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Supporting Information

Concave Nano-octahedral Alloys: Wet Chemical Synthesis of Bimetallic Pt-Pd Nanocrystals with High-index *{hhl}* Facets

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Experimental

1 Materials and Instrumentation

K_2PtCl_6, polyvinylpyrrolidone (K-30, PVP), glycine and polyoxyethylene lauryl ether (Brij) were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Polyvinyl alcohol (PVA) was obtained from Shantou Dahao Fine Chemical Co., Ltd. (Guangdong, China). Na_2PdCl_4 (>99.0%) was purchased from Kunming Institute of Precious Metals. All chemical reagents were obtained commercially and used without further purification. The water used in all experiments was ultrapure (>18.0 MΩ·cm).

The morphology, structure, and element distribution of the products were determined by scanning electron microscope (SEM, Hitachi S-4800) with an acceleration voltage of 15 kV, transmission electron microscope (TEM, JEOL-2100) with an acceleration voltage of 200 kV, and X-ray energy spectrometry (EDS, equipped in TECNAIF 30) with an accelerating voltage of 300 kV, respectively. The phases of products were determined by powder X-ray diffraction (XRD) using a Rigaku Ultima IV X-ray diffractometer with Cu K_α radiation (λ= 0.154178 nm). The coordination with ions in solution was measured by Fourier Transform Infrared Spectrometer (FT-IR) with a Nexus-870 from Thermo Nicolet. The Detection of surface substances on

nanocrystals was obtained by Fourier Transform Infrared Spectrometer (FT-IR) with a IS50 from Thermo Nicolet. The composition of products was analyzed by Inductively Coupled Plasma Mass Spectrometer (ICP-MS) with Agilent 7800. The X-Ray photoelectron spectroscopy (XPS) were operated by a Thermo Scientific K-Alpha+ equipped with a monochromatic aluminum anode X-ray source of K_α radiation (1486.6 eV). The electrochemical experiments were conducted with a potentiostat CHI 1030b (Shanghai ChenHua Instruments, Inc., China).

2 Synthesis of concave octahedral Pt-Pd alloys

200 mg of glycine and 50 mg of PVP were dissolved in 4 mL of water, together with preparing 2 mL of K_2PtCl_6 (5 mmol/L) and 2 mL of Na_2PdCl_4 solution (5 mmol/L). The above solution were mixed and was transferred into a 20 mL Teflon reactor, then heated to 180 °C within 45 min and kept for 20 h. The product was collected by centrifugation at 11,000 rpm for 10 min. After washing with deionized water five times, the final products were dispersed in ethanol.

3 Electrochemical measurement

Electrochemical experiments were performed in a three-electrode system, consisting of a glassy carbon working electrode (5 mm diameter), a platinum slice counter electrode, and a standard calomel electrode (SCE) serving as a reference electrode. To begin with, the glassy carbon electrode was carefully polished with 0.3 μm Al_2O_3 powder, followed by ultrasonic washing with ethanol and deionized water for one minute three times, respectively. Then the similar procedure was repeated for 50 nm Al_2O_3 powder. In the meanwhile, the catalysts were irradiated with a UV-ozone for 20 min to remove the surfactants that adsorbed on the surface. After that, the catalysts with a concentration of 2 mg mL^{-1} containing 99.5% water and 5% Nafion were prepared. Then 8 μL of the suspensions was transferred to the polished glassy carbon electrode, and dried at room temperature.

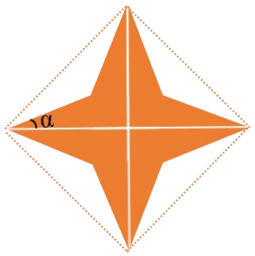
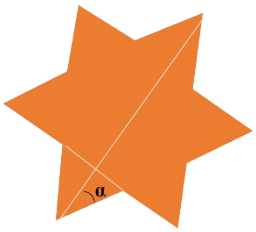
Electrochemical cleaning was carried out by running cyclic voltammetry scans from -0.25 V to 0.8 V (vs. SCE) at a scan rate of 50 mV s^{-1} in 0.5 M H_2SO_4 solution at 30 °C until a constant curve was obtained. The electrochemical active surface area (ECSA) is determined from the equation $ECSA=Q/q_0$, where Q is the electric charge

integrating from hydrogen desorption area and q_0 is defined as 210 μC cm^{-2}. After that, the performance of catalysts in formic acid oxidation was measured in a solution containing 0.5 M H_2SO_4 and 0.5 M HCOOH at 30 °C with a scan rate of 50 mV s^{-1}.

