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Highly active dye-sensitized photocatalytic H_2 evolution catalyzed by single-atom Pt cocatalyst anchored on g-C_3N_4 nanosheets under long-wavelength visible light irradiation

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1. Experimental

1.1 Preparation of photocatalysts

1.1.1 Chemicals and reagents

All reagents including triethanolamine (TEOA), Eosin Y (EY), $H_2PtCl_6·6H_2O$ and urea were of analytical grade and used without further purification. The deionized water was used throughout experiments.

1.1.2 Preparation of g-C_3N_4

The g-C_3N_4 was synthesized by pyrolyzing urea in an alumina crucible with a cover at 550 °C (ramp rate, 4 °C min^{-1}) for 2 h. The obtained product was washed with water and ethanol several times, and dried in vacuum oven at 60 °C overnight.

1.1.3 Preparation of Pt-CN

500 mg of g-C_3N_4 was dispersed into 150 mL of deionized water with ultrasonication for 30 min and then kept stirring for 5 min. After that, $H_2PtCl_6·6H_2O$ solution (4 mg mL^{-1}) was added into above g-C_3N_4 aqueous dispersion and the resulting mixture was heated at 70 °C in an oil bath for 1-10 h. Then the resulting Pt-CN product was filtered and washed with water and ethanol several times, and dried at 60 °C in vacuum oven overnight, followed by annealing at 125 °C for 1 h in N_2 atmosphere. The Pt loading measured by inductively coupled plasma-optical emission spectrometry (ICP-OES) for samples obtained with reaction time of 1, 2, 4, and 10 h was determined to be 0.17, 0.74, 1.22, and 1.70 wt%, respectively. The thus-obtained samples were labelled as *x*% Pt-CN, where *x* represents the Pt loading amount.

1.1.4 Preparation of Pt NPs-CN

The Pt NPs-CN was synthesized by photoreduction of $H_2PtCl_6·6H_2O$ (4 mg mL^{-1}) from 10 vol% TEOA solution (pH 7) containing g-C_3N_4 via illumination by 300 W Xe lamp (CEL-HXF300) with a cut-off filter of 420 nm for 6 h. The Pt loading for Pt NPs-CN was measured to be 2.88 wt% by ICP-OES. The obtained sample was labelled as 2.88% Pt NPs-CN.

1.2 Characterizations

The high-angle annular dark-field scanning transmission electron microscopy

(HAADF-STEM) characterization was performed on a FEI Titan TEM/STEM with a spherical aberration corrector. X-ray diffraction (XRD) patterns were obtained with a Rigaku Smartlab diffractometer with a nickel filtrated Cu K*β* radiation. X-ray photoelectron spectroscopy (XPS) measurements of the samples were performed on a K-Alpha surface analysis (Thermo Scientific Escalab-250Xi) using X-ray monochromatization. Fourier transform infrared spectroscopy (FT-IR) spectrum was obtained with a Thermo Nicolet Avatar 380 FT-IR spectrometer. The loading amount of Pt was measured by an inductively coupled plasma-optical emission spectrometry (ICP-OES) (Varian 710-ES). The specific surface area was determined with the Brunauer-Emmett-Teller (BET) equation at 77 K by using an adsorption apparatus (Micromeritics ASAP 2020 HD88). UV–vis diffuse reflectance spectra were recorded on a Shimadzu UV-3600 UV–vis-near-IR spectrophotometer equipped with an integrating sphere and $BaSO_4$ powders were used as a reflectance standard. UV–vis absorption spectra were taken with a Thermo Scientific–Evolution 220 spectrophotometer. The photoluminescence (PL) spectra were determined by a Horiba Scientific FluoroMax-4 spectrofluorometer.

