

Supporting Information for:

## Selective photocatalytic C-C coupling of benzyl alcohol into hydrobenzoin using Pt-deposited CdS nanosheets passivated with cysteamine

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# Experimental details

## Materials

All chemicals were used as purchased: cadmium acetate dihydrate ( $\text{Cd}(\text{Ac})_2 \cdot 2\text{H}_2\text{O}$ ,  $\geq 98.0\%$ ), oleic acid (OA, 95%), sulfide (S, 99.98%), 1-octadecene (ODE, technical grade, 90%), oleylamine (Oam, technical grade, 70%), platinum (II) acetylacetonate ( $\text{Pt}(\text{acac})_2$ , 98%), 1,2-hexadecanediol (HDD, technical grade, 90%), 4-mercaptopyridine (Mpy, 95%), cysteamine (MEA,  $\sim 95\%$ ), N-Methylformamide (NMF, 99%), sodium hydroxide (NaOH, reagent grade,  $\geq 98\%$ ) mercaptopropionic acid (MPA,  $\geq 99\%$ ), benzyl alcohol (BzOH, anhydrous, 99.8%), Tetraoctylammonium tetrafluoroborate ( $\geq 97.0\%$ ), 4-Methoxyacetophenone (99%), 1,1-Diphenylethylene (DPE, 97%), 2,3-Diphenyl-2,3-butanediol (APP), tert-Butyl hydroperoxide solution (5.0-6.0 M in decane) were purchased from Sigma Aldrich. 1,2-Dichlorobenzene ( $>99.0\%$ ), Phenyl ether (PE,  $>99.0\%$ ), were purchased from TCI. Triethanolamine (TEOA, 99+%) was purchased from Acros Organics. 1-Phenylethanol (PEOH) was purchased from Alfa Aesar.

## Preparation of CdS nanosheets (NSs):

Typically, 12.8 mg sulfur was dissolved in 20 mL ODE, followed by addition of 420 mg  $\text{Cd}(\text{Ac})_2 \cdot 2\text{H}_2\text{O}$  and 0.5 mL OA. The mixture was bubbled with argon gas for 30 min and heated to 260 °C within 15 mins under the argon atmosphere. The mixture was kept for 1 min for NSs synthesis and cooled down to room temperature. 1 mL OA was injected into the mixture to enhance the dispersion. The CdS NSs were purified by ethanol several times and dispersed in hexane.

## Pt deposition

20 mg CdS NSs were dispersed with 5 mg Pt acetylacetonate in 2 mL dichlorobenzene solution. Then, the solution was injected into a mixture of 0.2 mL OA, 0.4 mL OAm, 40 mg HDD, and 10 mL PE at 200 °C under an inert atmosphere. The reaction was kept for 3 min before cooled down to room temperature. The product was purified by ethanol and dispersed in hexane.

For the synthesis of isolated Pt NPs, the growth time was longer, typically 15 minutes because the homogeneous nucleation of Pt NPs was slower than the heterogeneous nucleation on the edges of CdS NSs. Chloroform (5 mL) and ethanol (30 mL) were then added under ambient conditions. The black product was precipitated and isolated by centrifugation. The pale-yellow supernatant was discarded, and the precipitate was dispersed in chloroform (5 mL) in the presence of oleic acid (0.05 mL) and oleylamine (0.05 mL). The nanoparticles were precipitated again by the addition of ethanol (20 mL) and centrifuged. The final nanoparticle product could be redissolved in nonpolar solvents like chloroform, toluene, and hexane.

## Ligand exchange

Thiol molecule (50 mM) and NaOH (0.1 M) were dissolved in NMF to form the ligand precursor solution. Equal volume of the ligand solution and CdS colloid solution (1– 2 mg/mL) were mixed to form a two-phase mixture. The mixture is vigorously stirred until the CdS were transferred completely from the hexane layer to the NMF layer. Then, the NMF layer was extracted and rinsed in hexane to remove the organic species. Finally, the ligand-exchanged Pt-CdS was collected by precipitation with acetone.

## Characterizations

Scanning transmission electron microscopy (STEM) was performed using a Talos F200X. Transmission electron microscopy images and high angle annular dark field scanning transmission electron microscopy (HAADF-STEM) images were recorded using field emission transmission electron microscopy (Tecnai F30, FEI company). Powder X-ray diffraction (XRD) patterns were obtained on High Resolution Powder X-Ray Diffractometer under Cu-K $\alpha$  radiation. UV-vis spectra were recorded on a Shimadzu UV-1601PC spectrophotometer. X-ray photoelectron spectroscopy (XPS) spectra were collected on Axis-Supra instrument (Kratos Kratos). Deconvolution was performed for accurate analysis, and for deconvolution, the spin-orbit splitting between the Pt 4f<sub>7/2</sub> and Pt 4f<sub>5/2</sub> peaks was set to  $\Delta=3.3$  eV, with the FWHM of both peaks set to the same value. Additionally, the area ratio between the two peaks was fixed at 3:4. Transient photocurrent responses were measured in a cell using a potentiostat (Ivium tech.) with three-electrode system: a platinum wire and an Ag/AgCl<sub>2</sub> electrode (protected from light) were used as the counter electrode and reference electrode, respectively. The 1.0 mg CdS NSs passivated with either cysteamine and MPA were dispersed in 1 mL methanol to obtain CdS slurry, which were dropped on ITO substrates (2.5 X 2.5 cm<sup>2</sup>) and used as working electrodes. The electrolyte for the transient photocurrent response studies was tetraoctylammonium tetrafluoroborate (1% m/v) in acetonitrile, and the light source was a solar light simulator (AM 1.5, 100 mW cm<sup>-2</sup>). The concentrations of the metal ions were measured using inductively-coupled plasma optical emission spectrometry (ICP-OES) recorded on an Agilent ICP-OES 720. The mass spectra were obtained by a gas chromatography (Trace1310-ISQ QD300, Thermo Fisher) equipped with a mass Spectrometer (MS).

