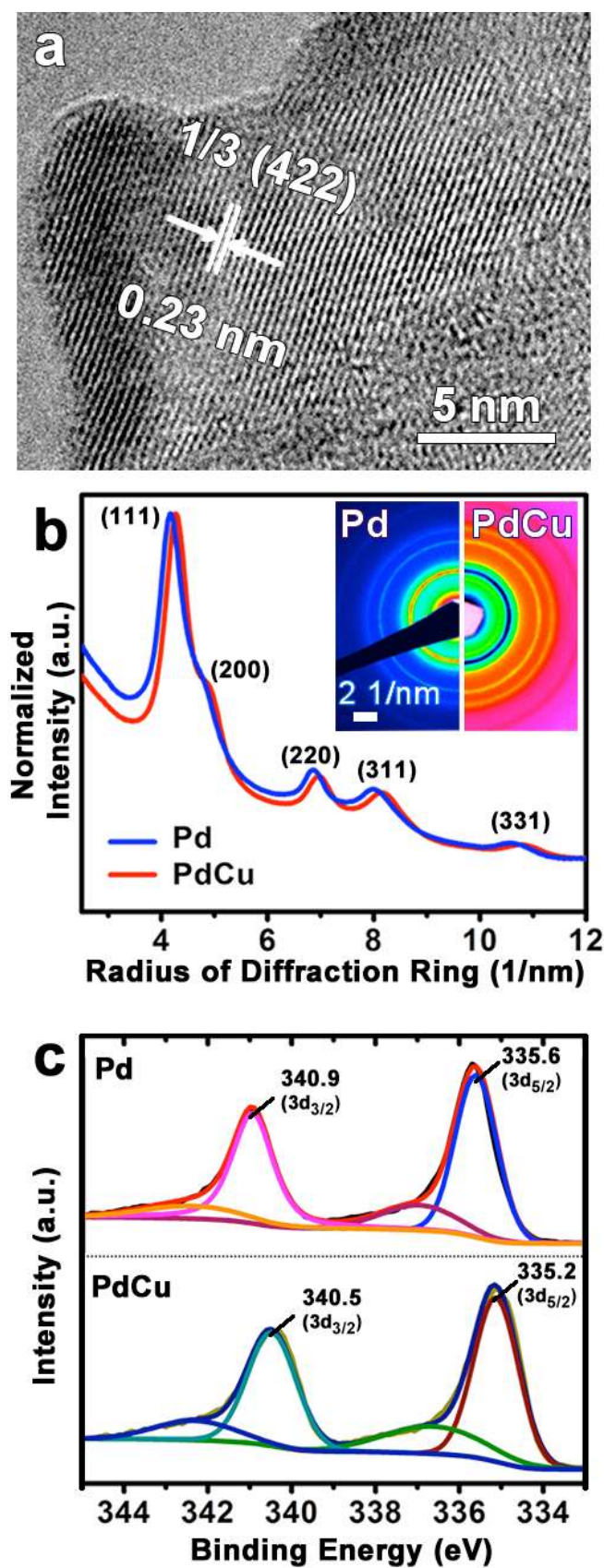


Figure 2. (a) HRTEM image of a typical PdCu nanosheet. (b) SAED patterns and 1D profile for Pd and PdCu nanosheets. (c) XPS analyses of Pd 3d in Pd and PdCu nanosheets. Here the PdCu nanosheets are from Sample 3.

