## **Supporting Information**

## Customizing Precise, Tunable, and Universal Cascade Charge Transfer Chain Towards Versatile Photoredox Catalysis

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### **1. Experimental section**

### **1.1 Materials**

Cadmium acetate dihydrate (C<sub>4</sub>H<sub>6</sub>CdO<sub>4</sub> 2H<sub>2</sub>O), Thiourea (CH<sub>4</sub>N<sub>2</sub>S), Hydrofluoric acid (HF 40 wt%), sodium borohydride (NaBH<sub>4</sub>), gold (III) chloride trihydrate (99.9%) hydrogen tetrachloroaurate (III) trihydrate (HAuCl<sub>4</sub> 3H<sub>2</sub>O), sodium tetrachloropalladate (Na<sub>2</sub>PdCl<sub>4</sub>), silver nitrate (AgNO<sub>3</sub>), sodium citrate, sodium chloride (NaCl), selenium (Se) powder, hydrazine hydrate (H<sub>4</sub>N<sub>2</sub> H<sub>2</sub>O  $\geq$  85%), nickel(II) nitrate hexahydrate (Ni(NO<sub>3</sub>)<sub>2</sub> 3H<sub>2</sub>O), cupric nitrate trihydrate (Cu(NO<sub>3</sub>)<sub>2</sub> 3H<sub>2</sub>O), cobaltous nitrate hexahydrate (Co(NO<sub>3</sub>)<sub>2</sub> 6H<sub>2</sub>O), Poly (diallyl-dimethylammonium chloride) (PDDA) (Mw = 200000 g/mol), methanol (CH<sub>4</sub>O), ethanol (C<sub>2</sub>H<sub>6</sub>O), ethylene glycol (C<sub>2</sub>H<sub>6</sub>O<sub>2</sub>), lactic acid (C<sub>3</sub>H<sub>6</sub>O<sub>3</sub>), sodium sulfide nonahydrate (Na<sub>2</sub>S 9H<sub>2</sub>O), sodium sulfite (Na<sub>2</sub>SO<sub>3</sub>), sodium sulfate (Na<sub>2</sub>SO<sub>4</sub>), triethanolamine (TEOA), acetonitrile (C<sub>2</sub>H<sub>3</sub>N), Ammonium formate (CH<sub>3</sub>NO<sub>2</sub>), 4-nitroaniline (4-NA), 3-nitroaniline (3-NA), 2-nitroaniline (2-NA), 3-nitrophenol (3-NP), 2-nitrophenol (2-NP), benzotrifluoride (BTF), benzyl alcohol (BA), *p*-methoxybenzyl alcohol (MOBA), *p*-fluorobenzyl alcohol (FBA), *p*-nitrobenzyl alcohol (NBA), and deionized water (DI H<sub>2</sub>O, Millipore, 18.2 MΩ cm resistivity) are used. All the materials are of analytical grade and used as received without further purification.

### 1.2 Preparation of CdS nano-leaves

Specifically, 5 mmol C<sub>4</sub>H<sub>6</sub>CdO<sub>4</sub> 2H<sub>2</sub>O, 6 mmol CH<sub>4</sub>N<sub>2</sub>S, 0.805 mL HF (40 wt%) and 79.2 mL of deionized water were added into a 100 ml Teflon autoclave to 80% volume. After stirring at room temperature for 1.5 h, the autoclave was sealed and maintained at 200 °C for 20 h, and then air cooled to room temperature. The precipitate obtained was filtered and washed several times with DI H<sub>2</sub>O and absolute ethanol, and then dried in vacuum at 60 °C for 8 h.<sup>1</sup>

### 1.3 Preparation of positively charged CdS@PDDA (C@P)

Pre-selected 0.2 g CdS as the substrate material and weighed PDDA according to its mass ratio, and then dispersed the two samples into 20 mL of 0.5 M NaCl solution and stirred for 1 h. Mixtures were labeled as C@P-X (X: 1, 5, 10, 15, 20 and 25) after centrifugal collection, and then dried in vacuum at 60 °C for 8 h.

### 1.4 Preparation of Negatively charged Au NCs (Au@citrate NCs)

The synthesis of Au NCs capped with negatively charged citrate ions was referred to a previously published method.<sup>2</sup> In brief, all glassware were cleaned thoroughly with aqua regia for 12 h and washed with DI H<sub>2</sub>O. In a 250 mL three flask, 1 mL HAuCl<sub>4</sub>  $3H_2O$  (40 mg/mL) and 99 mL DI H<sub>2</sub>O mixed solution were heated to boil under vigorous stirring (1500 rpm). Subsequently, sodium citrate (10 mL 38.8 mM) aqueous solutions was rapidly added into the gold solution under vigorous stirring (1500 rpm). After 20 s, the mixture became dark and then burgundy; heating was continued with vigorous stirring for 10 min. Finally, the solution was vigorously stirred under ambient conditions for another 15 min to finish the synthetic process. The asprepared Au NCs were stored in a refrigerator at 4  $\,^\circ$ C in a dark area.

## 1.5 Preparation of CdS@Au@citrate NCs (C@Au) and CdS@PDDA15@Au@citrate NCs (C@P15@Au) heterostructures

The construction of C@P@Au heterostructure was achieved by electrostatic self-assembly using C@P15 as the substrate and Au@citrate NCs as the anchoring block. Specifically, Au@citrate NCs aqueous solution was added dropwise to the 0.2 g C@P15 aqueous dispersion according to the mass ratio under vigorous stirring. After mixing for 2 h, the mixtures were centrifuged and labeled as C@P15@Au-X (X: 0.5, 1, 3, 5, 7, 10, 13 and 16), and then dried in vacuum at 60 °C for 8 h.