Table S1. Atomic ratio of concave octahedral Pt-Pd alloys based on the EDS anlysis and ICP-MS analysis.

Catalysts	EDS	ICP-MS
Pt-Pd concave octahedron	64.71%Pd:35.29%Pt	61.31%Pd:38.69%Pt

Table S2. Projection angles and geometrical parameters of concave octahedral NCs bounded by different *{hhl}* facets.

<table>
<tr><th>Polyhedral Projection direction</th><th>Geometrical model of polyhedron</th><th>Equations for the projection angles</th><th colspan="2">Calculated projection angle</th></tr>
<tr><td rowspan="5"><100></td><td rowspan="5">  </td><td rowspan="5">α = arctan(l/h)</td><td>(hhl)</td><td>α</td></tr>
<tr><td>(221)</td><td>26.5°</td></tr>
<tr><td>（332）</td><td>33.8 °</td></tr>
<tr><td>(775)</td><td>35.4°</td></tr>
<tr><td>(331)</td><td>18.4°</td></tr>
<tr><td rowspan="5"><111></td><td rowspan="5">  </td><td rowspan="5">α = arctan(l/h)</td><td>(hhl)</td><td>α</td></tr>
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<tr><td>(331)</td><td>18.4°</td></tr>
</table>

Table S3. Specific surface area activity of catalysts reported previously toward the electro-oxidation of formic acid.

Number	Catalysts	Specific surface area activity (mA/cm^2)	Reference
1	Octapod Pt nanocrystals with {411} facets	3.9	1
2	Pt concave nanocubes with {hk0} facets	0.57	2
3	Ultrafine decahedral Pt crystal decorated graphite nanosheets	0.72	3
4	Pt tetrapods	1.00	4
5	Pt hexapods	2.07	4
6	Pt octapods	2.81	4
7	Cubic PtPd alloy nanoparticles	1.09	5
8	Pt-Pd alloy flowers	5.42	6
9	Pt-Pd alloy dendrites	0.87	6
10	Pt-Pd alloy concave cubes	1.36	6
11	Pt-Pd alloy cubes	1.61	6
12	Pt-Pd alloy nanobars	3.92	6
13	Bimetallic 3D nano/micro-porous PtPd films	0.61	7
14	Concave octahedral Pt-Pd alloy nanocrystals with {hll} facets	2.73	this work

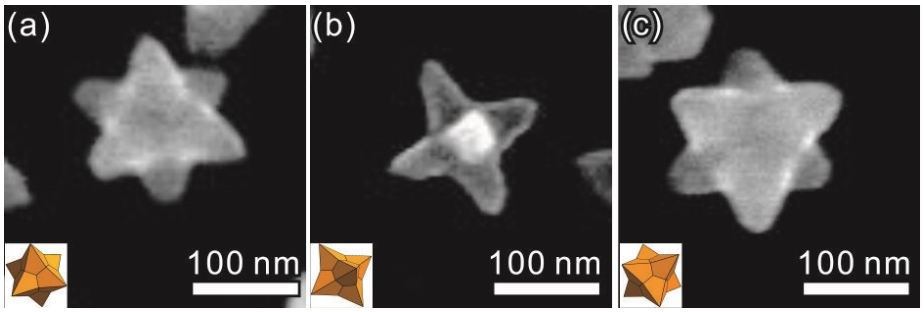

Fig. S1 SEM image of the as-prepared concave octahedral Pt-Pd alloys from different directions

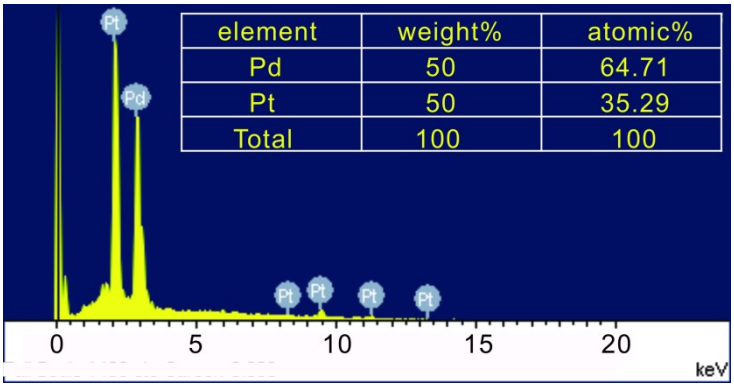

Fig .S2 EDS of the as-synthesized concave octahedral Pt-Pd alloys.