1.3 Photocatalytic hydrogen evolution reaction

The EY sensitized photocatalytic H_2 evolution experiments were performed in a 280 mL quartz reactor with a top flat quartz window for light irradiation and a silicone rubber septum was fixed on its side for sampling produced H_2 in the headspace of reaction cell. The 10 vol% TEOA (pH 7) was used as the sacrificial electron donor. In a typical procedure, 10 mg of as-prepared Pt-CN or Pt NPs-CN photocatalyst was dispersed into 100 mL of TEOA solution by ultrasonication for 5 min followed by addition of 0.4 mM EY as the photosensitizer. The reaction mixture was then thoroughly degassed by repeated evacuation-N_2 filling process and irradiated with a 30-W LED lamp (λ=520 nm). The H_2 gas produced was manually taken out by a gas-tight syringe (Agilent, 1.0 mL) and analyzed at given time intervals with a precalibrated gas chromatography (Tech comp; GC-7900) with a thermal conductivity detector, a 5 Å molecular sieve column (4 mm×5 m), and with N_2 as carrying gas.

The apparent quantum efficiency (AQE) of H_2 evolution was calculated from the ratio of the number of reacted electrons during H_2 evolution to the number of incident photons. The photon flux of incident light was determined using a Ray virtual radiation actinometer (Apogee MQ-500, silicon ray detector, light spectrum, 389–692 nm; measurement range, 0–4000 $\mu mol \cdot m^{-2} \cdot s^{-1}$).

2. Additional discussion and figures

2.1 Additional discussion

In aqueous solution, a sequential hydrolysis of $PtCl_6^{2-}$ ions may occur, giving rise to a series of hydrolytic species as shown in the following equations (1)~(6):[S1]

$$(1)\ PtCl_6^{2-} + OH^- \rightarrow Pt(OH)Cl_5^{2-} + Cl^-$$
$$(2)\ Pt(OH)Cl_5^{2-} + OH^- \rightarrow Pt(OH)_2Cl_4^{2-} + Cl^-$$
$$(3)\ Pt(OH)_2Cl_4^{2-} + OH^- \rightarrow Pt(OH)_3Cl_3^{2-} + Cl^-$$
$$(4)\ Pt(OH)_3Cl_3^{2-} + OH^- \rightarrow Pt(OH)_4Cl_2^{2-} + Cl^-$$
$$(5)\ Pt(OH)_4Cl_2^{2-} + OH^- \rightarrow Pt(OH)_5Cl_1^{2-} + Cl^-$$
$$(6)\ Pt(OH)_5Cl_1^{2-} + OH^- \rightarrow Pt(OH)_6^{2-} + Cl^-$$

On the basis of above hydrolysis mechanism of $PtCl_6^{2-}$, it is obvious that a higher pH value will lead to hydrolytic products with more chloride anions dissociated. Given that the pH value of the g-C_3N_4 dispersion in this study is about X (measured by a pH meter), it is reasonable that a series of Pt species containing fewer chloride ions such as $Pt(OH)_2Cl_4^{2-}$, $Pt(OH)_3Cl_3^{2-}$, $Pt(OH)_4Cl_2^{2-}$, $Pt(OH)_5Cl^{2-}$, and $Pt(OH)_6^{2-}$ will form during the reflux reaction (70 °C) of dispersed g-C_3N_4 nanosheets with H_2PtCl_6. In fact, the dissociation of Cl^- from $PtCl_4^{2-}$ ions due to the ion exchange with OH^- could be detected by adding $AgNO_3$ to the mixture of H_2PtCl_6 and g-C_3N_4 aqueous dispersions after reflux reaction. In the following heat-treatment at 125 °C in N_2, the dehydration and further dechlorination of the anchored Pt species would be expected to occur and the single Pt atoms formed within the g-C_3N_4 matrix, as evidenced in our paper and in the literature.[S2]

2.2 Additional figures

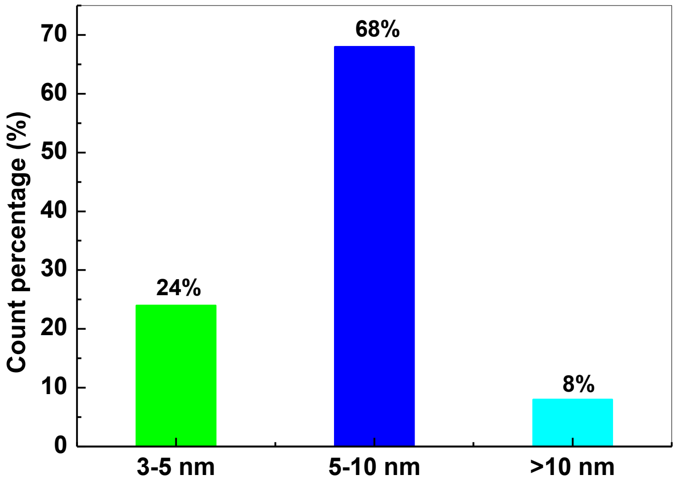

Fig. S1 The size distribution of Pt nanoparticles in Pt NPs-CN sample.