As a control sample, C@Au7 was prepared in the same way as described above.

### 1.6 Preparation of positively charged Ag NCs (Ag@citrate NCs)

Citrate-stabilized Ag NCs were synthesized based on an aqueous synthesis method reported previously.<sup>3</sup> Typically, 100 mL of a 1 mM aqueous AgNO<sub>3</sub> solution was mixed with 8 mL of a 40 mM aqueous sodium citrate solution used as stabilizer. Subsequently, A total of 2 mL of a 112 mM aqueous NaBH<sub>4</sub> solution was then added dropwise under vigorous stirring (2500 rpm) at ambient temperature, immediately yielding a yellowish brown Ag hydrosol. The Ag hydrosol was stocked in a refrigerator at 4  $\,^{\circ}$ C and aged for 24 h to decompose the residual NaBH<sub>4</sub> before it was used in subsequent steps.

### 1.7 Preparation of positively charged Pt NCs (Pt@citrate NCs)

Similarly, citrate-stabilized Pt NCs were synthesized according to the previously reported water synthesis Elliott's method.<sup>3</sup> In brief, a total of 26 mL of 2.8 mM aqueous sodium citrate solution was added to 50 mL of 0.4 mM aqueous hydrogen hexachloro-platinate solution at room temperature. Subsequently, 5 mL of 12 mM NaBH<sub>4</sub> was introduced dropwise with vigorous stirring (2500 rpm), and the pale-yellow solution turned dark-brown in 5 min. Finally, the dark-brown colloidal solution was stirred for 4 h and stored in a refrigerator at 4 °C until ready for further use.

### 1.8 Preparation of CdS@Ag NCs-7% (C@Ag7), CdS@PDDA15@Ag NCs-7% (C@P15@Au7), CdS@Pt NCs-7% (C@Pt7) and CdS@PDDA15@Pt NCs-7% (C@P15@Pt7) heterostructures

As expanded samples, C@Ag7, C@P15@Ag7, C@Pt7 and C@P15@Pt7 were prepared in the same way as C@P15@Au7, where the reagents used were Ag@citrate NCs and Pt@citrate NCs aqueous solution, respectively.

# 1.9 Preparation of CdS@M (Ni, Co and Cu NCs)-7% (C@M7) and CdS@PDDA15@M (Ni, Co and Cu NCs)-7% (C@P15@M7) heterostructures by photo-deposition method

C@P15@Ni7 was prepared by the photo-deposition method.<sup>4</sup> Briefly, 0.1 g of C@P15 powder was added to a 120 mL aqueous solution containing 25 mL of methanol to sonicate for 0.5 h, and then Ni(NO<sub>3</sub>)<sub>2</sub> 3H<sub>2</sub>O (3.468 mL 10 mg/mL) aqueous solution was injected into the above solution. After that, the suspension was transferred into a reaction bottle (250 mL in capacity), thoroughly degassed by N<sub>2</sub> for 0.5 h to eliminate the air inside the reactant system, and then irradiated by a 300 W Xe lamp ( $\lambda \ge 420$  nm) under continuous magnetic stirring. After reaction for 1 h, a solid sample was obtained through centrifugation, rinsed with pure water and alcohol more than three times, and dried in vacuum at 60 °C for 8 h.

As expanded samples, C@P15@Co7 and C@P15@Cu7 were prepared in the same way as C@P15@Ni7, where the reagents used were Co(NO<sub>3</sub>)<sub>2</sub> 6H<sub>2</sub>O (3.456 ml 10 mg/mL) and Cu(NO<sub>3</sub>)<sub>2</sub> 3H<sub>2</sub>O (2.664 mL 10 mg/mL) aqueous solution, respectively.

Similarly, C@Ni7, C@Co7 and C@Cu7 were prepared in the same way as described above, where the substrate material was chosen as CdS.

### 1.10 Preparation of NiSe2, CoSe2 and CuSe NCs

NiSe<sub>2</sub> NCs were synthesized also with reference to the previously reported method.<sup>5</sup> Specifically, 6.6 mmol selenium (Se) powder was added into 5 mL hydrazine hydrate ( $\geq$  85%) with ultrasonic processing for 0.5 h. Subsequently, 3.3 mmol Ni(NO<sub>3</sub>)<sub>2</sub> 6H<sub>2</sub>O was added to the above solution with ultra-sonication for 0.5 h. The solution was added to 100 ml Teflon autoclave, sealed and maintained at 180 °C for 24 h. After reaction, the black precipitate obtained was filtered and washed several times with DI H<sub>2</sub>O and absolute ethanol, and then dried in vacuum at 60 °C for 8 h.

CoSe<sub>2</sub> and CuSe NCs were synthesized in the same way as NiSe<sub>2</sub> NCs, where the reagents used were Co(NO<sub>3</sub>)<sub>2</sub> 6H<sub>2</sub>O and Cu(NO<sub>3</sub>)<sub>2</sub> 3H<sub>2</sub>O, respectively.