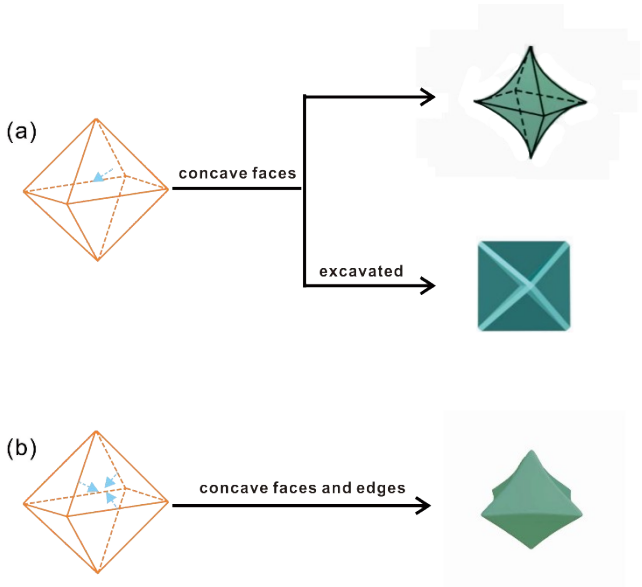

Fig. S3 Schematic diagram describing the evolution of octahedron to concave octahedron.

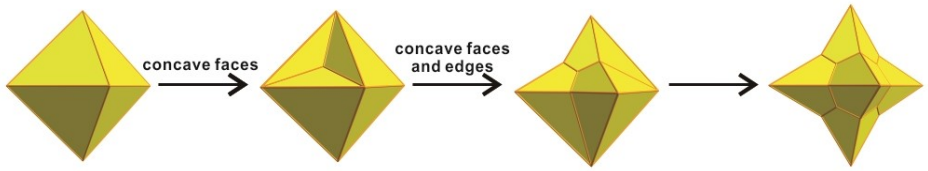

Fig. S4 The morphology evolution from octahedron to concave octahedron.

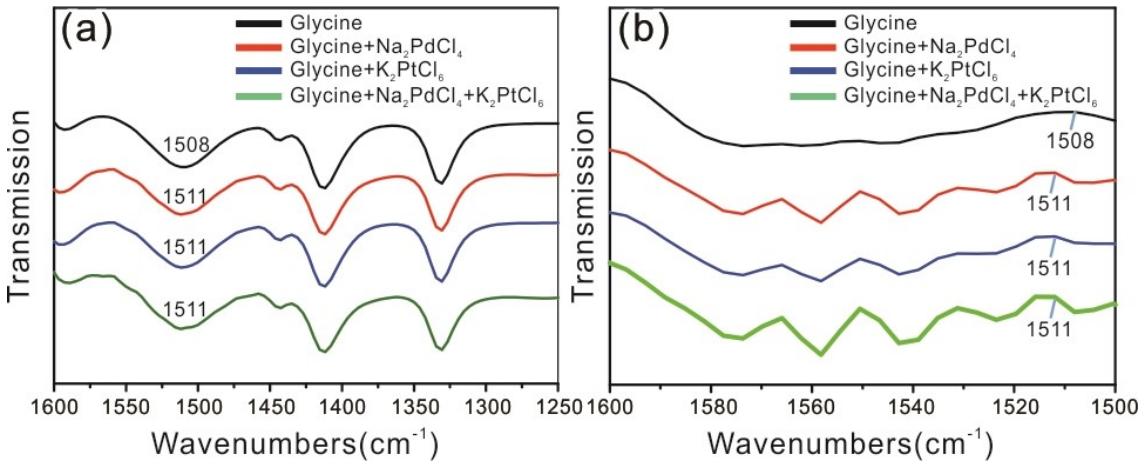

Fig. S5 (a) FT-IR and (b) its second derivative spectra of the different solutions.