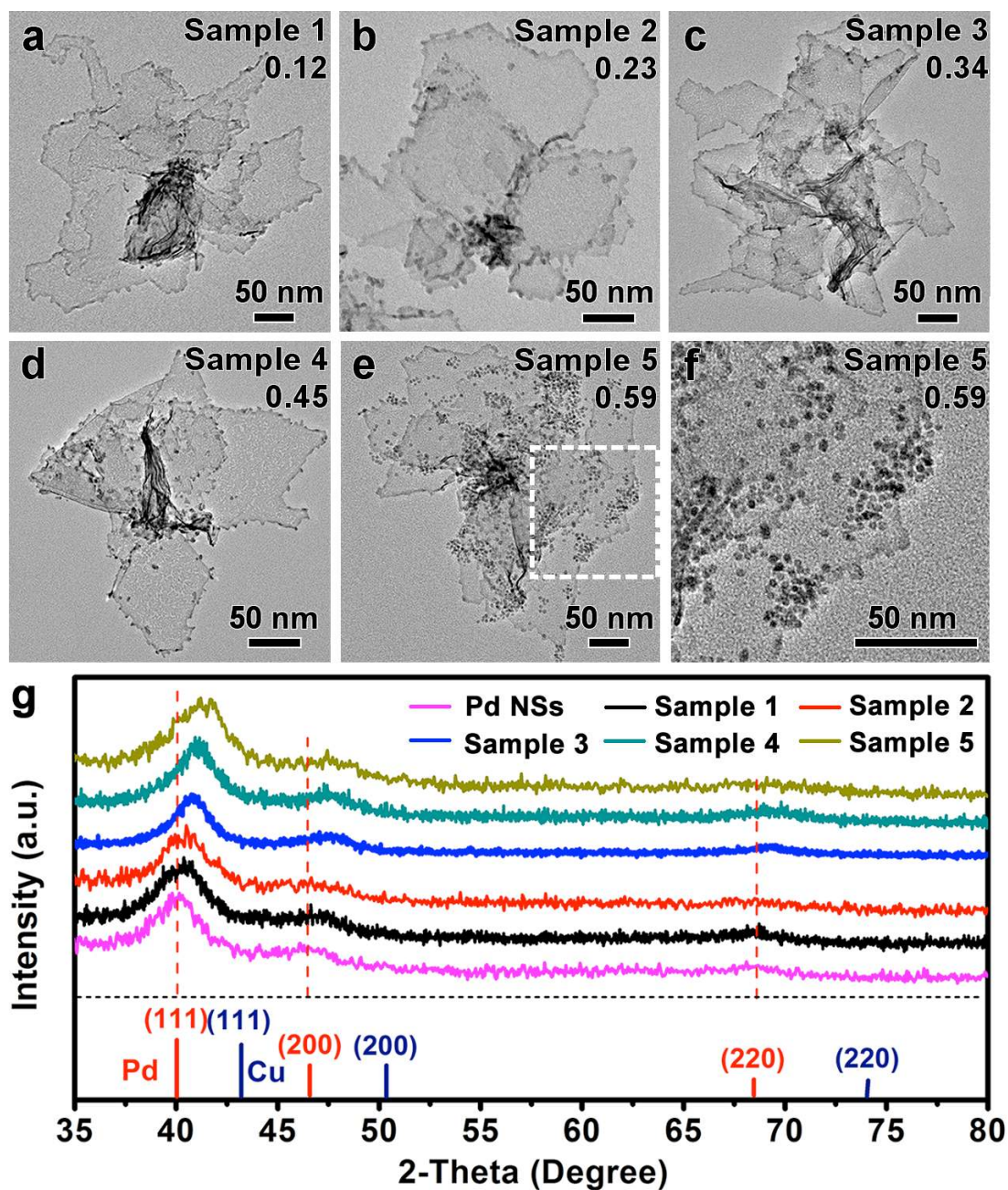


Figure 3. (a-e) TEM images of Samples 1-5 with different atomic ratios of Cu to Pd. (f) Magnified TEM image of the dashed square in (e). (g) The corresponding XRD data of Pd nanosheets (Pd NSs, Figure S3) and Samples 1-5. The molar ratios of Cu to Pd precursors are labeled in figures.