# 1.11 Preparation of CdS@X (NiSe<sub>2</sub>, CoSe<sub>2</sub> and CuSe NCs)-7% and CdS@PDDA@X (NiSe<sub>2</sub>, CoSe<sub>2</sub> and CuSe NCs)-7% heterostructures

Typically, 0.2 g of C@P15 and 0.014 g of NiSe<sub>2</sub> powder were dispersed to 100 mL DI H<sub>2</sub>O and sonicated for 0.5 h. Subsequently, the mixtures were collected by centrifugation after vigorous stirring (1000 rpm) for 2 h and vacuum dried at 60  $^{\circ}$ C for 8 h. Finally, the sample was labeled as C@P15@NiSe<sub>2</sub>7.

As expanded samples, C@P15@CoSe<sub>2</sub>7 and C@P15@CuSe7 were prepared in the same way as C@P15@NiSe<sub>2</sub>7, where the reagents used were CoSe<sub>2</sub> (0.014 g) and CuSe (0.014 g) powder, respectively.

Similarly, C@NiSe<sub>2</sub>7, C@CoSe<sub>2</sub>7 and C@CuSe7 were prepared in the same way as described above,

where the substrate material was chosen as CdS.

### 1.12 Photocatalytic hydrogen evolution

Specifically, 10 mg of the catalyst was dispersed in 6 mL of aqueous solution containing 1 mL of lactic acid as the sacrificial reagent and stirred (1000 rpm) throughout the reaction to ensure that the catalyst was in suspension throughout the experiment. The reaction system was evacuated to eliminate other impurity gases, and the distance between the reactor and the light source was set to 15 cm. Photocatalytic activities were evaluated based on the  $H_2$  evolution amount in the first 2 h of the reaction. The stability of the cycle was tested as follows: the photocatalytic system was completely degassed again after the first run without separating the catalyst and then the next set of light irradiation test was performed.

Apparent quantum yield (A.Q.Y) of the reaction was defined by the following equation:

$$A.Q.Y(\%) = \frac{\text{number of reacted electrons}}{\text{number of incident photons}} \times 100\%$$
(1)
$$= \frac{\text{number of enolved hydrogen molecules} \times 2}{\text{number of incident photons}} \times 100\%$$

Solar-to-hydrogen (S.T.H) efficiency was calculated according to the formula below:

$$S.T.H = \frac{n_{H_2} \text{ (mmol)} \times \triangle G \text{ (KJ/mol)}}{S \text{ (cm}^2) \times P \text{ (mW/cm}^2) \times t \text{ (s)}} \times 100\%$$
(2)

where  $n_{H_2}$  is the amount of H<sub>2</sub> molecules,  $\Delta G$  is the Gibbs free energy per mol of H<sub>2</sub> (at 25 °C,  $\Delta G = 237$  kJ mol<sup>-1</sup>), S is the irradiation area, P is the light intensity, and t is the reaction time.

A.Q.Y and S.T.H values are measured under the same photocatalytic reaction conditions except for using the monochromatic light with different wavelength (i.e., 400, 420, 450, 500, 550, 600, 650, and 700 nm) as the light source. In a typical calculation of A.Q.Y and S.T.H, the number of incident photons is measured using a radiant power energy meter (Perfect light, PLS-MW2000) with an irradiation spot diameter of 2 cm.

### **1.12 Photoreduction performances**

Specifically, 10 mg of catalyst and 40 mg of ammonium formate (NH4HCO2) were mixed with 40 mL of

4-NA aqueous solution (30 ppm) in a glass reactor under N<sub>2</sub> bubbling. After vigorously stirring in dark for 30 min to reach the adsorption-desorption equilibrium, the glass vessel was irradiated by visible light ( $\lambda > 420$  nm). 2 mL of the sample solution was collected at regular time intervals (0, 20, 40, 60, 80 and 100 s), centrifuged (12000 rpm), and the supernatant was analyzed by a UV-vis absorption spectrophotometer. Photoreduction of other aromatic nitro compounds were also carried out under the same conditions. Photoactivities of samples was defined by following formula.

Conversion (%) = 
$$\frac{C_0 - C_{alcohol}}{C_0} \times 100\%$$
 (3)

### 1.13 Selection photocatalytic oxidation performances

Specifically, 8 mg of catalyst was dispersed in a mixed solution of BTF (1.5 mL) bubbled with oxygen before use and aromatic alcohols (0.1 mmol). After vigorously stirring in dark for 20 min to reach the adsorption-desorption equilibrium, the glass vessel was subjected to light irradiation ( $\lambda > 420$  nm) for 4 h and the catalyst was kept in suspension under vigorous stirring (1000 rpm) during the photoreaction. After the reaction, the mixture solution is centrifuged at 12000 rpm to remove the catalyst, and the supernatant is analyzed with a gas chromatograph (SHIMADZU, GC-2014C). Conversion, yield and selectivity of the reaction are calculated by the following formulas.

Conversion (%) = 
$$\frac{C_0 - C_{alcohol}}{C_0} \times 100\%$$
 (4)

Yield (%) = 
$$\frac{C_{aldehyde}}{C_0} \times 100\%$$
 (5)

### 1.14 Photocatalytic CO<sub>2</sub> reduction

Specifically, 10 mg of the catalyst was dispersed in mixed solution (DI H<sub>2</sub>O (2 mL), triethanolamine (TEOA, 3 mL) and C<sub>2</sub>H<sub>3</sub>N (5 mL) and stirred (1000 rpm) throughout the reaction to ensure that the catalyst was in suspension throughout the experiment. The reaction system was evacuated to eliminate other impurity gases. Then, high purity CO<sub>2</sub> was introduced to the reaction system with a partial pressure of 1 atm. After light irradiation ( $\lambda > 420$  nm) for 2 h, the generated products were sampled and quantified by an gas chromatograph

(SHIMADZU, GC-2014C). The stability of the cycle was tested as follows. After the first run, the photocatalytic system was again subjected to complete degassing, introduction of  $CO_2$ , and replenishment of acetonitrile without separating the catalyst, and then the next set of light irradiation tests were performed.