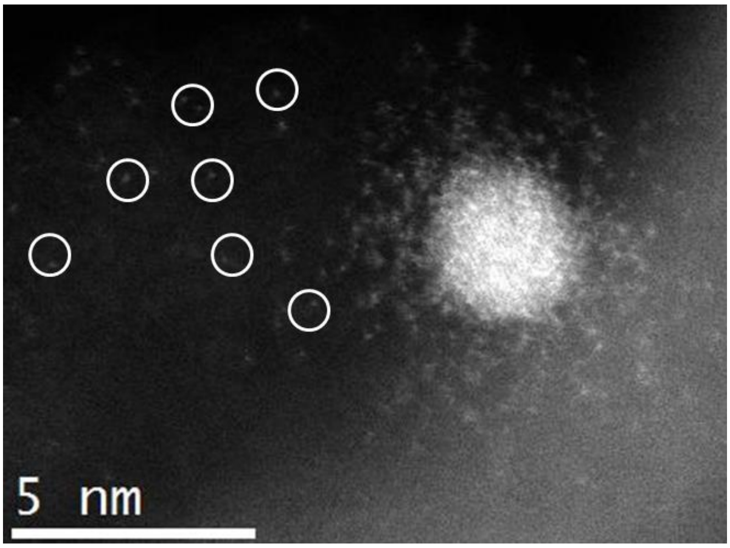

Fig. S2 HAADF-STEM image Pt NPs-CN photocatalyst. The single Pt atoms were marked by white cycles.

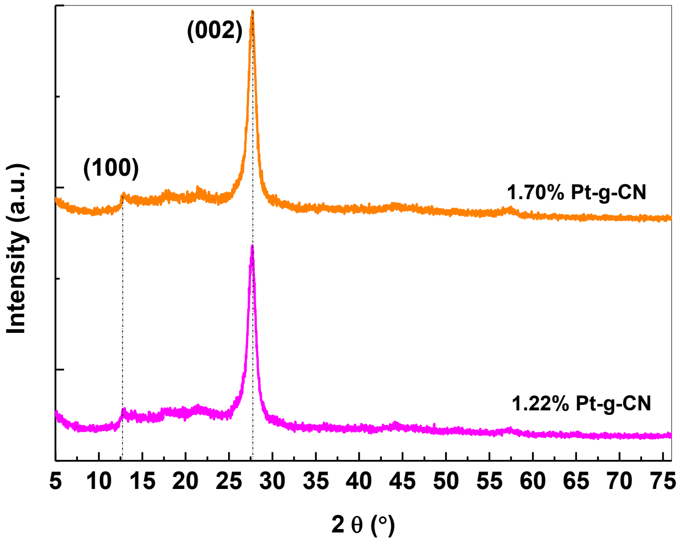

Fig.S3 XRD patterns of Pt-CN with higher Pt loadings of 1.22% and 1.70%.

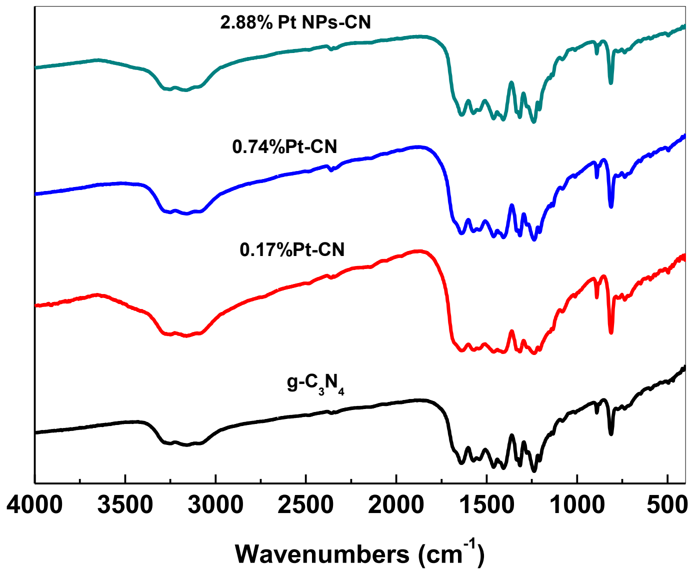

Fig.S4 FTIR spectra of g-C_3N_4, Pt-CN, and Pt NPs-CN photocatalysts.