## Photocatalytic BzOH conversion

Generally, 1 mg Pt/CdS was dispersed in ACN with sonication. Then, the solution was transferred into a 10-mL quartz vial, followed by the addition of 25  $\mu$ L (0.24 mmol) BzOH and a magnetic bar. Then, the vial was sealed, and the solution was bubbled with Ar gas to form an inert atmosphere. The photoreactor was stirred and irradiated by a solar light simulator (AM 1.5, 100 mW cm<sup>-2</sup>). The produced hydrogen gas was quantified through the headspace gas analysis (25  $\mu$ L) by gas chromatography (YL6500 GC system, Younglin Chromass) equipped with a thermal conductivity detector (TCD). 4-Methoxy acetophenone solution in toluene as the internal standard was added into the electrolyte, followed by centrifugation to discard the photocatalyst. The supernatant was analyzed quantitatively by a GC equipped with a flame ionization detector (FID). For the radical capture experiment, 104  $\mu$ L (1 mmol) BzOH and 353  $\mu$ L (2 mmol) DPE were used instead of 25  $\mu$ L BzOH.

## Photocatalytic hydrogen evolution reaction (HER)

The experimental procedure is same as the photocatalytic BzOH conversion, with the exception that ACN and BzOH were replaced with water and TEOA, respectively.

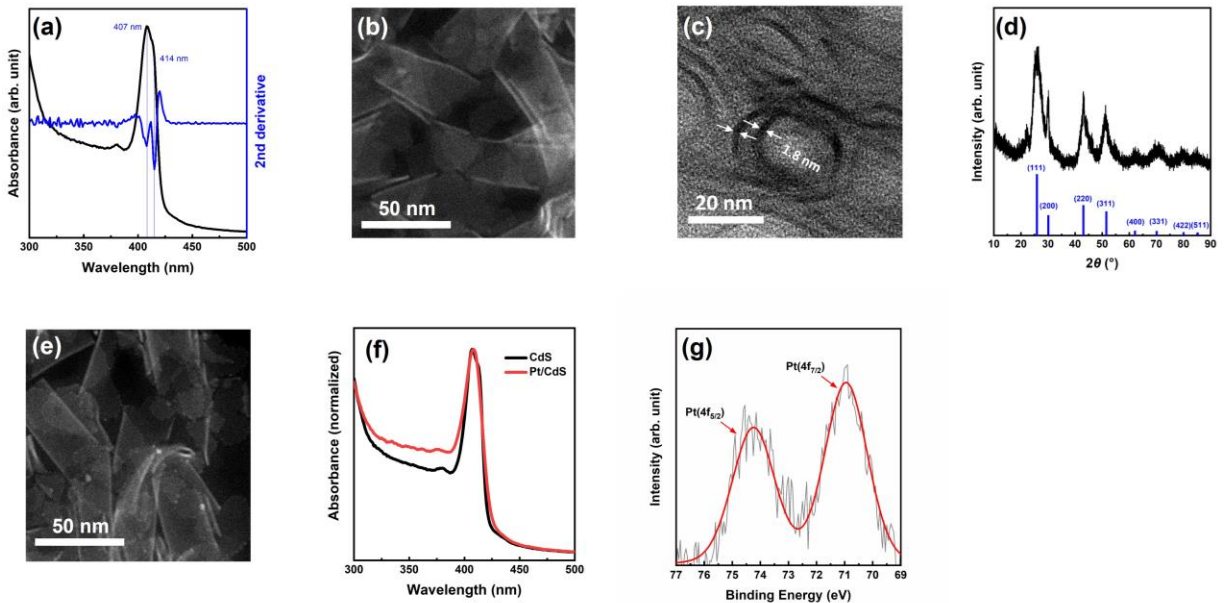
## Transient absorption measurements

Pump and probe beams were generated from a pulsed regeneratively-amplified Ytterbium-doped potassium gadolinium tungstate (Yb:KGW) laser (Pharos, Light conversion), which produced photon pulses with a wavelength of 1028 nm, a pulse duration of 196 fs, and a repetition rate of 200 kHz. This beam used as a fundamental source to seed an Optical Parametric Amplifier (OPA) equipped with a second harmonic module (Orpheus, Light Conversion) for the pump beam generation. The pump beam was adjusted to a wavelength of 320 nm, and its beam radius was approximately 130  $\mu$ m. The intensity per

pump pulse was adjusted to  $\sim 2 \mu\text{J}/\text{cm}^2$  to prevent multi-exciton generation. A fraction of the fundamental beam, which was used as a probe beam, was transmitted through a delay line and focused onto a sapphire to generate white-light continuum generation with TA spectrometer (Harpia, Light Conversion). This beam (a beam radius of  $105 \mu\text{m}$ ) was then focused onto the sample and overlapped with the pump beam area. After the transmission through the sample, the probe beam was collected with a detector (Kymera 193i, Andor).

