Supporting Information

Directed Self-assembly of Dual Metal Ions with Ligands: towards the Synthesis

of Noble Metal/Metal Oxide Composites with Controlled Facet

Fang Cui, Jiajia Zhang, Qing Shao, Linxu Xu, Xinzi Pan, Xiaoqiang Wang, Xiao Zhang and Tieyu Cui*

School of Chemistry and Chemical Engineering, Harbin Institute of Technology, Harbin 150001, P. R. China.

E-mail: cuit@hit.edu.cn; Fax: (+86) 451-86403646; Tel: (+86) 451-86403646;

Experimental Section

Chemicals. Palladium chloride (PdCl₂, 60% Pd basis) was purchased from Aldrich Chemistry Co. Ltd.. Zinc Oxide (ZnO, 99%), methacrylic acid (HMA), absolute ethanol, and isopropanol were all commercially available products. HMA was distilled and stored at 4 °C before use. Other chemicals were used as received without further purification. The water used in the experiments was deionized with a resistivity of 18.2 M Ω cm⁻¹.

Preparation of aqueous solution containing Zn^{2+} and MA⁻. At room temperature, ZnO powder (8.1 g, 0.1 mol) was added to a mixture of deionized water (200 mL) and HMA (17 mL, 0.2 mol) under magnetic stirring. After stirring for at least 2h, the ZnO solid was dissolved completely and the mixture became turbid white to colorless and transparent. The mixture was then filtrated to remove the trace insoluble substance. The obtained aqueous containing Zn^{2+} and MA⁻ ions with a molar ration of about 1:2 was used as the precursor solution for preparing Zn(MA)₂ assemblies.

Preparation of Zn(MA)_2 FHS. For a typical preparation, 25 mL absolute ethanol was added into 4 mL the aforementioned aqueous solution containing Zn^{2+} and MA⁻ ions with a molar ration of 1:2. The mixture was stored at room temperature to maintain the growth of self-assemblies. After 18 h storage, the $Zn(MA)_2$ FHS were prepared. The precipitates of $Zn(MA)_2$ FHS could be collected by centrifugation and washed extensively with absolute ethanol. Finally, the products were dried in a vacuum oven at room temperature overnight.

Preparation of Zn(MA)₂/**Pd(II) FHS and Pd/ZnO(001) FHS.** Typically, 50 mL of ethanol solution of PdCl₂ (10 mmol L⁻¹) was placed in a flask first, and then 30 mg Zn(MA)₂ FHS was added under stirring at room temperature. The mixture was stored at room temperature to maintain the coordination of Pd²⁺ with the chemically soft alkene units. After 24 h storage, dual metal coordination polymers Zn(MA)₂/Pd(II) were prepared. The resulted grey black

precipitate was collected by centrifugation and washed with absolute ethanol. Finally, the products were dried in a vacuum oven at room temperature to give the final products. This solid product was then examined by Raman spectra to reveal the successful coordination of soft Pd(II) ions and soft alkene units. Part of this solid product was also dissolved in nitrohydrochloric acid for ICP elemental analysis, which indicated a Zn: Pd molar ratio of 11: 1. The asprepared Zn(MA)₂/Pd(II) FHS were transferred to a furnace and were heated-treated at target temperature (400 °C) under air (heating rate: 1 °C min⁻¹ below 200 °C, and 10 °C min⁻¹ in the temperature range of 200-400 °C). After keeping at the target temperature for 10 min, the materials were immediately cooled to room temperature.

Catalytic activity tests for 4-nitrophenol reduction. Typically, 30 μ L of 4nitrophenol (10.0mM) and 30 μ L of NaBH₄ (1.0 M) were added into a quartz cuvette containing 2 mL water. Then 10 μ L of an aqueous solution of catalytic sample (1.0 mg mL⁻¹) was injected into the cuvette to start the reaction. The intensity of the absorption peak at 400 nm in UV-vis spectroscopy was used to monitor the process of the conversion of 4-nitrophenol to 4-aminophenol.

Characterization. Transmission electron microscopy (TEM) was conducted by a FEI Tecnai G2 F30 electron microscope at an acceleration voltage of 300 kV with a CCD camera. An energy-dispersive X-ray spectroscopy (EDS) detector coupled with high magnification TEM was applied for elemental analysis. Scanning electron microscope (SEM) images were taken by a JEOL JSM-6700F electron microscope using primary electron energy of 3 kV. Fourier-transform infrared (FTIR) spectra were recorded with KBr disks containing the powder sample with a Nicolet AVATAR 360 FT-IR spectrometer. ¹H NMR spectra were recorded on a Bruker AVANCE500 500 MHz NMR spectrometer. X-ray powder diffraction (XRD) investigation was carried out on a Rigaku D/Max-2500 X-ray diffractometer using Cu K radiation (λ = 1.5418 Å). X-ray photoelectron spectroscopy (XPS) was investigated with a VG ESCALABMKII spectrometer. Inductively coupled plasma atomic emission spectroscopy (ICP)

measurements were performed on an Optima 7000 DV. UV-visible adsorption spectra were acquired using a SHIMADZU 3100 UV-vis-near-IR spectrophotometer.