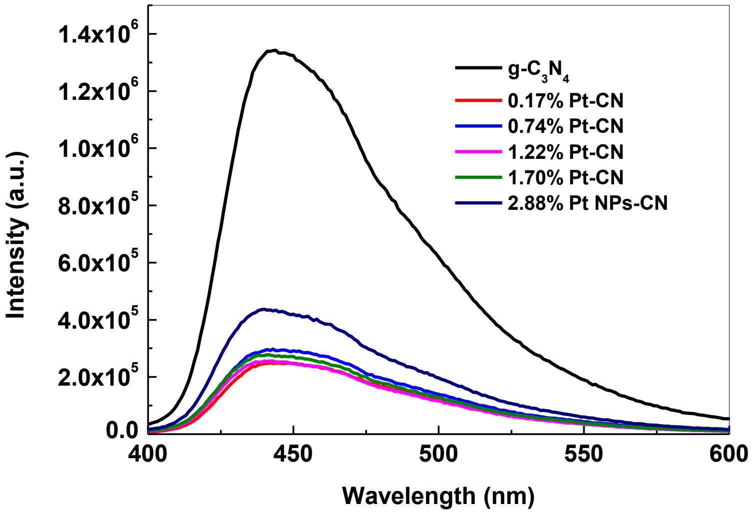

Fig. S5 Photoluminescent spectra of g-C_3N_4, Pt-CN, and Pt NPs-CN samples. The excitation wavelength is 380 nm.

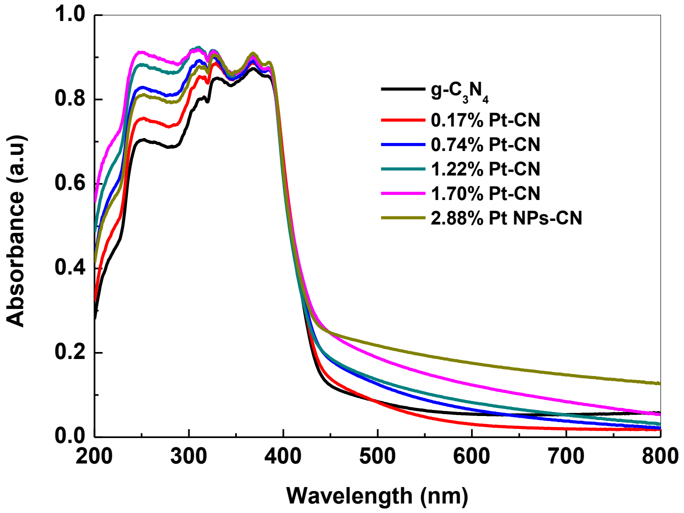

Fig. S6 UV-vis diffuse reflectance spectra of the Pt-CN and Pt NPs-CN catalysts.

