Electronic Supplementary Material (ESI) for Analytical Methods.

Supporting Information

Highly dispersed palladium nanoparticles generated in situ on layered double hydroxide nanowalls for ultrasensitive electrochemical detection of hydrazine

Liang Xu, Zongkai Qu, Jun Chen, Xu Chen,* Feng Li and Wensheng Yang*

State Key Laboratory of Chemical Resource Engineering, Beijing University of Chemical Technology, Beijing 100029, China

*Corresponding Author. Tel.: +86 10 64435271; fax. +86 10 64425285.

E-mail address: chenxu@mail.buct.edu.cn (X. Chen)

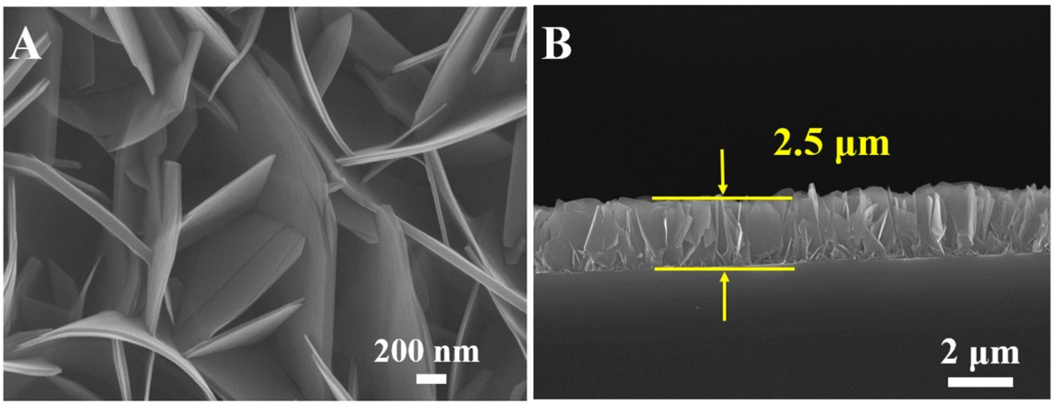
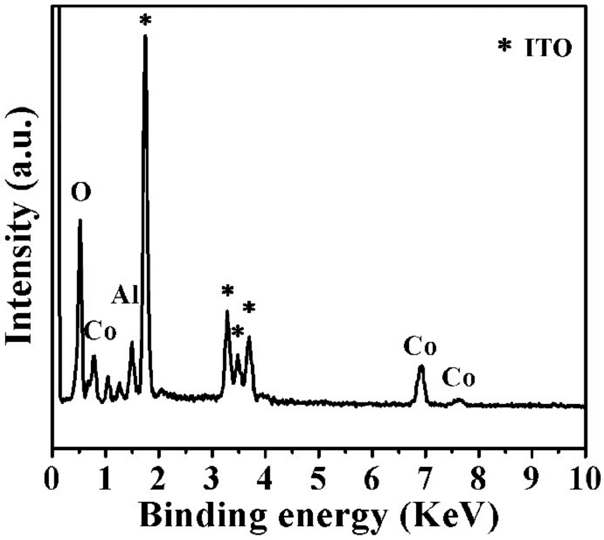


Fig. S1 (A) SEM image of the CoAl-LDHNWs at high magnification. (B) A typical cross-sectional SEM image of the CoAl-LDHNWs.



Samples	Element	Wt%	At%
CoAl-LDHNW/ITO	O K	76.89	90.97
	Al K	4.24	2.98
	Co K	18.87	6.05

Fig. S2 The EDS results of CoAl-LDHNW/ITO sample.