### 1.15 Photoelectrochemical (PEC) measurements

Specifically, 15 mg of the sample was dispersed in 3 mL of ethanol by sonication to get slurry which was spread onto the pretreated FTO glass. After air drying, the Scotch tape was unstuck and the uncoated part of the electrode was isolated with nail polish. The exposed area of the working electrode was 1 cm<sup>2</sup>. Finally, the working electrode was vertically dipped into the electrolyte and irradiated with visible light ( $\lambda > 420$  nm) (PLS-SXE300D, Beijing Perfect Light Co. Ltd., China). Potentials of the electrode were calibrated against the reversible hydrogen electrode (RHE) based on the following formula:

$$E_{\rm RHE} = E_{\rm Ag/AgCl} + 0.059 \text{pH} + E^{\circ}_{\rm Ag/AgCl} (E^{\circ}_{\rm Ag/AgCl} = 0.1976 \text{ V at } 25 \text{ °C})$$
(7)



**Scheme S1.** Schematic flowcharts for fabrication of CdS@PDDA@M (M: Ni, Co, Cu NCs) and CdS@PDDA@X (X: NiSe<sub>2</sub>, CoSe<sub>2</sub>, CuSe NCs) heterostructures.



Figure S1. Zeta potentials ( $\xi$ ) of (a) CdS, C@P15 and Au@cirate NCs and (b) Ag@citrate NCs and Pt@citrate NCs.



Figure S2. Structure model of hexagonal CdS.



Figure S3. UV-vis absorption spectrum of Au@citrate NCs with photograph in the inset.



Figure S4.  $N_2$  adsorption-desorption isotherms & pore size distribution curves (inset) of (a) CdS and (b) C@P15@Au7 heterostructure.



Figure S5. (a-e) XRD patterns of CdS, C@P15@M (M: Ag, Pt)-7, C@P15@M (M: Ni, Co, Cu)-7 and C@P15@X (X: NiSe<sub>2</sub>, CoSe<sub>2</sub>, CuSe)-7 heterostructures.

**Note:** Figure S5a presents the XRD patterns of C@P15@Ag7 and C@P15@Pt heterostructures. The characteristic diffraction peaks of Pt@citrate and Ag@citrate NCs are difficult to be detected due to their low loading. In addition, these characteristic diffraction peaks may be shielded by the substantial peaks of the CdS substrate. Similarly, as shown in Figure S5b, characteristic peaks of Ni, Co, and Cu NCs are not observed in the XRD patterns of C@P15@M7 (M: Ni, Co, Cu NCs) heterostructures due to the same reason. As displayed in Figure S5c, the peaks at 20 of 30.15, 33.68, 37.01, 42.99, 50.94, 55.69, 57.95 and 72.70° can be indexed to (200), (210), (211), (220), (311), (230), (321) and (421) crystal planes of cubic NiSe<sub>2</sub> (PDF# 11-552). Noteworthily, the peaks of NiSe<sub>2</sub> are also observed in the XRD pattern of C@P15@NiSe<sub>2</sub>7, indicating NiSe<sub>2</sub>have been successfully anchored on the C@P15. Analogously, as mirrored in Figure S5d-e, the peaks attributed to CoSe<sub>2</sub> and CuSe are observed in the XRD patterns of C@P15@CoSe<sub>2</sub>7 and C@P15@CuSe7 heterostructures, respectively. In summary, the above analysis strongly confirms the successful preparation of C@P15@X7 (X: Ag, Pt, Ni, Co, Cu, NiSe<sub>2</sub>, CoSe<sub>2</sub>, and CuSe) ternary heterostructures.



**Figure S6.** (a-b) UV-vis absorption spectra of Ag@citrate NCs and Pt@citrate NCs with photographs in the inset.



Figure S7. UV-vis absorption spectrum of PDDA aqueous solution with photograph in the inset.



Figure S8. UV-vis absorption spectra of citrate.



Figure S9. Molecular structure of PDDA.



Figure S10. Molecular structure of citrate.



**Figure S11.** (a) Survey spectra and high-resolution (b) Cd 3d, (c) S 2p, (d) Ag 3d, (e) C 1s and (f) Cl 2p spectra of (I) CdS and (II) C@P15@Ag7 heterostructure.

Note: As displayed in **Figure S9d**, high-resolution of Ag 3d spectrum for C@P15@Ag7 shows two peaks at 373.0 (Ag  $3d_{3/2}$ ) and 367.0 eV (Ag  $3d_{5/2}$ ), which correspond to the Ag<sup>0</sup> and Ag<sup>+</sup> species, respectively, confirming the Ag@citrate NCs deposition on the C@P15. Among them, the appearance of Ag<sup>+</sup> specie may be due to the oxidation of Ag nanoparticles by long-term exposure to air.<sup>6</sup>



**Figure S12.** (a) Survey spectra and high-resolution (b) Cd 3d, (c) S 2p, (d) Pt 4f, (e) C 1s and (f) Cl 2p spectra of (I) CdS and (II) C@P15@Pt7 heterostructure.