Fig. S1 Molecular structure of the methacrylate anion (MA⁻).

The six atoms (non-hydrogen) in MA⁻ tend to form a coplanar conjugated structure to achieve the lowest energy state, thus MA⁻ can be a semi-rigid and structurallyconstrained ligand available to achieve the ordered assemblies. Moreover, each MA⁻ ligand combines two end groups with distinct hard and soft characters. The ionic, chemically hard carboxylate groups are predisposed, as the primary groups, to interact with Zn²⁺ ions for framework formation, while leaving chemically soft alkene units as freestanding, secondary donors, for selective anchoring Pd²⁺. In addition, the "Janusfaced" characters of MA⁻ not only embody in hard-soft combination, but also in hydrophilic-hydrophobic, as well as hydrogen bond (H-bond) receptor–donor combinations. Consequently, the assembly manipulation of MA⁻ with Zn²⁺ ions is expected by rationally adjusting the compositions and properties of the solvents.



Fig. S2 (a) ¹H NMR spectrum of the aqueous solution of Zn^{2+} and MA⁻, which is prepared by using D₂O as solvent instead of H₂O. (b) FTIR spectrum of Zn(MA)₂ powder obtained by rotary evaporation of the aqueous solution of Zn²⁺ and MA⁻ at 45 °C. The peaks at 1569 and 1413 cm⁻¹ belong to the asymmetrical and symmetrical stretching vibrations of carboxylate groups. The peak at 1643 cm⁻¹ is the symmetrical stretching vibration of C=C double bonds.



Fig. S3 SEM image (a) and XRD pattern (b) of $Zn(MA)_2$ FHS. Inset of (b): schematic diagram of the layered structure in $Zn(MA)_2$ flake.



Fig. S4 ¹³C solid-state NMR spectrum of Zn(MA)₂ FHS.



Fig. S5 FTIR (a) and ¹H NMR spectra (b) of the $Zn (MA)_2$ FHS.

In the FTIR spectrum the peaks at around 1555 and 1409 cm⁻¹ attributed to the characteristic bands of the asymmetric and symmetric stretching vibrations of carboxylate groups are clearly presented, confirming the successful coordination of – COO⁻ with Zn²⁺ ions. The $\Delta_{asym-sym}$ is 145 cm⁻¹, which confirms the MA⁻ ligands adopt a bridging coordination mode in Zn(MA)₂ flakes. In the ¹H NMR spectrum, the signals appearing at 1.795, 5.583 and 5.976 ppm, with an integral ratio close to 3:1:1, are assigned to the methyl protons H^a and methylene protons H^b, H^c of the MA⁻ ions respectively.

Table S1. Element analysis of the Zn (MA)₂ FHS.

Element	Zn	С	Н
Calculated (%)	27.77	40.79	4.28
Found (%)	27.76	41.15	4.11



Fig. S6 The XRD pattern and X-ray crystal structure of the layered assemblies of MA⁻ ligands with Pb^{2+} ions.



Fig. S7 SEM images of the $Zn(MA)_2$ FHS prepared by using isopropanol (a) and DMF (b) as the initiation solvents.



Fig. S8 FTIR spectra of $Zn(MA)_2$ FHS (a) and $Pd(II)/Zn(MA)_2$ FHS (b). After Pd (II) uptake, two new peaks appear at 1386 and 1373 cm⁻¹ respectively, which belong to the vibrations of PdCl₂.



Fig. S9 XPS spectra of $Zn(MA)_2$ FHS (a) and $Pd(II)/Zn(MA)_2$ FHS (b).



Fig. S10 Raman spectra of $Zn(MA)_2$ FHS (a) and $Pd(II)/Zn(MA)_2$ FHS (b). The peak around 380 cm⁻¹ corresponds to the Pd(II)-alkene stretching frequency, and is highlighted by the dotted line.



Fig. S11 (a) Proposed formation mechanism of Pd/ZnO (001) flakes from $Pd(II)/Zn(MA)_2$ flakes, SEM images of $Pd(II)/Zn(MA)_2$ FHS before (b) and after (c) thermal treatment.



Fig. S12 SEM image of $Pd(II)/Zn(MA)_2$ FHS (a) and the corresponding size distribution (b). SEM image of Pd/ZnO (001) FHS (c) and the corresponding size distribution (d).



Fig. S13 XRD patterns of pure ZnO (001) FHS powder (a) and Pd/ZnO (001) FHS powder (b). The high intensity of the (001) peak, indicating the predominantly polar (001) facet covers the flake structures.