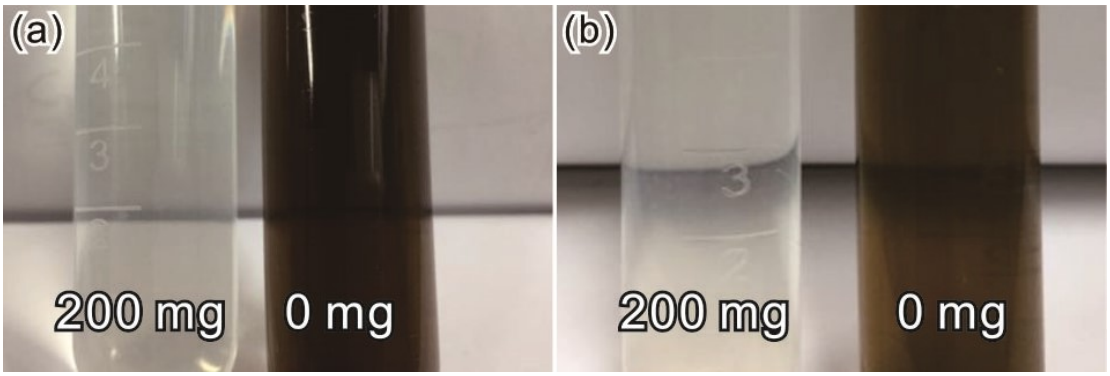

Fig. S6 Photoes of reaction solutions after reaction 1h (a) K_2PtCl_6+200 mg/0 mg glycine, (b) Na_2PdCl_4+200 mg/0 mg glycine.

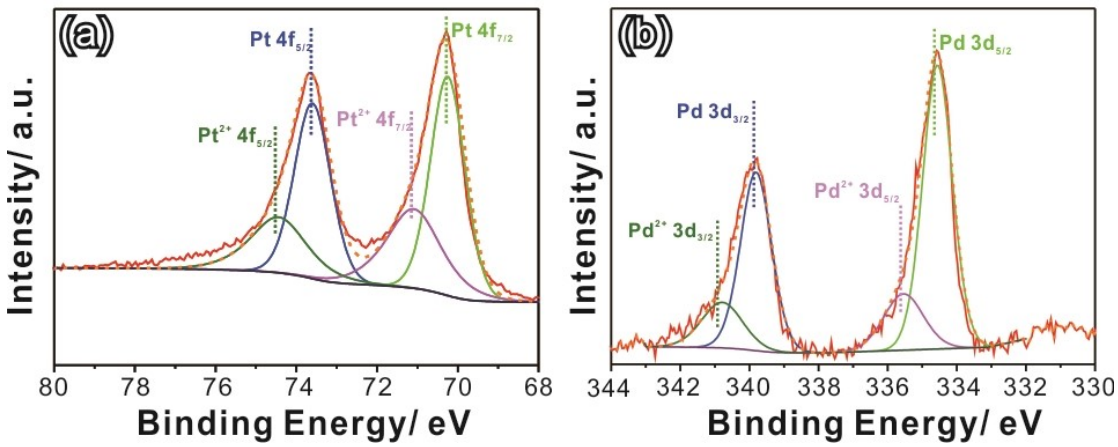

Fig. S7 (a) Pt 4f XPS spectra and (b) Pd 3d XPS spectra of the as-synthesized concave octahedral Pt-Pd alloys.