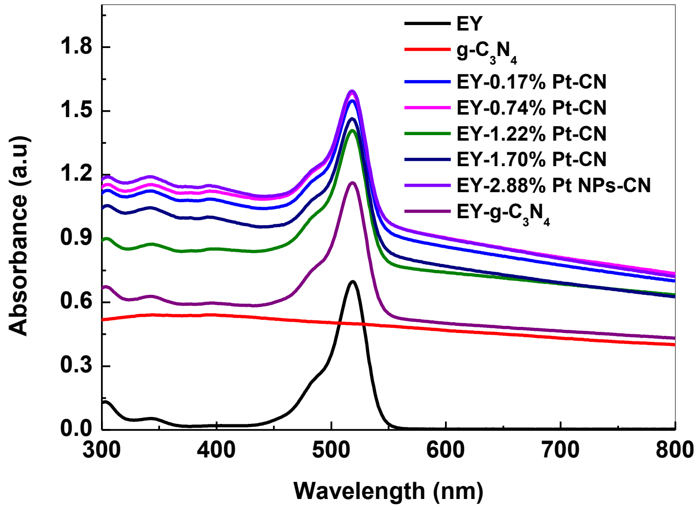

Fig. S7 UV-vis absorption spectra of reaction solution containing EY, g-C_3N_4, EY-g-C_3N_4, EY-Pt-CN, and EY-Pt NPs-CN. EY, 10 μM; g-C_3N_4, Pt-CN, or Pt NPs-CN, 100 μg mL^{-1}.

Table S1 The comparison of photocatalytic H_2 evolution in different photocatalytic systems composed of EY or ErB as photosensitizer, g-C_3N_4 as Pt loading matrix, and Pt as H_2 evolution cocatalyst.

Photocatalyst	Reaction conditions	Light source	H_2 evolution rate (μmol h^{-1} mg_{Pt}^{-1})	Ref.
EY-mpg-C_3N_4/Pt	EY, 0.4 mM; mpg-C_3N_4/Pt, 30 mg; Pt, 7 wt.%; TEOA (15 vol.%, pH 7)	250-W high pressure Hg lamp, >420 nm	371.7	S3
EY-g-C_3N_4/Pt	EY, 12.5 μM; g-C_3N_4/Pt, 100 mg; Pt, 7 wt.%; TEOA (0.79 M, pH 7)	400-W high pressure Hg lamp, >420 nm	22.8	S4
ErB-g-C_3N_4/Pt	ErB, 2.27 mM; g-C_3N_4/Pt, 100 mg; Pt, 1.25 wt.%; TEOA (5 vol.%, pH 9)	300-W Xe lamp, >420 nm	522.0	S5
EY-g-C_3N_4 NS/Pt	EY, 2.27 mM; g-C_3N_4/Pt, 30 mg; Pt, 1.0 wt.%; TEOA (10 vol.%, pH 8)	300-W Xe lamp, >420 nm	943.0	S6
EY-g-C_3N_4/Pt	EY, 0.72 mM; g-C_3N_4/Pt, 50 mg; Pt, 0.5 wt.%; TEOA (20 vol.%, pH 7)	300-W Xe lamp, >420 nm	362	S7
EY-0.17%Pt-CN EY-0.74%Pt-CN EY-1.22%Pt-CN EY-1.70%Pt-CN EY-2.88%Pt NPs-CN	EY, 0.4 mM; Pt-CN or Pt NPs-CN, 10 mg; TEOA (10 vol.%, pH 7)	30-W LED 520 nm	283.5 458.1 309.3 225.9 94.9	This work

Table S2 Physicochemical properties of g-C_3N_4, Pt-CN, and Pt NPs-CN samples.

Sample	S_{BET} (m^2g^{-1})[a]	Average pore size (nm)[b]	Total pore volume (cm^3 g^{-1})[c]
g-C_3N_4	83.5	17.7	0.369
0.17% Pt-CN	64.0	24.2	0.387
0.74% Pt-CN	72.1	21.2	0.382
1.22% Pt-CN	87.1	21.2	0.473
1.70% Pt-CN	101.4	23.5	0.595
2.88% Pt NPs-CN	83.2	23.1	0.479

[a] BET surface area is calculated from the linear part of the BET plot.

[b] Adsorption average pore width (4 V/A by BET).

[c] Single point total pore volume of the pores at p/p_0=0.99.