Fig. S14 (a) Time-dependent UV-vis absorption spectra of the reaction solution in the presence of Pd/Zn (001) FHS composite catalysts. (inset: plot of $\ln(C_t/C_0)$ against the reaction time). (b) The proposed mechanism of the reduction of the 4-NP by NaBH₄ using Pd/ZnO (001) FHS catalyst.



Fig. S15 FTIR spectrum of ZnO (001) plates after reacting with 4-nitrophenol. The sample was washed centrifugally washed with ethanol for several times before FTIR measurement. The characteristic vibrations of 4-NP are clearly observed, indicating the existence of strong interactions between 4-NP and ZnO (001) plates. The antisymmetric stretching and symmetric stretching vibration of -NO₂ are observed at 1552 and 1364 cm⁻¹. The C=C stretching vibration presents at 1622 cm⁻¹. The C-H deformation vibration is observed at 1410 cm⁻¹. The C-H out-of-plane bending vibrations are observed at 860 and 735 cm⁻¹. The C-O stretching vibration is observed at 1263 cm⁻¹. The Zn-O stretching vibrations are observed at 1455 and 478 cm⁻¹.

Entry	Catalyst	k ^a (s ⁻¹)	<i>k</i> ' ^b (s ⁻¹ g ⁻¹)	Ref.
1	Pd/ZnO@Zn	4.63×10 ⁻³	76.6	S 1
2	Pd/carbon nanotube	10.5×10 ⁻³	124.65	S2
3	PdAu/graphene	6.5×10 ⁻³	130	S 3
4	Pd/mesoporous silica SBA-15	1.2×10^{-2}	750	S4
5	Pd/fibrous nano-silica	8.0×10 ⁻³	1026	S 5
6	Pd/Fe ₃ O ₄ -Ag	3.3×10 ⁻²	1736	S 6
7	tube/flower/star-like Pd/ZnO	4.3×10 ⁻³ ~7.8×10 ⁻³	1610-2328	S 7
8	Pd/ZnO (001)	3.2×10 ⁻³	2817	This work

Table S2. Comparison of catalytic performances of different Pd-based catalysts from the literature in the reduction reaction of 4-NP.

 k^a , the kinetic rate constant was calculated from the ralationships between $\ln C_{(t)}/C_{(0)}$ and reaction time in the reduction reaction of 4-NP.

 $k^{b'}$, the catalytic activity factor was calculated by using eqn $k' = k/m_{pd}$.

References:

[S1] Q. Y. Hu, X. W. Liu, L. Tang, D. W. Min, T. C. Shi and W. Zhang, Pd-ZnO

Nanowire Arrays as Recyclable Catalysts for 4-Nitrophenol Reduction and Suzuki Coupling Reactions. *RSC Adv.*, 2017, **7**, 7964–7972.

[S2] X. M. Gu, W. Qi, X. Z. Xu, Z. H. Sun, L. Y. Zhang, W. Liu, X. L. Pan, and D. S. Su, Covalently Functionalized Carbon Nanotube Supported Pd Nanoparticles for Catalytic Reduction of 4-nitrophenol, *Nanoscale*, 2014, **6**, 6609 – 6616.

[S3] C. Liu, R. Liu, Q. Sun, J. Chang, X. Gao, Y. Liu, S. Lee, Z. Kang and S. Wang, Controlled Synthesis and Synergistic Effects of Graphene-supported PdAu Bimetallic Nanoparticles with Tunable CatalyticProperties. *Nanoscale*, 2015, **7**, 6356–6362.

[S4] J. Morère, M. J. Temorio, M. J. Torralvo, C. Pando, J. A. R. Renuncio and A. Cabaňas, Deposition of Pd into Mesoporous Silica SBA-15 using Supercritical Carbon Dioxide. *J. Supercrit. Fluids*, 2011, 56, 213–222.

[S5] X. D. Le, Z. P. Dong, X. L. Li, W. Zhang, M. D. Le and J. T. Ma, Fibrous Nano-silica Supported Palladium Nanoparticles: An Efficient Catalyst for the Reduction of 4-Nitrophenol and Hydrodechlorination of 4-Chlorophenol under Mild Conditions. *Catal. Commun.*, 2015, 59, 21–25.
[S6] K. Jiang, H. Zhang, Y. Yang, R. Mothes, H. Lang and W. Cai, Facile Synthesis of Ag@Pd Satellites–Fe3O4 Core Nanocomposites as Efficient and Reusable Hydrogenation Catalysts. *Chem. Commun.*, 2011, 47, 11924 – 11926.

[S7] Z. Bao, Y. Yuan, C. Leng, L. Li, K. Zhao and Z. Sun, One-Pot Synthesis of Noble Metal/Zinc Oxide Composites with Controllable Morphology and High Catalytic Performance, *ACS Appl. Mater. Interfaces*, 2017, **9**, 16417-16425.