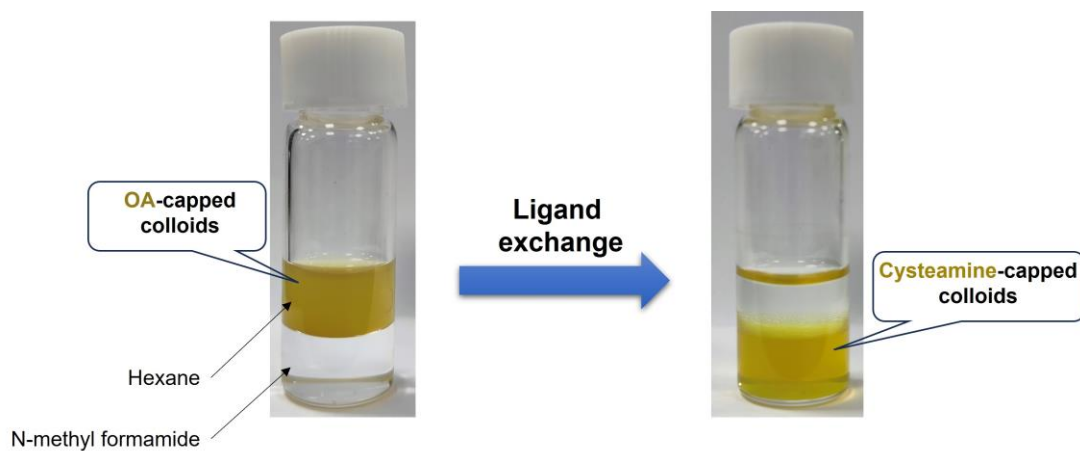
# Supporting experimental results

Fig. S1



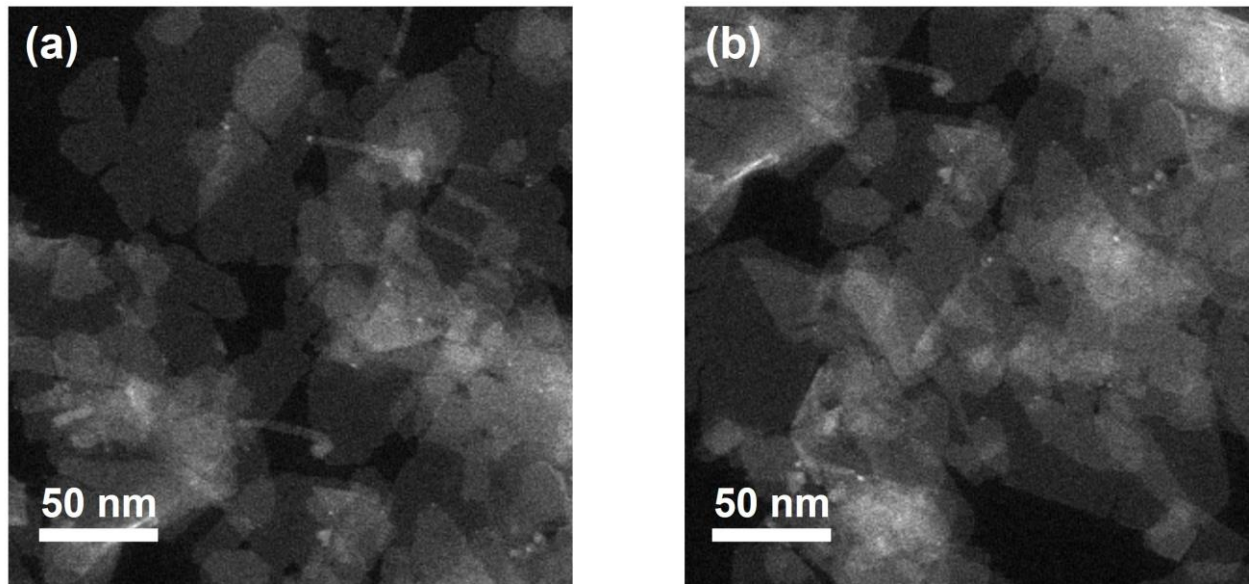
**Fig. S1** (a). Normalized absorption spectrum of CdS NSs colloid solution in hexane (black line). The 2<sup>nd</sup> derivative of the absorption spectra shown as the blue line indicates the electron/light-hole and overlapping electron/heavy-hole transitions at 407 nm and 414 nm, respectively. (b) STEM image of CdS NSs. (c) The TEM image of upright nanosheet to measure the thickness. (d) X-ray diffraction patterns of CdS NSs. The standard diffraction peaks of CdS with the zinc blende structure (PDF#: 10-0454) are inserted as blue lines for reference. (e) TEM image of Pt/CdS NSs. (f) Normalized absorption spectra of CdS NSs (black line) and Pt/CdS NSs (red line) colloid solution in hexane. (g) XPS spectra of Pt 4f ( $4f_{5/2}$  and  $4f_{7/2}$ ) in Pt/CdS NSs.

**Fig. S2**



**Fig. S2** Ligand exchange process. The Pt/CdS NS capped by OA has a hydrophobic surface, making it soluble in hexane (the upper solution). By stirring, the surface capping ligand changes from OA to cysteamine, resulting in the phase transfer from hexane to N-methyl formamide (NMF). Then the surface become hydrophilic, making it soluble in NMF (bottom solution).

