Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information

N-doped Graphene-Supported PdCu Nanoalloy as Efficient Catalyst for Reducing Cr(VI) by Formic Acid

Shuangzhi Li,[a] Lijun Liu,[ab*] Qing Zhao,[a] Chiyang He,[a] and Weikai Liu[a]

[a] *College of Chemistry and Chemical Engineering, Wuhan Textile University, Wuhan 430200, People's Republic of China*

[b] *Hubei Key Laboratory of Biomass Fibers and Eco-dyeing & Finishing, Wuhan Textile University, Wuhan, 430073, Hubei, China.*

Corresponding author: Lijun Liu
E-mail: liulj@wtu.edu.cn, eduliu@163.com
Tel: +86-27-59367685; Fax: +86-27-59367343.
Address: 1 Yangguang Avenue, Jiangxia District, Wuhan 430200, P. R. China.

1. Synthesis of GO

Typically, graphite powder (1.5 g) was added to concentrated H_2SO_4 (35 mL) under stirring in an ice bath. Under vigorous agitation, $KMnO_4$ (4.5g) was added slowly to keep the temperature of the suspension lower than 20 °C Successively, the reaction system was transferred to a 40 °C water bath and vigorously stirred for about 0.5 h. Then, 75 mL water was added, and the solution was stirred for 15 min at 95 °C. Additional 250 mL water was added and followed by a slow addition of 7.5 mL H_2O_2 (30%), turning the color of the solution from dark brown to yellow. The mixture was centrifuged and washed with 5 wt.% HCl aqueous solution (250 mL) at 5000 rpm for 10 min to remove metal ions. The resulting solid was centrifuged and washed with deionized water at 25000 rpm for 10 min to remove acids and other impurities, and diluted to 600 mL, making a graphite oxide aqueous dispersion. Finally, it was dried in an oven at 40°C to demarcate the content of GO.

2. Calculation based on the Vegard's law

The XRD pattern of Pd_6Cu_4/NG was recorded and calibrated with standard silicon reference. As shown in Fig. 1b, the (111) reflection of Pd_6Cu_4/NG shows an obvious positive shift by ~1.08°. According to the (111) reflection of Pd_6Cu_4/NG, the lattice constant (a_{PdCu}) of Pd_6Cu_4 nanoalloy is estimated to be a_{PdCu} = 3.791 Å. Considering that Cu and Pd has the same fcc crystalline structure, we estimate the alloy composition according to the Vegard's law (eq. 1):

$$a_{PdCu} = xa_{Pd} + (1 - x)a_{Cu} \qquad \text{(eq. 1)}$$

where a_{Pd}(3.890 Å), a_{Cu}(3.615 Å) and a_{PdCu} are the lattice constants of Pd, Cu and PdCu nanoalloy with fcc crystalline structures, respectively; *x* represents the atomic ratio of Pd/Cu.

The Pd/Cu atomic ratio (*x*) is thus calculated to be 0.63/0.37, which is close to the value

measured by ICP-OES. The result further proves the formation of PdCu alloy on N-doped graphene.

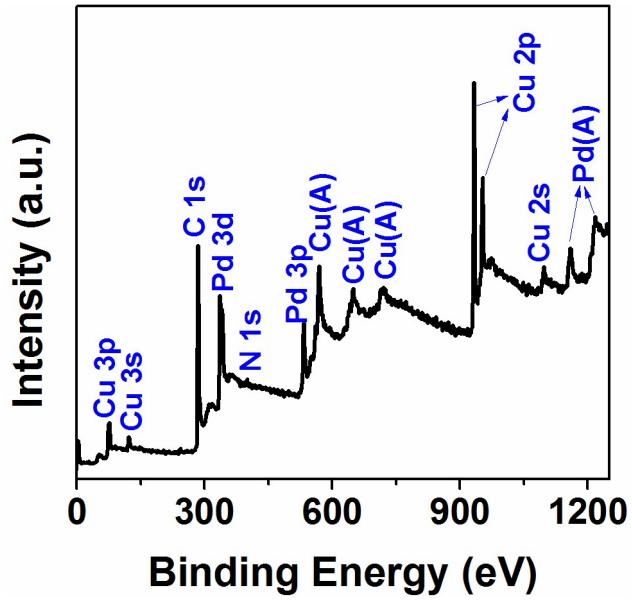

Fig. S1. The survey XPS spectrum of the resulting Pd_6Cu_4/NG, showing the presence of Cu, Pd, C and a minority of N in the catalyst.