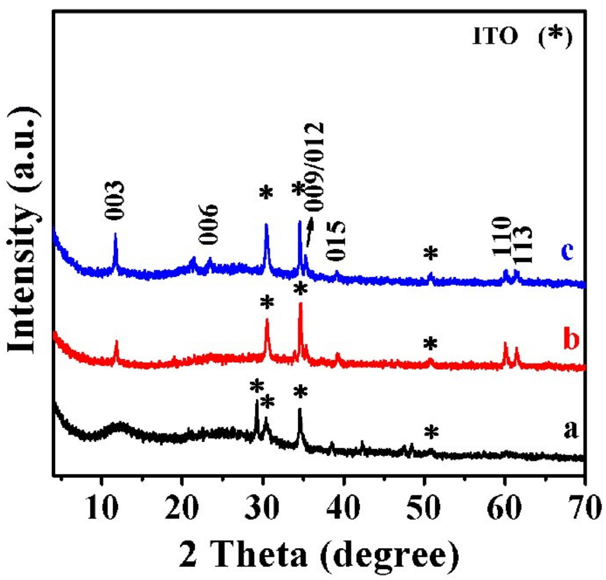


Fig. S3 The XRD patterns of the (a) bare ITO substrate, (b) CoAl-LDHNW/ITO, and (c) CoAl-LDHs powder.

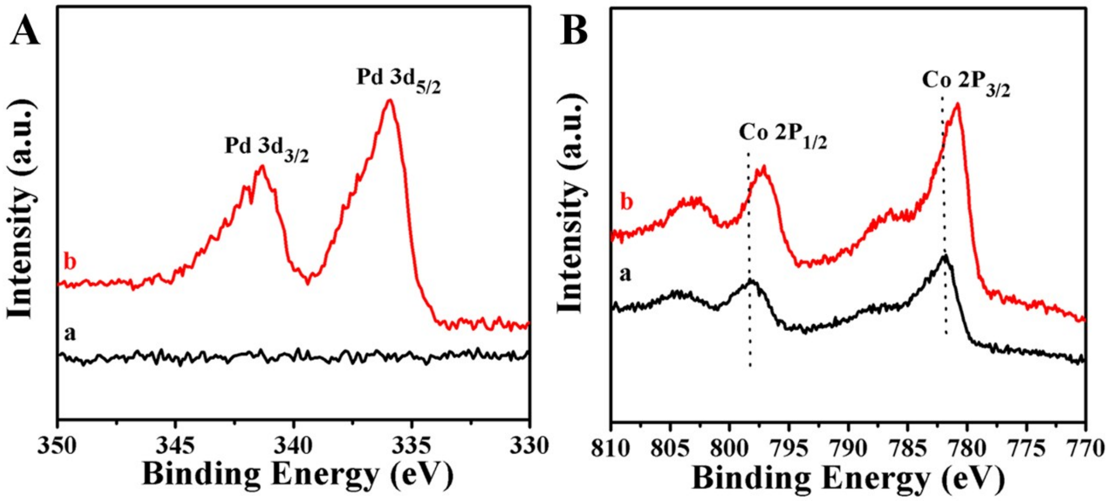


Fig. S4 The XPS spectra of (A) Pd 3d and (B) Co 2p in (a) CoAl-LDHNWs and (b) PdNP/CoAl-LDHNW composite samples.

X-ray photoelectron spectroscopy (XPS) was employed to further study the surface characterization of the PdNP/CoAl-LDHNW composite and CoAl-LDHNWs. From curve b of Fig. S4A, Pd 3d$_{5/2}$ and Pd 3d$_{3/2}$ of the metallic Pd(0) state were observed at the binding energies of 336.0 and 341.5 eV, respectively, indicating the presence of metallic Pd.[1] Fig. S4B shows the Co 2p XPS spectrum of CoAl-LDHNWs, which exhibits two typical Co 2p$_{3/2}$ and Co 2p$_{1/2}$ peaks at 782.0 eV and 797.8 eV, respectively.[2] The presence of the satellite bands originated from a high-spin Co^{2+} state in CoAl-LDHs. While the Co 2p$_{3/2}$ and Co 2p$_{1/2}$ peaks of PdNP/CoAl-LDHNW composite slightly shifted to lower energy levels (780.8 and 797.1eV, respectively), which demonstrates Co^{2+} in CoAl-LDHNWs was oxidized to Co^{3+} when mixing with PdCl$_4^{2-}$.[3] All XPS results suggested that PdCl$_4^{2-}$ could be in situ reduced by Co^{2+} in CoAl-LDHNWs and form Pd nanoparticles on the layers of CoAl-LDHNWs.