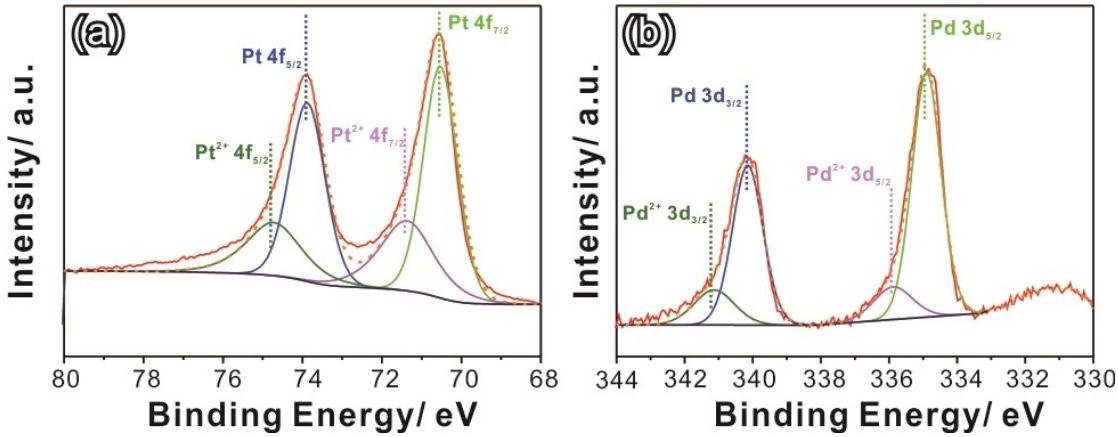

Fig. S8 (a) Pt 4f XPS spectra and (b) Pd 3d XPS spectra of the as-synthesized octahedral Pt-Pd alloys.

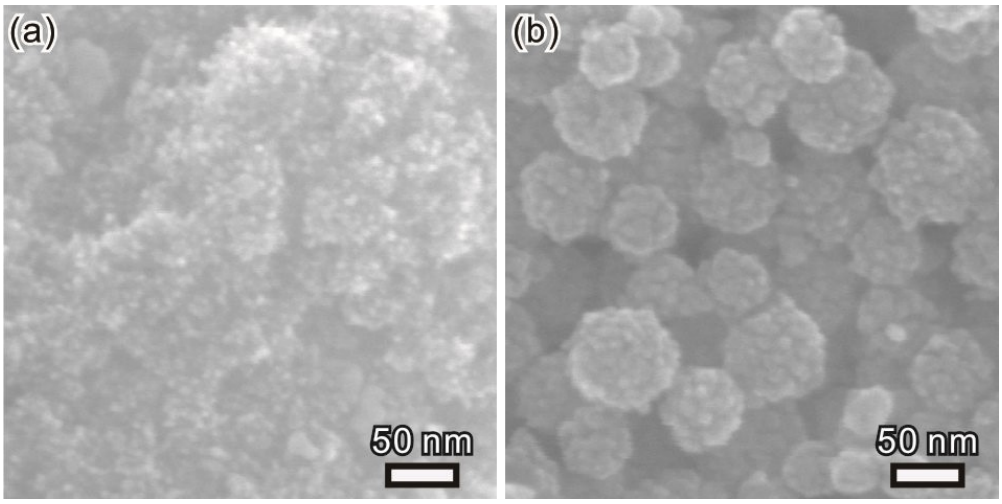

Fig. S9 SEM images of Pt-Pd nanocrystals collected from the reaction with the same condition used in the synthesis of concave octahedral Pt-Pd alloys but prepared by replacing glycine with (a) 2 mL 30% methylamine and (b) 0.2 mL octylame.

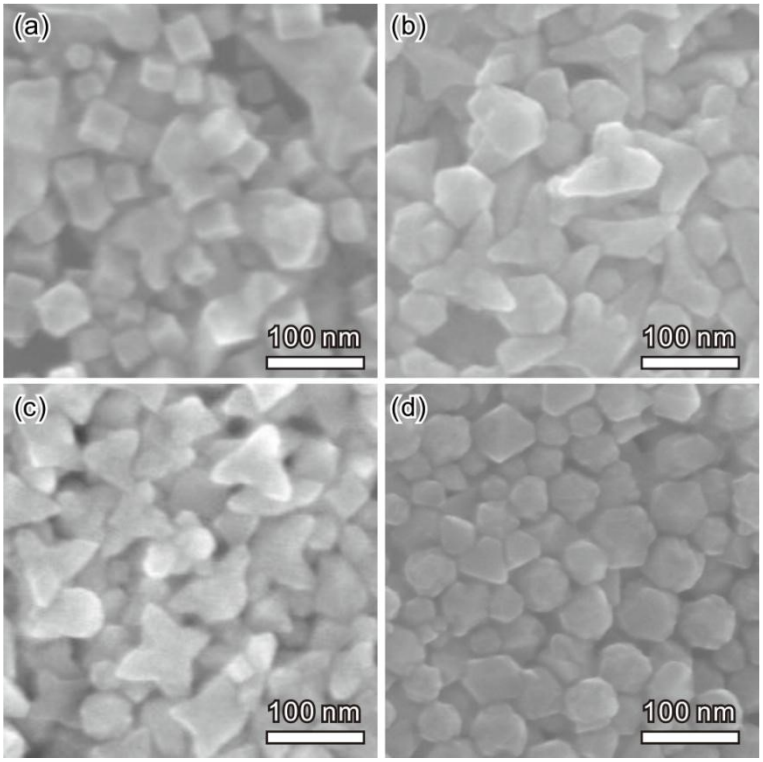

Fig. S10 SEM images of NCs that were prepared with different molar ratios of Pt to Pd salt precursors: (a) pure Pt NCs, (b) 1:2, (c) 2:1, (d) pure Pd NCs.