**Note:** Figure S12d shows the high-resolution spectrum of Pt 4f for C@P15@Pt7 heterostructure, wherein two peaks at 70.87 (Pt 4f<sub>7/2</sub>) and 74.17 eV (Pt 4f<sub>7/2</sub>) are assigned to Pt<sup>0</sup>, indicating the deposition of Pt@citrate NCs on the C@P15.<sup>7</sup> Alternatively, one doublet of peaks at 72.01(Pt 4f<sub>5/2</sub>) and 75.25 (Pt 4f<sub>7/2</sub>) eV are assigned to partially oxidized Pt<sup> $\delta$ +</sup> (Pt<sup>2+</sup> and Pt<sup>4+</sup>).<sup>8</sup>



**Figure S13.** (a) Survey spectra and high-resolution (b) Cd 3d, (c) S 2p, (d) Ni 2p, (e) C 1s and (f) Cl 2p spectra of (I) CdS and (II) C@P15@Ni7 heterostructure.

**Note:** Figure S13d shows the high-resolution spectrum of Ni 2p for C@P15@Ni7 heterostructure, wherein two peaks at 855.50 (Ni  $2p_{3/2}$ ) and 873.39 eV (Ni  $2p_{1/2}$ ) are assigned to the Ni<sup>2+</sup> species.<sup>9</sup> The other characteristic peaks located at 852.62 (Ni  $2p_{3/2}$ ) and 869.62 eV (Ni  $2p_{1/2}$ ) correspond to the metallic Ni<sup>0</sup>,<sup>10</sup> indicating that we have successfully deposited Ni NCs onto C@P15 using photo-induced reduction.



**Figure S14.** (a) Survey spectra and high-resolution (b) Cd 3d, (c) S 2p, (d) Co 2p, (e) C 1s and (f) Cl 2p spectra of (I) CdS and (II) C@P15@Co7 heterostructure.

**Note:** As depicted in **Figure S14d**, high-resolution Co 2p spectrum of C@P15@Co7 can be deconvoluted into two typical components, 779.1 (Co  $2p_{3/2}$ )/794.4 (Co  $2p_{1/2}$ ) eV and 781.0 (Co  $2p_{3/2}$ )/796.8 (Co  $2p_{1/2}$ ) eV, corresponding to the Co<sup>0</sup> and Co<sup>2+</sup> species, respectively.<sup>11</sup> The Co<sup>0</sup> signal can be observed , proving that Co nanoparticles have been successfully deposited on the C@P15 by photo-induced reduction. The Co<sup>2+</sup> could be attributed to the slight oxidation (CoO) on the surface of Co NCs.



**Figure S15.** (a) Survey spectra and high-resolution (b) Cd 3d, (c) S 2p, (d) Cu 2p, (e) C 1s and (f) Cl 2p spectra of (I) CdS and (II) C@P15@Cu7 heterostructure.

**Note:** High-resolution spectrum of Cu 2p (**Figure S15d**) exhibits two peaks at 930.60 (Cu  $3p_{3/2}$ ) and 951.61 eV (Cu  $2p_{1/2}$ ), wherein the peak centered at 951.61 eV could be assigned to Cu<sup>0.12</sup> The peak at 931.60 eV could be attributed to CuO which might from oxidized Cu NCs after exposure to ambient air.<sup>12</sup> Thus, the result suggests that C@P15@Cu7 heterostructure has been successfully prepared.



**Figure S16.** High-resolution (a) Cd 3d, (b) S 2p, (c) Ni 2p, (d) Se 2d, (e) C 1s and (f) Cl 2p spectra of (I) CdS and (II) C@P15@NiSe<sub>2</sub>7 heterostructure.

**Note:** As shown in **Figure S16c**, high-resolution Ni 2p spectrum of C@P15@NiSe<sub>2</sub>7 is fitted into four characteristic peaks, and the peaks at 855.54 (Ni  $2p_{3/2}$ ) and 873.28 eV (Ni  $2p_{1/2}$ ) are indexed to Ni<sup>2+.9</sup> Moreover, the peaks at 54.20 (Se  $3d_{5/2}$ ) and 54.90 (Se  $3d_{3/2}$ ) eV in the high-resolution Se 2d spectrum (**Figure S16d**) correspond to the Se-metal bonds, and the peak at around 59.4 13 eV are ascribed to the Se-O bond (SeO<sub>x</sub>).<sup>13</sup> Thus, the result suggests that the C@P15@NiSe<sub>2</sub>7 heterostructure has been successfully prepared.



Figure S17. High-resolution (a) Cd 3d, (b) S 2p, (c) Co 2p, (d) Se 2d, (e) C 1s and (f) Cl 2p spectra of (I) CdS and (II) C@P15@CoSe<sub>2</sub>7 heterostructure.

**Note:** As observed in **Figure S17c**, two characteristic peaks at 778.46 (Co  $2p_{3/2}$ ) and 796.27 eV (Co  $2p_{1/2}$ ) in the high-resolution Co 2p spectrum of C@P15@CoSe<sub>2</sub>7 can be ascribed to the Co<sup>2+</sup> species.<sup>14</sup> **Figure S17d** displays the high-resolution Se 2d spectrum, in which the peaks at 54.20 (Se  $3d_{5/2}$ ) and 55.0 eV (Se  $3d_{3/2}$ ), result from the Se-metal bonds. The wide peak at 59.13 eV is assigned to the SeO<sub>x</sub>.<sup>14</sup> Thus, the result suggests that the C@P15@CoSe<sub>2</sub>7 heterostructure has been successfully prepared.