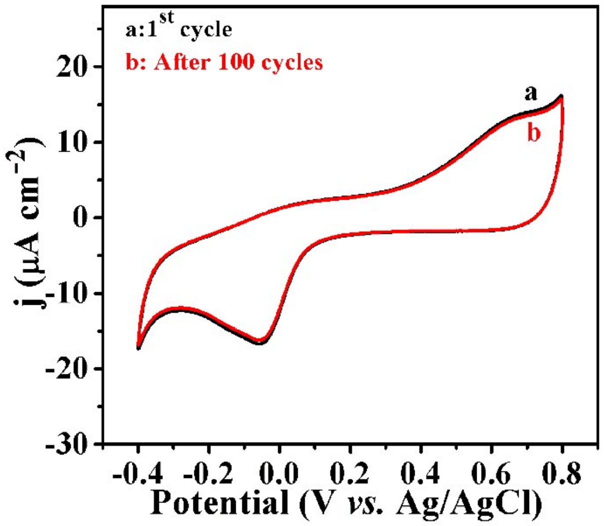


Fig. S5 CVs of the PdNP/CoAL-LDHNW/ITO electrode in 0.1 M phosphate buffer solution (pH 7.0) at 100 mV s^{-1} before and after continuous 100 cycles.

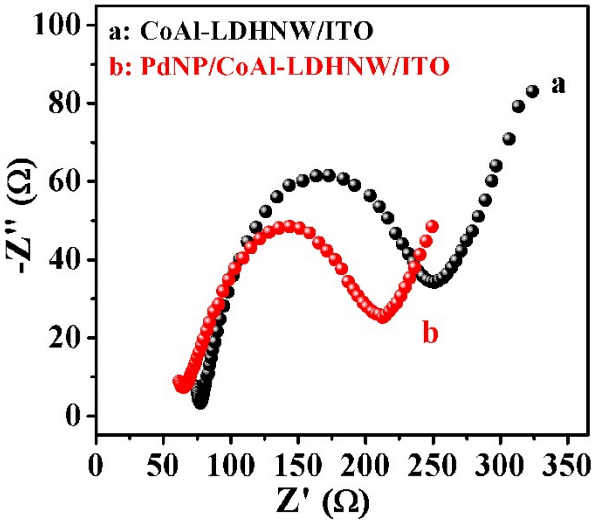


Fig. S6 Nyquist plots of the CoAl-LDHNW/ITO (a) and PdNP/CoAl-LDHNW/ITO electrodes (b) in 5.0 mM $[Fe(CN)_6]^{3-/4-}$ containing 0.1 M KCl in the frequency range of 0.1−10 kHz with an AC voltage of 5 mV.

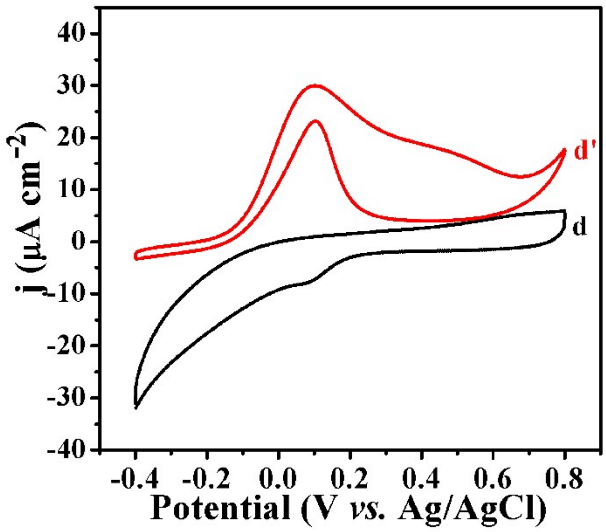


Fig. S7 CVs of PdNP/CoAl-LDH power-modified ITO electrode in 0.1 M phosphate buffer solution (pH 7.0) in the absence (d) and presence (d') of 0.5 mM hydrazine at 100 mV s^{-1}.