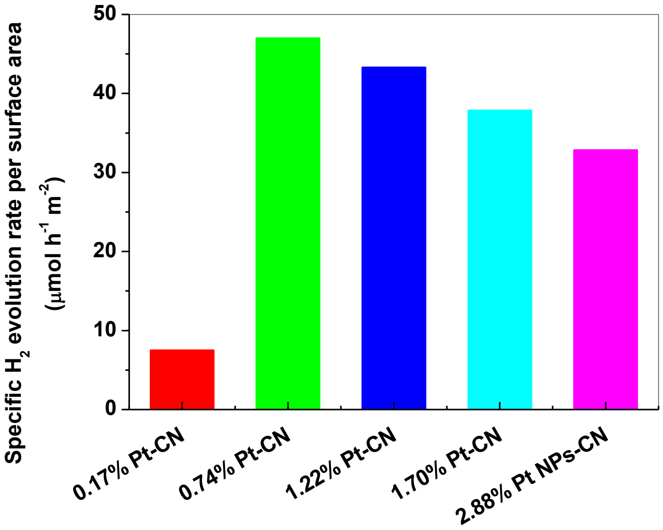

Fig. S8 Surface-specific photocatalytic H_2 evolution activity of Pt-CN and Pt NPs-CN samples.

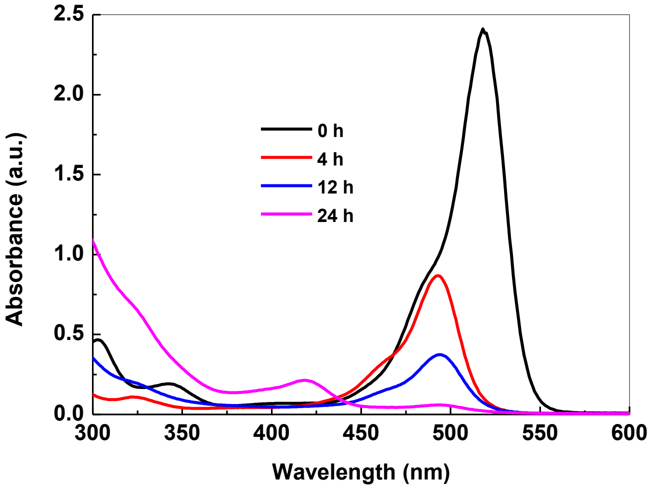

Fig. S9 UV-vis absorption spectra of EY during the photocatalytic H_2 reaction from EY sensitized 0.74% Pt-CN under 520 nm irradiation as a funtion of reaction time. The 0.74% Pt-CN was removed by centrifiguation and the remaining EY solution was diluted 10 times.

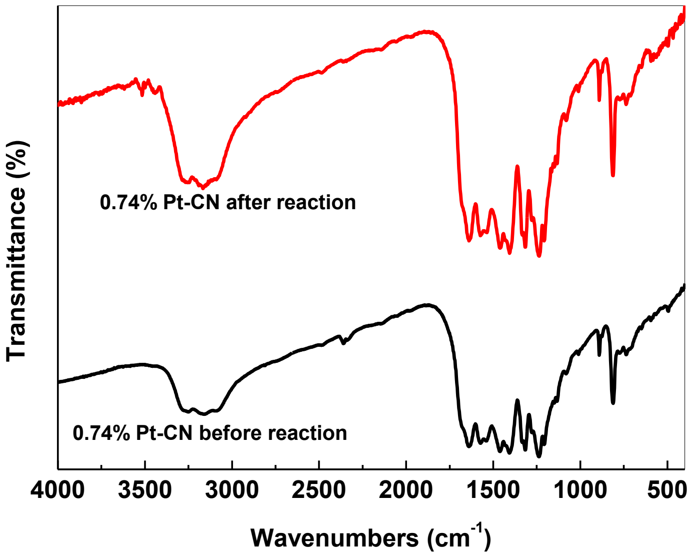

Fig. S10 FTIR spectra of 0.74% Pt-CN before and after reaction.

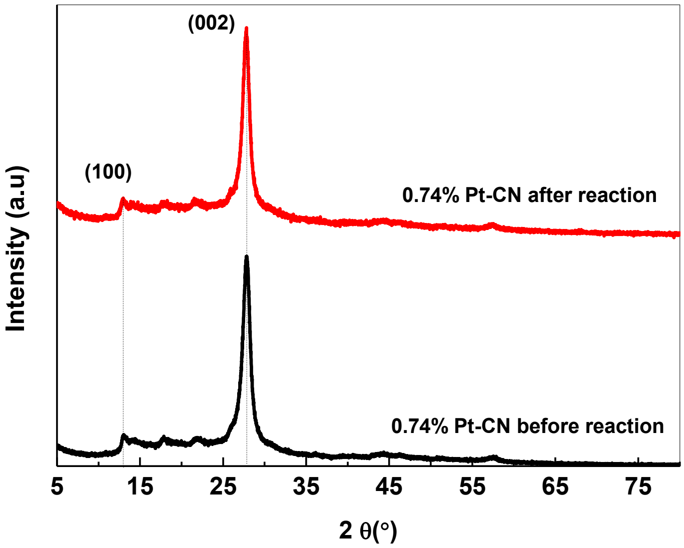

Fig. S11 XRD patterns of 0.74% Pt-CN before and after reaction.