Figure S18. High-resolution (a) Cd 3d, (b) S 2p, (c) Ni 2p, (d) Se 2d, (e) C 1s and (f) Cl 2p spectra of (I) CdS and (II) C@P15@CuSe7 heterostructure.

**Note:** As mirrored in **Figure 18c**, high-resolution Cu 2p spectrum of C@P15@CuSe7 can be deconvoluted into four peaks located at 931.20 (Cu  $3p_{3/2}$ ), 934.10 (Cu  $3p_{3/2}$ ), 951.45 (Cu  $3p_{12}$ ) and 953.97 (Cu  $3p_{1/2}$ ) eV. Among them, the two peaks at 934.10 (Cu  $3p_{3/2}$ ) and 953.97 (Cu  $3p_{1/2}$ ) eV belong to the Cu<sup>2+</sup> species.<sup>15</sup> Likewise, as shown in **Figure S18d**, high-resolution Se 2d spectrum can be divided into two peaks at 54.2 and 55.0 eV, which can be ascribed to the Se<sup>2-</sup> species, proving the formation of Cu-Se bands.<sup>15</sup> Thus, these results suggest that C@P15@CuSe7 heterostructure has been successfully prepared.



Figure S19. EDX images of (a) C@P15 and (b) C@P15@Au7.



Figure S20. (a) HRTEM image of Au@citrate NCs with (b) size distribution histogram.



Figure S21. (a) HRTEM image of Ag@citrate NCs with (b) size distribution histogram.



Figure S22. (a) HRTEM image of Pt@citrate NCs with (b) size distribution histogram.



**Figure S23.** (a) FESEM images of C@P15@Au7 heterostructure with (b) EDS and (c-h) elemental mapping results.



**Figure S24.** (a) FESEM images of C@P15@Ag7 heterostructure with (b) EDS and (c-h) elemental mapping results.



Figure S25. (a) FESEM images of C@P15@Pt7 heterostructure with (b) EDS and (c-h) elemental mapping results.



**Figure S26.** (a) FESEM images of C@P15@Ni7 heterostructure with (b) EDS and (c-h) elemental mapping results.



**Figure S27.** (a) FESEM images of C@P15@Co7 heterostructure with (b) EDS and (c-h) elemental mapping results.



**Figure S28.** (a) FESEM images of C@P15@Cu7 heterostructure with (b) EDS and (c-h) elemental mapping results.



**Figure S29.** (a) FESEM images of C@P15@NiSe<sub>2</sub>7 heterostructure with (b) EDS and (c-i) elemental mapping results.



Figure S30. (a) FESEM images of C@P15@CoSe<sub>2</sub>7 heterostructure with (b) EDS and (c-i) elemental mapping results.



**Figure S31.** (a) FESEM images of C@P15@CuSe7 heterostructure with (b) EDS and (c-i) elemental mapping results.



Figure S32. The contact angle images of CdS, C@Au7 and C@P15@Au7 heterostructures.



Figure S33. TGA curve of C@P15@Au7 heterostructure.



**Figure S34.** Photocatalytic H<sub>2</sub> evolution performances of CdS <sub>VS</sub> CdS-450 °C, C@Au7 <sub>VS</sub> C@Au7-450 °C, and C@P15@Au7 <sub>VS</sub> C@P15@Au7-450 °C heterostructures under visible light irradiation ( $\lambda > 420$  nm).



Figure S35. A.Q.Y result of C@P15@Au7 heterostructure under different monochromatic light irradiation.



Figure S36. (a) Photographs of CdS and (b) C@P15@Au7 heterostructure after cyclic light irradiation.



**Figure S37.** (a) XRD patterns and (b) FTIR spectra of C@P15@Au7 heterostructure (II) before and (III) after cyclic photoreduction reactions.



**Figure S38.** (a) Survey spectra and high-resolution (b) Cd 3d, (c) S 2p, (d) Au 4f, (e) Cl 2p and (f) C 1s spectra of C@P15@Au7 heterostructure (II) before and (III) after cyclic photoreduction reactions.



**Figure S39**. (a) FESEM images, (b-c) low-magnification TEM images, (d-e) HRTEM images, (f) HADF-TEM image and (g) elemental mapping results of C@P15@Au7 heterostructure after cyclic photoreduction reactions.

Note: Figure S39d & e show the HRTEM images of C@P15@Au7 after photoreactions, wherein ultra-thin

PDDA layer is integrated between CdS and Au@citrate NCs, with visible lattice stripes of ca. 0.358 and 0.236

nm corresponding to the (100) and (111) crystal planes of hexagonal CdS and cubic Au NCs, respectively.



**Figure S40.** Photocatalytic activities of C@P15@Au7 heterostructure toward photoreduction of 4-NA under visible light irradiation ( $\lambda > 420$  nm) with and without adding AgNO<sub>3</sub> as an electron scavenger and N<sub>2</sub> bubbling at ambient conditions.



**Figure S41.** Photocatalytic activities of C@P15@Au7 and C@P15@Au7-450 °C heterostructures toward photoreduction of 4-NA under visible light irradiation ( $\lambda > 420$  nm) with the addition of ammonium formate as hole scavenger and N<sub>2</sub> bubbling at ambient conditions.



**Figure S42.** Photocatalytic CO<sub>2</sub> reduction performances of C@P15@Au7 and C@P15@Au7-450 °C heterostructures under visible light irradiation ( $\lambda > 420$  nm).