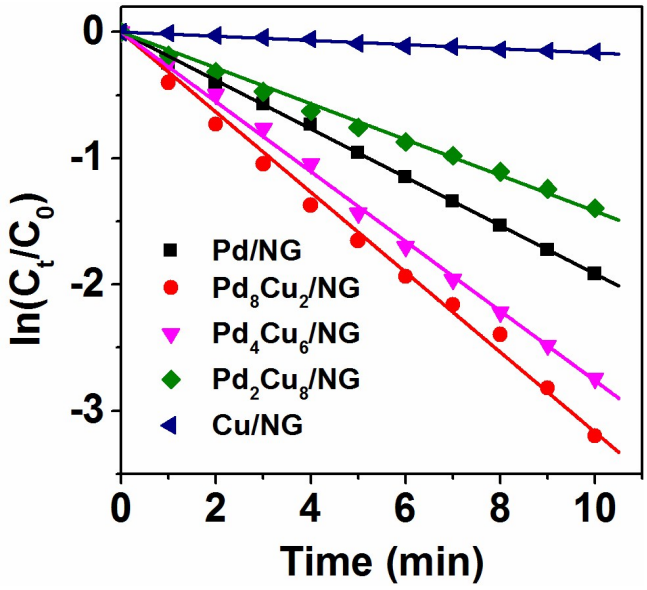

Fig. S2. Plots of ln(A_t/A_0) *versus* reaction time of the Cr(VI) reduction over PdCu/NG with various Pd/Cu atomic ratios.

Table S1 The physical properties of PdCu/NG with various Pd/Cu atomic ratios.

catalysts	metal loading[a] (wt.%)	S_{BET} ($m^2 \cdot g^{-1}$)
Pd/NG	31.3	173
Pd_8Cu_2/NG	31.2	161
Pd_6Cu_4/NG	31.4	164
Pd_4Cu_6/NG	31.0	169
Pd_2Cu_8/NG	31.8	161
Cu/NG	29.9	165

[a] The metal loading was measured by ICP-OES

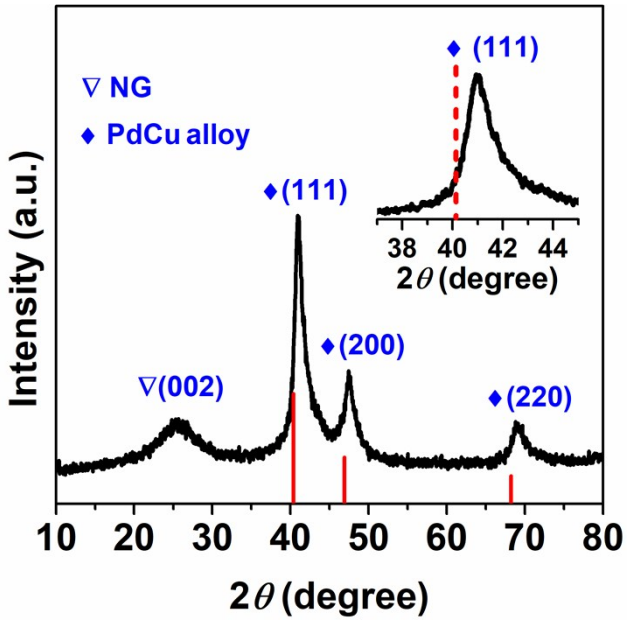

Fig. S3. XRD pattern of Pd_6Cu_4/NG after five times of cycling uses, which shows characteristic diffractions belonging to Pd_6Cu_4 nanoalloy and NG support. No phase change is observed after cycling uses.

Table S2 Comparison of the normalized rate constants ($k_n = k / m_{metal}$) of Pd_6Cu_4/NG with the prior catalysts reported for reduction of Cr(VI) by FA.

catalyst		k_n[a]	Ref.
active metals	support	(min^{-1} mg^{-1})	
Pd NWs	–	7.05	1
Pt NPs	carbon	6.68	2
PtAu/rGO	rGO	13.1	2
AuPd@Pd NPs	–	2.40	3
PdCu nanoalloy	–	11.2	4
Pd NPs	SiO_2-NH_2	1.72	5
Pd tetrapods	–	14.3	6
Pd NPs	N-doped graphene	11.0	this work
Pd_6Cu_4 nanoalloy	N-doped graphene	23.2	this work

[a] k_n is the normalized reaction rate constant, $k_n = k / m_{metal}$.

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