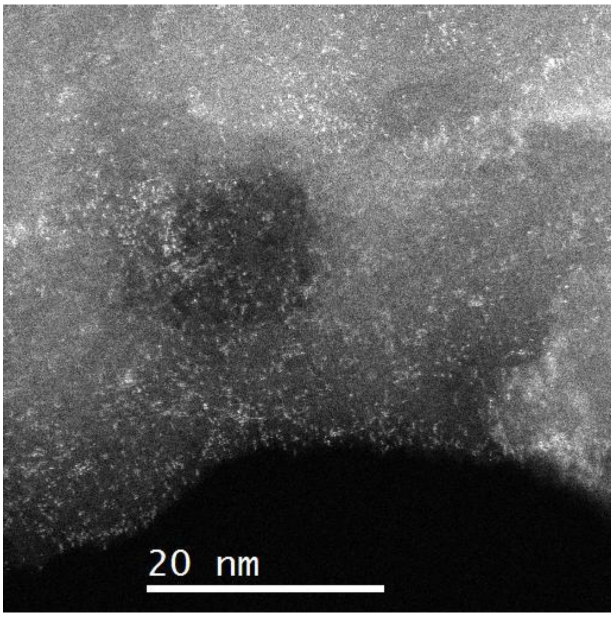

Fig. S12 HAADF-STEM image of 0.74% Pt-CN after reaction.

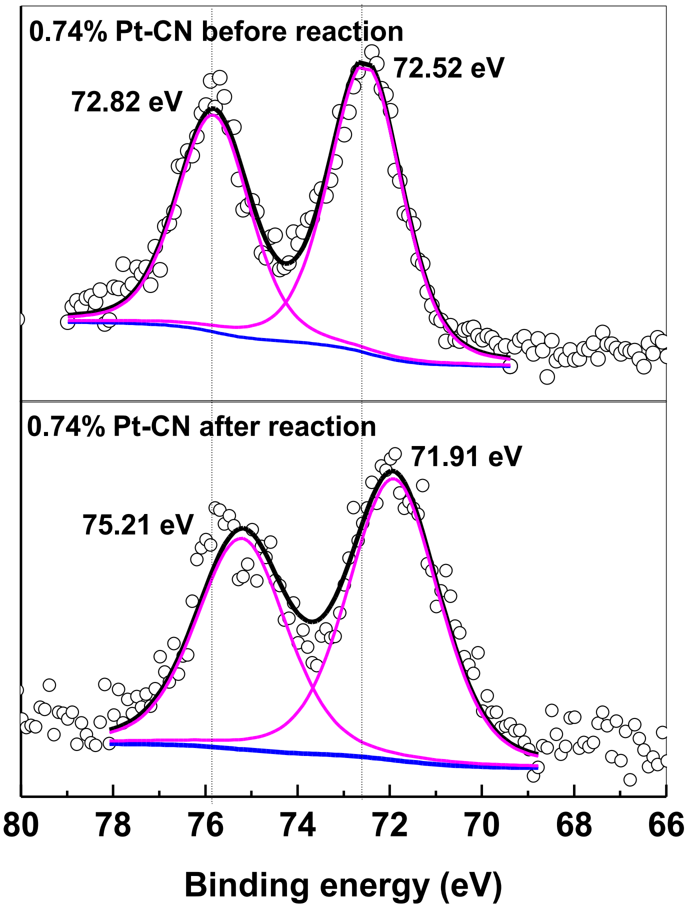

Fig. S13 High-resolution XPS spectra of Pt 4f core level of 0.74% Pt-CN before and after reaction.

References

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