**Figure S43.** Photocatalytic activities of CdS, C@Au7 and C@P15@Au7 heterostructures towards selective oxidation of a series of aromatic alcohols to aldehydes under visible light irradiation ( $\lambda > 420$  nm), including (a) benzyl alcohol, (b) p-methoxybenzyl alcohol, (c) p-fluorobenzyl alcohol and (d) p-nitrobenzyl alcohol, along with (e) reaction model under current experimental conditions.



**Figure S44.** Conversion of BA and yield of BAD over C@P15@Au7 heterostructures on adding different scavengers under visible light irradiation ( $\lambda > 420$  nm).



Figure S45. Mott-Schottky plots of C@Au7 and C@P15@Au7 heterostructures (1500 Hz).



**Figure S46.** (a & b) TA spectra of C@Au7 and C@P15@Au7 heterostructures recorded at several representative time delays.



**Figure S47.** (a) Mott-Schottky plots of CdS along with (b) transformed plots based on the Kubelka-Munk function vs. the energy of light for CdS and (c) energy level diagram of CdS.



Figure S48. Schematic illustration of the charge migration mechanism.

**Note:** Upon light irradiation, free electrons over CdS could partly transfer from the bulk to the surface due to unsaturated dangling bonds and sudden breakage of the periodic lattice on the surface.<sup>16</sup> The surface electron accumulation leads to the band bending of CdS and formation of built-in electric field due to the uneven space charge distribution, the direction of which is directed from the bulk to the surface.<sup>17</sup> However, the structure is detrimental to the electrons transfer from the bulk CdS to the surface, thus limiting the photoactivity. In order to break this dilemma, we choose PDDA to encapsulate the CdS substrate. As an electron traction "pump", PDDA shows the powerful electron-withdrawing ability, which can extract the electrons enriched on the CdS surface in time, thus effectively eliminating the influence of built-in electric field.



Figure S49. Photocatalytic mechanism of hydrogenation of nitroaromatics.

**Note:** According to the previous works,<sup>18,19</sup> there are two possible pathways for photocatalytic reduction of aromatic nitro compounds, which involve direct and indirect reaction pathways. The direct route involves gradual formation of nitrosobenzene (Ph-NO), phenylhydroxylamine (Ph-NHOH) and finally aniline (Ph-NH<sub>2</sub>), following three consecutive hydrogenation steps. The second pathway, commonly named indirect or condensation route, involves the condensation of nitrosobenzene (Ph-N=NO-Ph), sequence azo (R-N=N-R), hydrazo (R-NH-NH-R), and finally aniline.



**Figure S50.** Schematic illustration for (a) CO<sub>2</sub> photoreduction into CO and CH<sub>4</sub> through the use of metal-site M (Au & Cd) and (b) carbene generation pathway.

**Note:** Adsorption and activation of CO<sub>2</sub> molecules on catalyst surface are the critical kinetic factors in producing solar fuels. As shown in **Figure S50a**, metal sites M (Cd & Au) tends to bond weakly with the sole C or O atom of adsorbed CO<sub>2</sub>, which produces a series of reactive intermediates. Compared with the highly stable C=O bonds, the relatively weak M-C or M-O bonds are easily cleaved, facilitating the formation of free CO molecules as well as hydrocarbon species such CH<sub>4</sub> after protonation. At present, the possible CO<sub>2</sub> reduction pathway of carbene-pathway (fast deoxygenation pathway) is generally accepted (as depicted in **Figure S50b**).<sup>20,21</sup> The CO<sub>2</sub> reduction reaction may undergo the route of CO<sub>2</sub>·-→CO→C·→CH<sub>3</sub>·→CH<sub>4</sub>, which is characteristic of first deoxygenation reaction and then hydrogenation reaction. In carbene pathway, intermediate CO is commonly prone to desorb and transforms to the final product due to the weak affinity between photocatalyst surface and CO product.<sup>22</sup> Besides, CO can act as an intermediate to further interact with protons and electrons to form CH<sub>4</sub> when the surface atoms of photocatalyst demonstrates strong CO adsorption capacity. The above analysis is consistent with the CO<sub>2</sub> reduction products actually detected by us, which confirms that the whole reduction reaction follows the carbine pathway.



Figure S51. Schematic depicting photooxidation mechanism of the C@P15@Au7 heterostructures.

**Note:** It is worth noting that photoelectrons enriched on the Au@citrate NCs surface can directly combine with the dissolved  $O_2$  molecules to engender superoxide ( $O_2^-$ ) radicals [ $E(O_2/O_2^-) = -0.284 \text{ V} vs.$  NHE] in terms of suitable energy level position of CdS.<sup>23</sup> The thus-formed  $O_2^-$  radicals take part in the photocatalytic oxidation of aromatic alcohols to aldehydes and then attack the carbon radicals to form the intermediate, for which the interaction between the C-O bonds of alcohol and O-O bonds of dioxygen may be synergistically realized through the oxygen-bridged structure.<sup>24</sup> Furthermore, holes in the VB of CdS can also directly oxidize the aromatic alcohols to aldehydes considering their high oxidation capability, fulfilling the photocatalytic selective oxidation process.

Peak position (cm <sup>-1</sup> )	Vibrational mode	Functional groups/Ingredient
1387	δ <sub>C-H</sub>	-CH- & -CH <sub>3</sub> <sup>25</sup>
1633	δ <sub>0-H</sub>	O-H <sup>25</sup>
2855 & 2923	₽с-н	-CH2- <sup>25</sup>
3426	υ <sub>Ο-Η</sub>	О-Н <sup>25</sup>

 Table S1. Peak position with corresponding functional group.

v: Stretching vibration.