**Fig. S3**



**Fig. S3** STEM images of Pt/CdS NSs capped with (a) MPA and (b) cysteamine.



Fig. S4

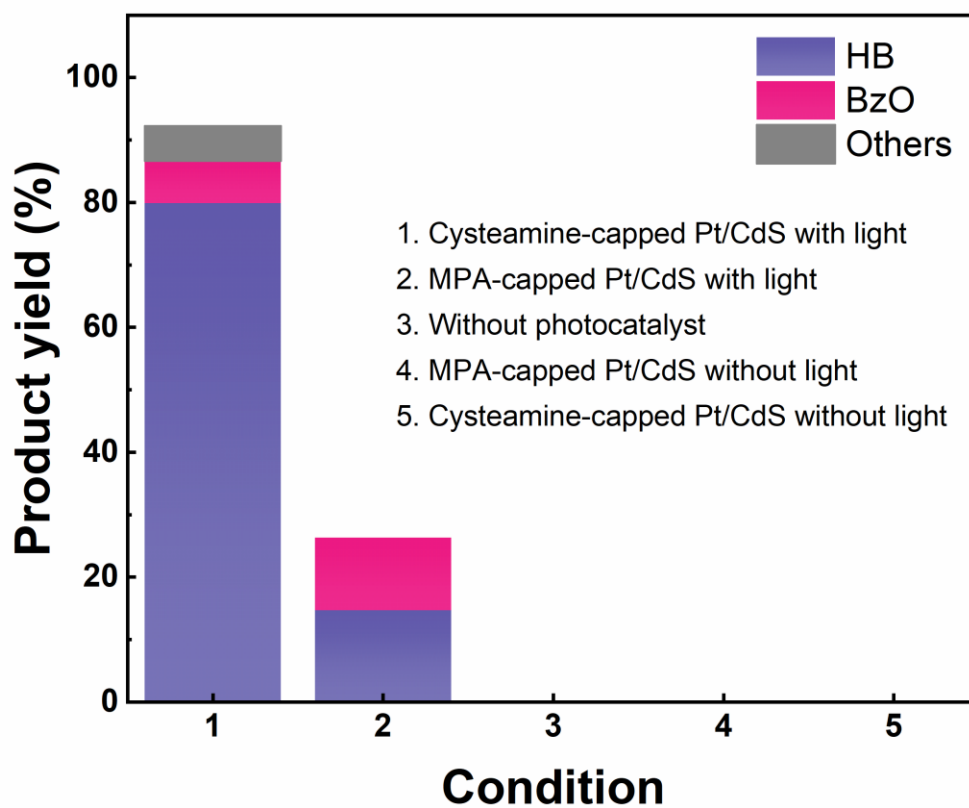
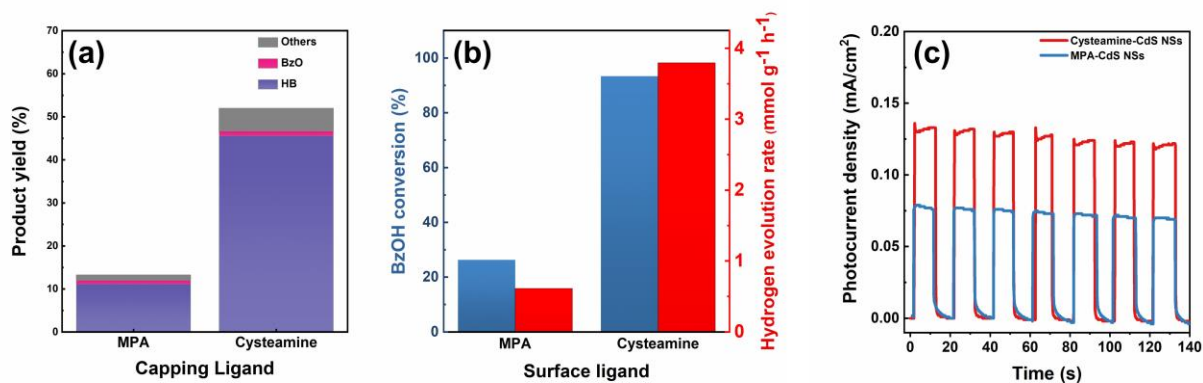


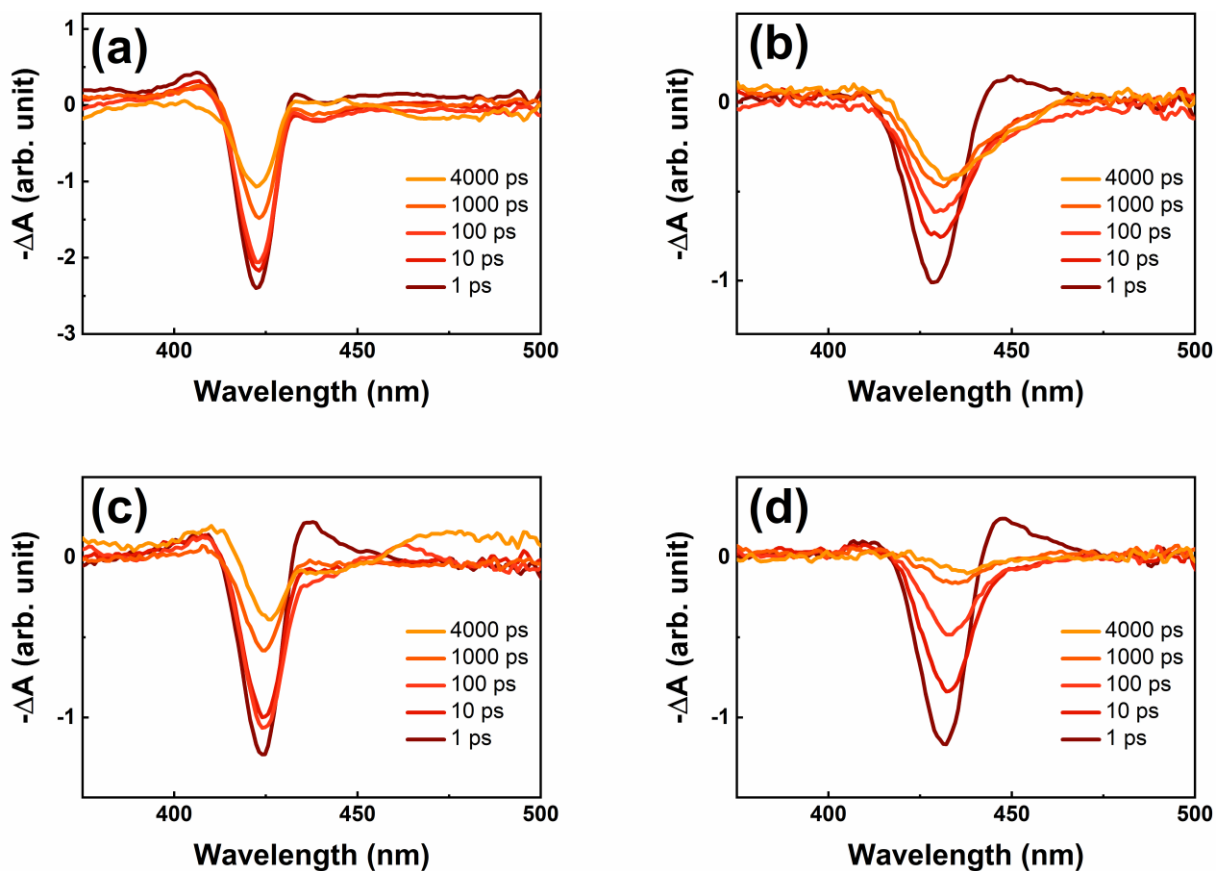
Fig. S4. Products distribution of photocatalytic BzOH conversion at difference experiment conditions