The PdNP/CoAl-LDHs power were obtained by scraping from the PdNP/CoAl-LDHNW/ITO substrate (1 cm×1 cm). Then the power was dispersed in 150 μL of deionized water and sonicated for ~20 min to form a homogeneous suspension. The PdNP/CoAl-LDH power-modified ITO electrode was prepared by casting all the 150 μL of the LDH suspension on the surface of clean ITO electrode, and dried at room temperature.

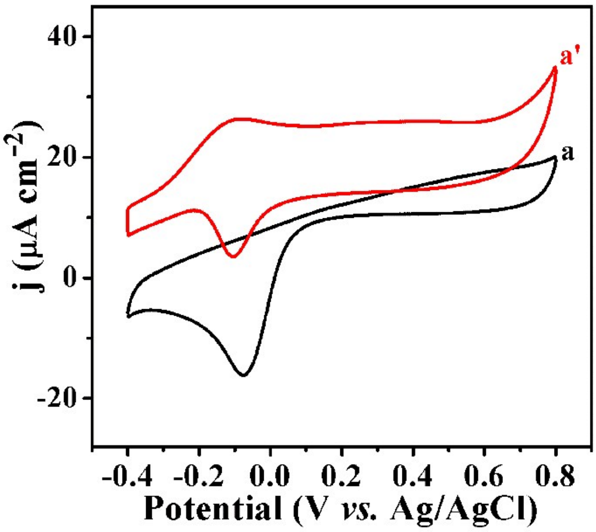


Fig. S8 CVs of the PdNP/ITO electrode in 0.1 M phosphate buffer solution (pH 7.0) in the absence (a) and presence (a') of 0.5 mM hydrazine at 100 mV s^{-1}.

The sample of pristine PdNPs was prepared by dissolving the PdNP/CoAl-LDHNW in 10 wt% hydrochloric acid (HCl) solution to remove the LDH support. Then, the PdNPs (washed 3 times with water) was dropped on the ITO electrode again and dried at room temperature, denoted as the PdNP/ITO. The electrocatalytic oxidation performance of the PdNP/ITO electrode toward hydrazine was studied. As shown in Fig. S8, the oxidation peak current intensity of the PdNP/ITO electrode was about 20 μA cm^{-2} for 0.5 mM hydrazine, which was much lower than 85 μA cm^{-2} obtained from the PdNP/CoAl-LDHNW/ITO electrode. This result indicates that the presence of LDHNW as support is important for the improved hydrazine sensing performance.

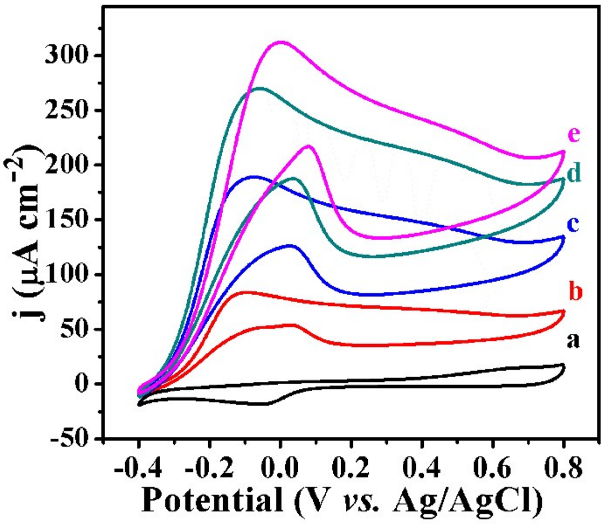


Fig. S9 CVs of PdNP/CoAl-LDHNW/ITO electrode in 0.1 M phosphate buffer solution (pH 7.0) with various hydrazine concentrations (a, 0 mM; b, 0.5 mM; c, 1.0 mM; d, 1.5 mM and e, 2.0 mM) at 100 mV s^{-1}.