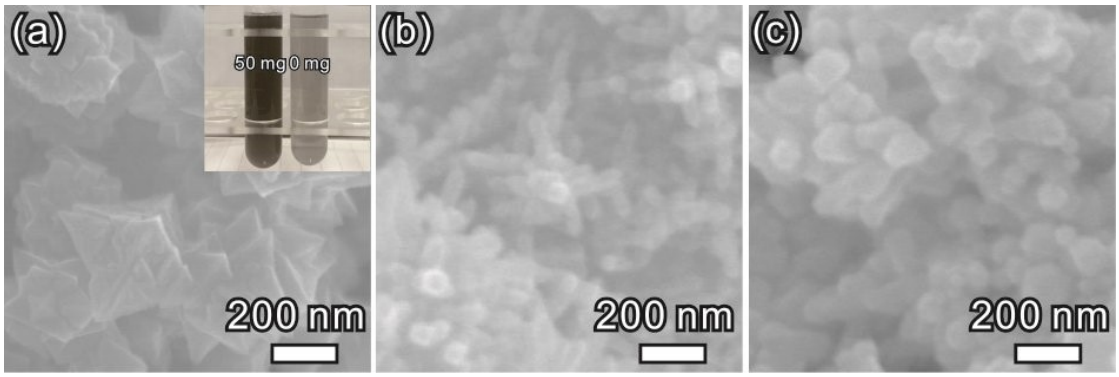

Fig. S11 SEM images of Pt-Pd nanocrystals collected from the reaction with the same condition used in the synthesis of concave octahedral Pt-Pd alloys but prepared by replacing PVP with (a) 0 mg PVP, the inset is the photo of reaction solutions with 50 mg PVP and 0 mg PVP after reaction for 5 h, (b) Brij and (c) PVA.

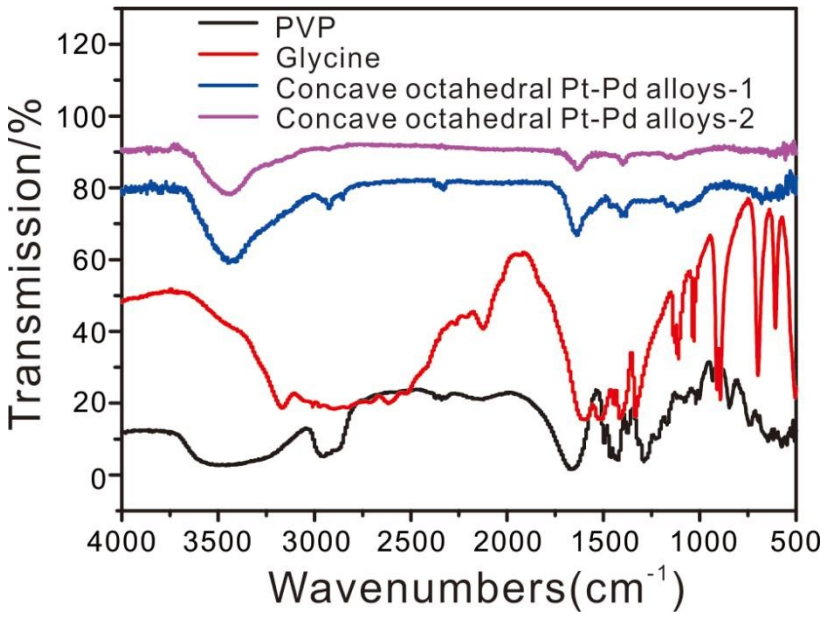

Fig. S12 FT-IR characterization for the concave octahedral Pt-Pd alloys-1 (without UV treatment), concave octahedral Pt-Pd alloys-2 (with UV treatment), PVP and glycine. It's seen that the typical absorption bands of glycine and PVP especially in the range of 2000～1200 cm^{-1} and 3250～2750 cm^{-1} could be observed from the FT-IR spectra.

Reference:

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