Fig. S5



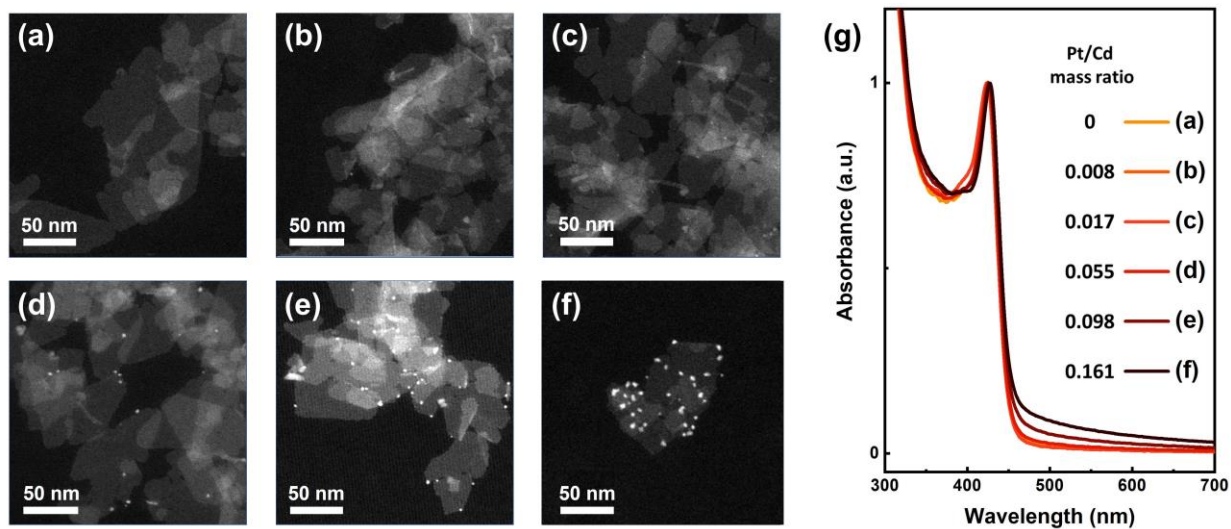
**Fig. S5** (a) Products distribution of photocatalytic BzOH conversion by CdS NSs with different surface ligands. (b) Comparison between the photocatalytic activities of BzOH (Blue, 3h) and HER (red) conversion by using Pt/CdS NSs with different ligands. (c) Transient photocurrent response to on-off illumination of CdS NSs with different ligands (solar light simulator, AM 1.5, 100 mW cm<sup>-2</sup>).

Fig. S6



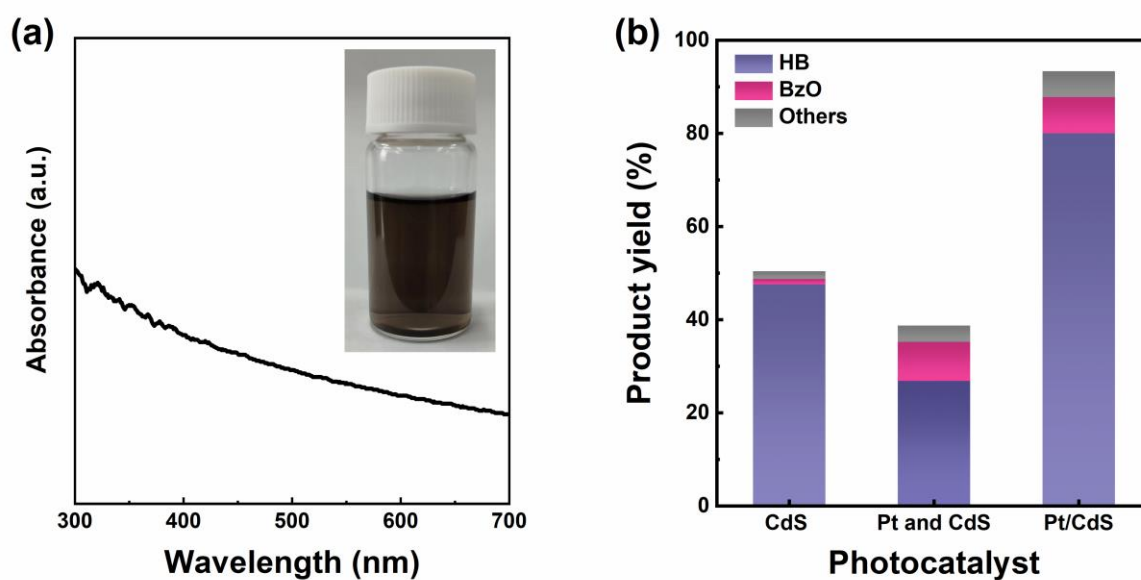
**Fig. S6** TA spectra at indicated delay time of (a) MPA-capped CdS NSs, (b) cysteamine-capped CdS NSs, (c) MPA-capped Pt/CdS NSs, and (d) cysteamine-capped Pt/CdS NSs in DMSO. The main feature observed in the TA spectra is the exciton bleach (XB), which corresponds to the transition of electrons and holes. The XB of CdS NSs originates from state-filling of conduction band electron levels.