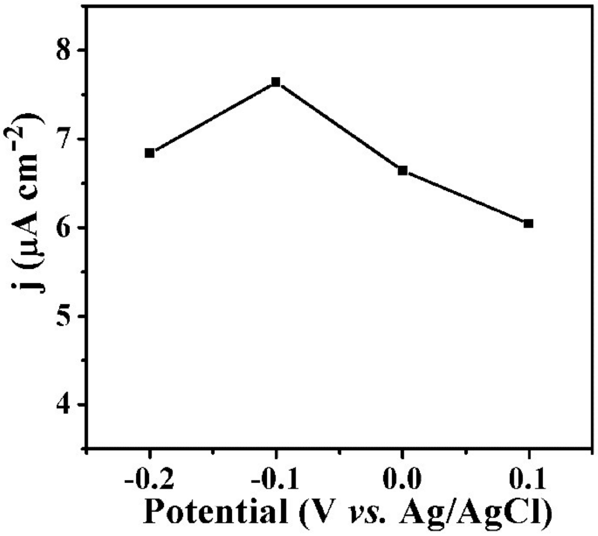


Fig. S10 Effect of applied potential for PdNP/CoAl-LDHNW/ITO electrode with the response of 50 μM hydrazine in 0.1 M phosphate buffer solution (pH 7.0).

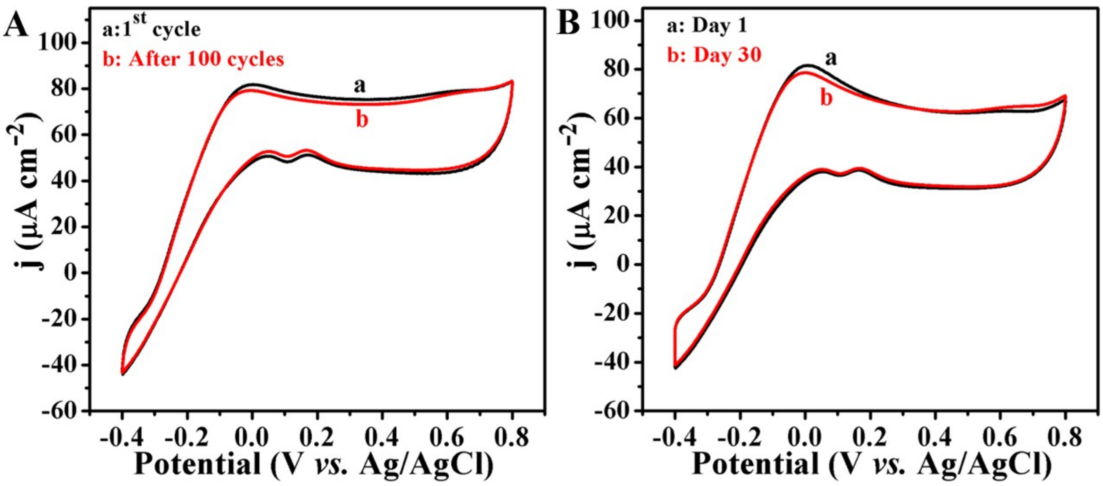


Fig. S11 CVs of the PdNP/CoAL-LDHNW/ITO electrode in the presence of 0.5 mM hydrazine in 0.1 M phosphate buffer solution (pH 7.0) at 100 mV s^{-1}. (A) Before and after continuous 100 cycles; (B) Before and after 30 days storage at room temperature.

References:

1 H. Meng, C. Wang, P. K. Shen and G. Wu, *Energy Environ. Sci.*, 2011, **4**, 1522−1526.

2 Q. Tang, Q. Zhang, P. Wang, Y. Wang and H. Wan, *Chem. Mater.*, 2004, **16**, 1967−1976.

3 R. Ma, J. Liang, K. Takada and T. Sasaki, *J. Am. Chem. Soc.*, 2011, **133**, 613−620.