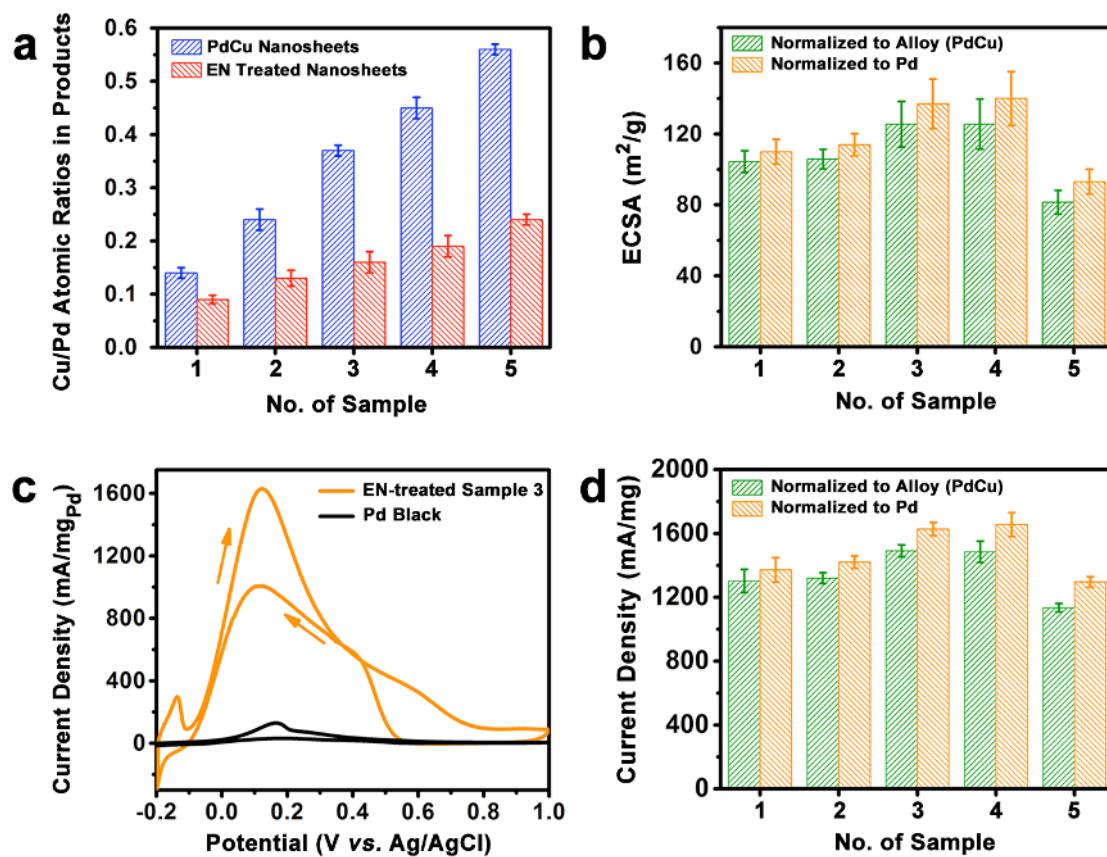


Figure 4. (a) ICP-OES results of Samples 1-5 with different atomic ratios of Cu to Pd. (b) ECSAs of Samples 1-5 recorded in 0.5 M H₂SO₄ aqueous solution at scan rate of 50 mV/s. (c) CV curves of EN-treated Sample 3 and Pd black, and (d) peak current densities of EN-treated Samples 1-5 in electrocatalytic FAO recorded in aqueous solution containing 0.5 M H₂SO₄ and 0.25 M HCOOH at scan rate of 50 mV/s.

Table 1. Summary of Cu/Pd atomic ratios in different PdCu alloy nanosheets and their electrocatalytic activities after EN treatment.

| No. of Sample | Cu/Pd atomic ratio | | ECSA (m ² /g) | | | Mass activity (mA/mg) | |
|------------------|--------------------|-------------|--------------------------|-------------------------------|---------------------|-------------------------------|---------------------|
| | Precursor | Product | After EN treatment | Normalized to alloy (PdCu) | Normalized to Pd | Normalized to alloy (PdCu) | Normalized to Pd |
| 1 | 0.12 | 0.14 ± 0.01 | 0.09 ± 0.01 | 104.5 ± 6.9 | 110.2 ± 7.3 | 1301.4 ± 72.7 | 1371.9 ± 76.6 |
| 2 | 0.23 | 0.24 ± 0.02 | 0.12 ± 0.02 | 106.6 ± 6.1 | 114.3 ± 6.5 | 1325.5 ± 36.6 | 1421.2 ± 39.2 |
| 3 | 0.34 | 0.37 ± 0.01 | 0.15 ± 0.02 | 126.2 ± 12.5 | 137.6 ± 13.6 | 1493.5 ± 38.0 | 1628.3 ± 41.4 |
| 4 | 0.45 | 0.45 ± 0.02 | 0.19 ± 0.02 | 125.5 ± 13.4 | 139.8 ± 14.9 | 1485.9 ± 66.9 | 1655.7 ± 74.6 |
| 5 | 0.59 | 0.56 ± 0.01 | 0.24 ± 0.01 | 81.7 ± 6.3 | 93.5 ± 7.2 | 1133.7 ± 28.1 | 1297.4 ± 32.1 |

ToC

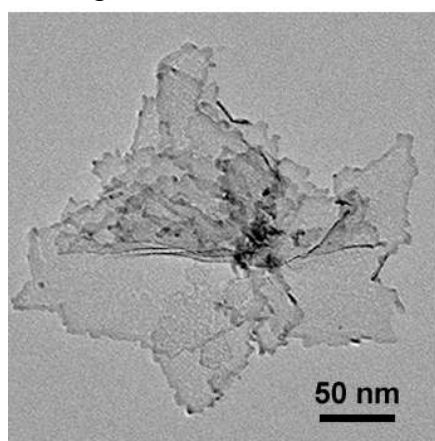
Ultrathin PdCu alloy nanosheets have been synthesized via a facile wet-chemistry method. These nanosheets after treated with ethylenediamine exhibit superior electrocatalytic activity toward the formic acid oxidation.

Keyword: Two-dimensional; Nanosheets; PdCu alloy; Electrocatalysts; Formic acid oxidation

Nailiang Yang, Zhicheng Zhang, Bo Chen, Ying Huang, Junze Chen, Zhuangchai Lai, Ye Chen, Melinda Sindoro, An-Liang Wang, Hongfei Cheng, Zhanxi Fan, Xiaozhi Liu, Bing Li, Yun Zong, Lin Gu, Hua Zhang*

Title: Synthesis of Ultrathin PdCu Alloy Nanosheets Used as Highly Efficient Electrocatalyst for Formic Acid Oxidation

ToC figure



PdCu Alloy Nanosheets