Fig. S7



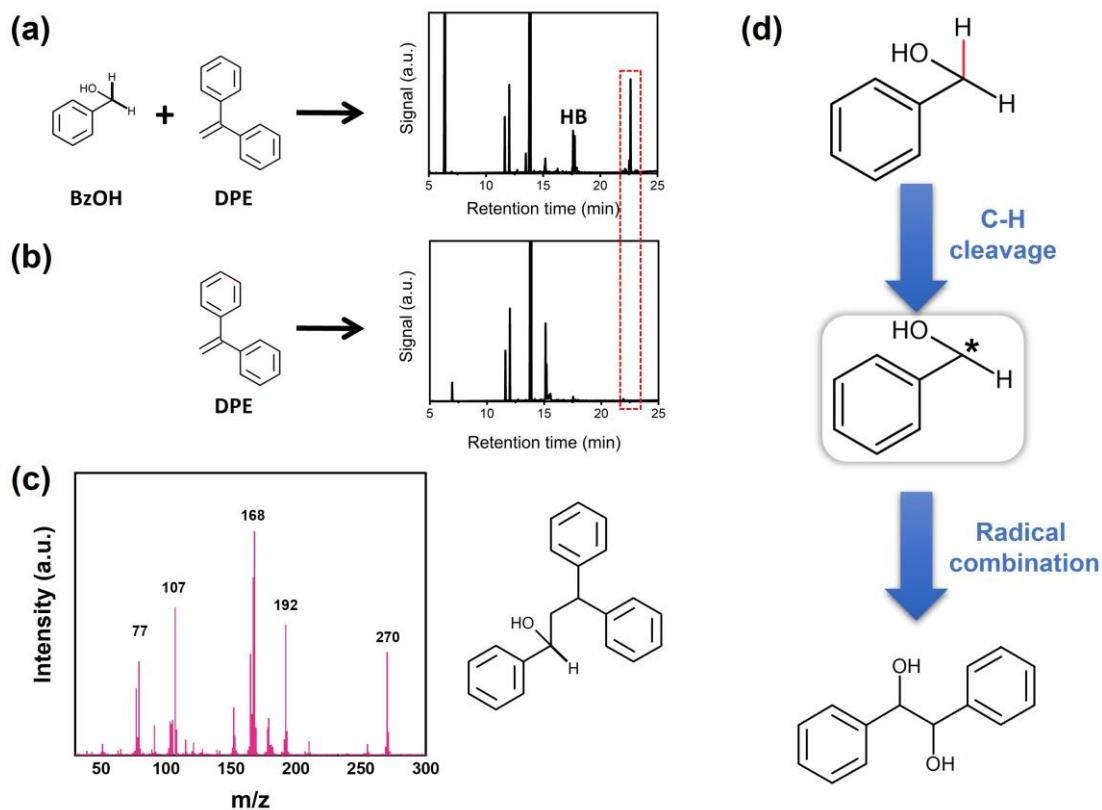
**Fig. S7** STEM images of Pt/CdS with varying mass fractions of Pt (a-f), and the corresponding normalized absorption spectra with Pt/Cd mass ratios(g). The sizes of Pt NPs sizes from (b) to (f) are  $1.3 \pm 0.2$  nm,  $2.3 \pm 0.3$  nm,  $3.5 \pm 0.5$  nm,  $4.1 \pm 0.9$  nm,  $5.6 \pm 1.7$  nm, respectively.

Fig. S8



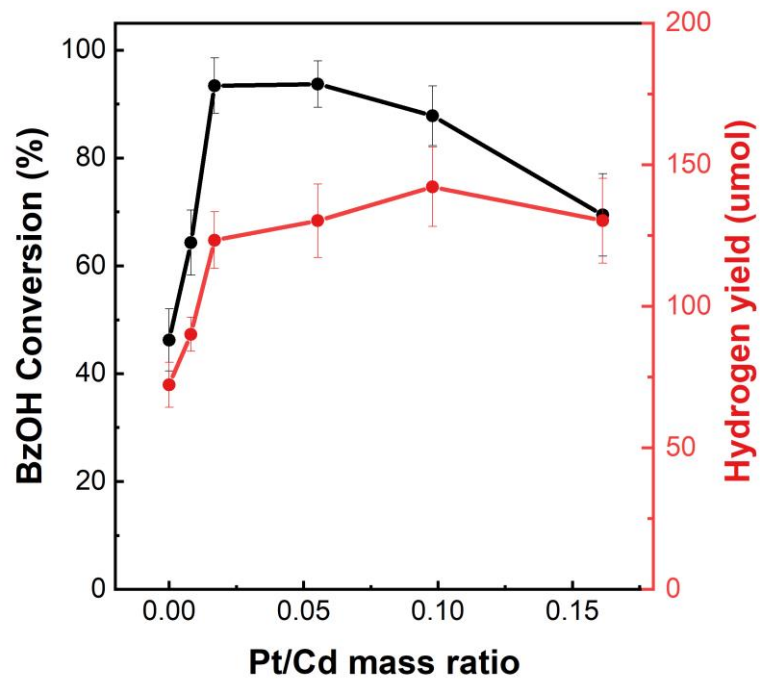
**Fig. S8** (a) Absorption spectrum of Pt nanoparticles colloids in hexane. Inset indicates the photograph of Pt colloid solution. (b) Photocatalytic BzOH conversion with 1 mg CdS, 0.013 mg Pt and 1 mg CdS, and 1 mg Pt/CdS of a mass ratio of 0.017.

Fig. S9



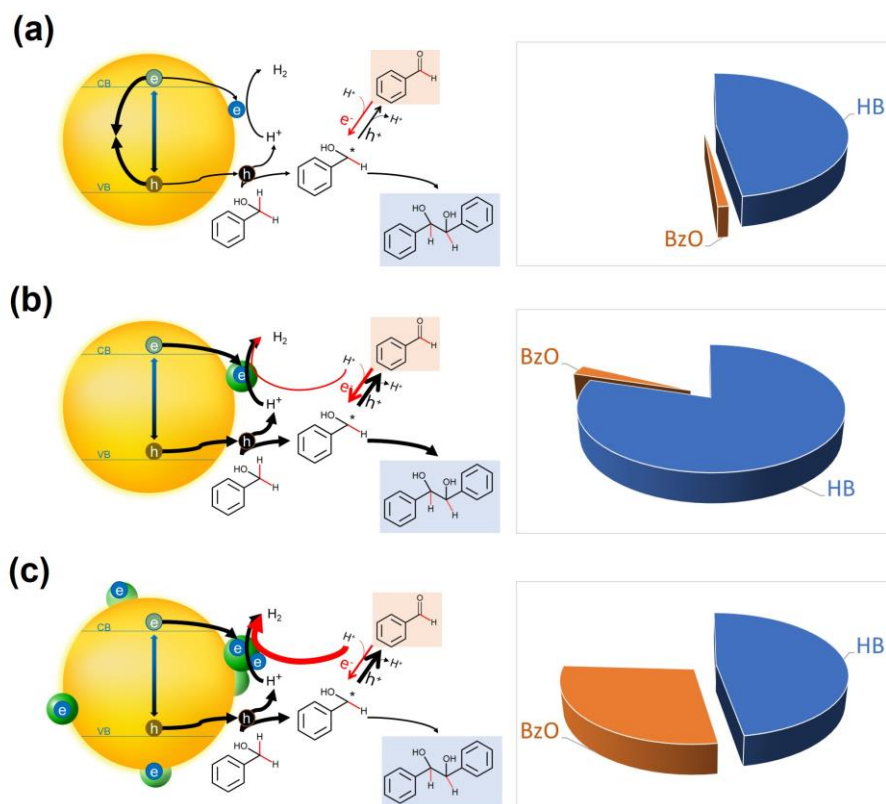
**Fig. S9** (a) Radical capture reaction and the corresponding GC spectrum after the reaction. The peaks corresponding to HB are located at around 17 min, marked as "HB" in the spectrum. (b) Control experiment with only DPE and the corresponding GC spectrum. The red dot marks the product from the radical capture reaction by comparing the two GC spectra. (c) Mass spectrum of the product from the radical capture reaction and the corresponding molecule. (d) Reaction mechanism of the ketyl radical as the intermediate in the C-C coupling reaction of BzOH for HB production.

Fig. S10



**Fig. S10** Photocatalytic BzOH conversion (black line) and hydrogen yield (red line) by Pt/CdS with varying mass fractions of Pt.

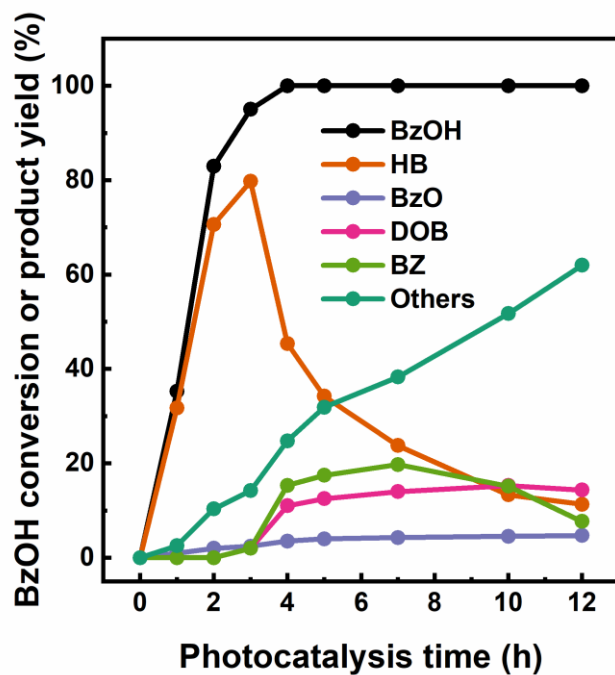
Fig. S11



**Fig. S11** Postulated reaction mechanism of conversion of BzOH. (a) Charge recombination inside CdS slows down the reaction activity. The well-preserved redox equilibrium between ketyl radical and BzO results in high selectivity toward HB. (b) Moderate Pt deposition suppresses the charge recombination allows for high reaction rate. The HER reaction is intensified by Pt but give minor effect to the redox equilibrium between the ketyl radical and BzO. (c) Although the over-loaded Pt deposition can also suppress the charge recombination but the Pt-intensified HER reaction diminishes the electron supply available for BzO reduction, leading to the accumulation of BzO and subsequently decreasing the selectivity toward HB.



Fig. S12



**Fig. S12** Photocatalytic BzOH conversions and products of Pt/CdS NSs with Pt/Cd mass ratio of 0.017 during 12 h reaction. Conversion (BzOH) =  $(n_0(\text{BzOH}) - n(\text{BzOH})) \times 100\%$ ; Yield (HB) =  $2 \times n(\text{HB}) / n_0(\text{BzOH}) \times 100\%$ ; Yield (BzO) =  $n(\text{BzO}) / n_0(\text{BzOH}) \times 100\%$ ; Yield (DOB) =  $2 \times n(\text{DOB}) / n_0(\text{BzOH}) \times 100\%$ ; Yield (BZ) =  $2 \times n(\text{BZ}) / n_0(\text{BzOH}) \times 100\%$ ; Yield (Others) =  $100\% - \text{Yield (HB)} - \text{Yield (BzO)} - \text{Yield (DOB)} - \text{Yield (BZ)}$ .

# Supplementary table

**Table S1.** Fitting parameters for multiple exponential decay from TA data

		A <sub>1</sub>	$\tau_1$	A <sub>2</sub>	$\tau_2$	A <sub>3</sub>	$\tau_3$	A <sub>4</sub>	$\tau_4$
MPA	CdS	36.7%	0.48±0.04	15.5%	272±23	47.8%	7814±301		
	Pt/CdS	39.6%	0.48	15.9%	272	42.6%	7814	1.9%	10.5±18.2
Cysteamine	CdS	36.8%	0.63±0.15	21.8%	162±18	41.4%	12,156±1182		
	Pt/CdS	42.7%	0.63	36.6%	162	9.9%	12,156	10.8%	12.9±4.8

# Supplementary note

## Note 1. Analysis of transient absorption data

The exponential fitting equation:

$$y(x) = \int_{-\infty}^{\infty} \frac{e^{-\frac{t^2}{2\sigma}}}{\sigma\sqrt{2\pi}} \times \left\{ \sum_{i=1}^n A_i e^{-\frac{(x-x_0)-t}{\tau_i}} \right\} dt \quad (S1)$$

, where  $n$  is the number of total exponential components. Initially, the decay components of CdS NSs capped with MPA and cysteamine were fitted using this equation with three exponential components ( $n = 3$ ). For the Pt/CdS NSs samples, an additional decay component attributed to electron transfer from CdS to Pt was included, alongside the existing decay components associated with electron trapping ( $\tau_1, \tau_2$ ) and carrier recombination ( $\tau_3$ ). As there were no other changes to the sample apart from the introduction of Pt, we assumed the original three decay lifetimes remained unchanged in the case of Pt/CdS NSs.

To isolate and identify the specific decay component associated with electron transfer from CdS to Pt, we then fitted the Pt/CdS samples capped with MPA and cysteamine using the same equation, but with four exponential components ( $n = 4$ ). In this process, the first three decay lifetimes ( $\tau_1, \tau_2, \tau_3$ ) were kept consistent with those obtained from the corresponding CdS samples. As shown in Table S1, a notable observation is that for Pt/CdS, the amplitudes of  $\tau_1$  and  $\tau_2$  should ideally be similar to or reduced compared to those of the original CdS NSs due to the competition between electron trapping and electron transfer from CdS to Pt. However, an increase in the amplitudes of  $\tau_1$  and  $\tau_2$  was observed. This suggests that the timescales of  $\tau_1$  and  $\tau_2$  are similar to that of  $\tau_4$ , and thus, the fitting process could not perfectly attribute the electron transfer from CdS to Pt to  $\tau_4$ , resulting in some contribution to  $\tau_1$  and  $\tau_2$ .

Based on this, we consider the difference between  $A_1+A_2+A_4$  for Pt/CdS and  $A_1+A_2$  for CdS to represent the quantity of electrons transferred from CdS to Pt. Consequently, for MPA-capped CdS NSs, the sum of the fast decay amplitudes increased from 52.2% before Pt deposition to 57.4% after Pt deposition, reflecting a 5.2% increase in electron transfer to Pt. In contrast, for cysteamine-capped CdS NSs, the sum of the fast decay amplitudes increased from 58.6% before Pt deposition to 90.1% after Pt deposition, demonstrating a 31.5% increase in electron transfer to Pt. This indicates that electron transfer from CdS to Pt is significantly more pronounced in the cysteamine-capped samples.

## Note 2. Python code for reaction rate simulation

```
import numpy as np
import matplotlib.pyplot as plt
import scipy as sp
from scipy.integrate import odeint
from scipy.integrate import solve_ivp

def dHdt(t,H):
    return k1*(B0*h/(2*k1*t*B0*h**2+1))**(2)-k2*h*H
B0=0.24
k1=5
k2=1
H0 = 0

t = np.linspace(0.1, 20, 100)
h=0.1
sol_m4 = odeint(dHdt, y0=H0, t=t, tfirst=True)
h=0.2
sol_m3 = odeint(dHdt, y0=H0, t=t, tfirst=True)
h=0.5
sol_m2 = odeint(dHdt, y0=H0, t=t, tfirst=True)
h=0.7
sol_m1 = odeint(dHdt, y0=H0, t=t, tfirst=True)

H_sol_m1 = sol_m1.T[0]
H_sol_m2 = sol_m2.T[0]
H_sol_m3 = sol_m3.T[0]
H_sol_m4 = sol_m4.T[0]

plt.figure()
plt.plot(t, H_sol_m1, label='h = 0.7')
plt.plot(t, H_sol_m2, label='h = 0.5')
plt.plot(t, H_sol_m3, label='h = 0.2')
plt.plot(t, H_sol_m4, label='h = 0.1')
plt.xlabel('t')
plt.ylabel('[HB]')
plt.legend()
plt.show()
```