 $\delta$ : Deformation vibration.

Table S2. Summary of specific surface area, pore volume and pore size of CdS and C@P15@Au7.

Samples	$S_{BET} (m^2 g^{-1})^a$	Total pore volume (cm <sup>3</sup> g <sup>-1</sup> ) <sup>b</sup>	Average pore size (nm) <sup>c</sup>
CdS	4.325	0.006	6.548
C@P15@Au7	3.587	0.006	7.214

<sup>a</sup> BET surface area is calculated from the linear part of BET plot.

<sup>b</sup> Single point total pore volume of the pores at  $P/P_0 = 0.95$ .

<sup>c</sup> Adsorption average pore width (4V/A by BET).

Element	CdS	C@P15@Au7	Chemical Bond Species
C 1s A	284.8	284.8	C-C <sup>26</sup>
C 1s B	286.7	286.2	C-O <sup>26</sup>
C 1s B	288.46	288.0	C=O <sup>26</sup>
Cd 3d <sub>5/2</sub>	405.32	404.70	Cd <sup>2+ 27</sup>
Cd 3d <sub>3/2</sub>	412.0	411.38	Cd <sup>2+ 27</sup>
S 2p <sub>3/2</sub>	161.74	162.91	S <sup>2- 28</sup>
S 2p <sub>1/2</sub>	161.08	162.25	S <sup>2- 28</sup>
Au 4f7/2	N.D.	82.83	Au <sup>0 2</sup>
Au 4f <sub>5/2</sub>	N.D.	86.58	Au <sup>0 2</sup>
Cl 2p <sub>3/2</sub>	N.D.	198.0	Cl <sup>- 29</sup>
Cl 2p <sub>1/2</sub>	N.D.	199.86	Cl <sup>- 29</sup>

Table S3. Chemical bond species vs. B.E. for CdS and C@P15@Au7.

Element	C@P15@Ag7	C@P15@Pt7	Chemical Bond Species
C 1s A	284.8	284.8	C-C <sup>26</sup>
C 1s B	286.0	286.2	C-O <sup>26</sup>
C 1s B	288.42	288.22	C=O <sup>26</sup>
Cd 3d <sub>5/2</sub>	404.65	405.0	Cd <sup>2+ 27</sup>
Cd 3d <sub>3/2</sub>	411.38	411.78	Cd <sup>2+ 27</sup>
S 2p <sub>3/2</sub>	160.96	161.22	S <sup>2- 28</sup>
S 2p <sub>1/2</sub>	162.13	162.33	S <sup>2- 28</sup>
Ag 3d5/2	367.0	N.D.	Ag <sup>0 6</sup>
Ag 3d <sub>3/2</sub>	373.0	N.D.	Ag <sup>+ 6</sup>
Pt 4f7/2	N.D.	70.87	Pt <sup>0</sup> <sup>7</sup>
Pt 4f <sub>7/2</sub>	N.D.	74.17	Pt <sup>0 7</sup>
Pt 4f5/2	N.D.	72.01	Pt <sup>2+ 8</sup>
Pt 4f5/2	N.D.	75.25	Pt <sup>4+ 9</sup>
Cl 2p3/2	197.97	198.10	Cl <sup>- 29</sup>
Cl 2p1/2	199.60	199.65	Cl <sup>- 29</sup>

Table S4. Chemical bond species vs. B.E. for C@P15@Ag7 and C@P15@Pt7.

Element	C@P15@Ni7	C@P15@Co7	C@P15@Cu7	Chemical Bond Species
C 1s A	284.8	284.8	284.8	C-C <sup>26</sup>
C 1s B	286.2	286.2	286.28	C-O <sup>26</sup>
C 1s B	288.28	288.12	288.23	C=O <sup>26</sup>
Cd 3d <sub>5/2</sub>	404.84	404.83	404.75	Cd <sup>2+ 27</sup>
Cd 3d <sub>3/2</sub>	411.59	411.59	411.49	Cd <sup>2+27</sup>
S 2p <sub>3/2</sub>	161.25	161.30	161.28	S <sup>2- 28</sup>
S 2p <sub>1/2</sub>	162.38	162.46	162.34	S <sup>2- 28</sup>
Ni 2p <sub>3/2</sub>	852.62	N.D.	N.D.	Ni <sup>0 10</sup>
Ni 2p <sub>3/2</sub>	855.50	N.D.	N.D.	Ni <sup>2+ 9</sup>
Ni 2p1/2	869.62	N.D.	N.D.	Ni <sup>0 10</sup>
Ni 2p <sub>1/2</sub>	873.39	N.D.	N.D.	Ni <sup>2+ 9</sup>
Co 2p3/2	N.D.	779.10	N.D.	Co <sup>0 11</sup>
Co 2p3/2	N.D.	781.0	N.D.	Co <sup>2+ 11</sup>
Co 2p1/2	N.D.	794.4	N.D.	Co <sup>0 11</sup>
Co 2p1/2	N.D.	796.8	N.D.	Co <sup>2+ 11</sup>
Cu 2p <sub>3/2</sub>	N.D.	N.D.	931.60	Cu-O <sup>12</sup>
Cu 2p1/2	N.D.	N.D.	951.61	Cu <sup>0</sup> <sup>12</sup>
Cl 2p <sub>3/2</sub>	198.20	198.0	198.0	Cl <sup>- 29</sup>
Cl 2p1/2	200.0	199.86	199.93	Cl <sup>- 29</sup>

Table S5. Chemical bond species vs. B.E. for C@P15@Ni7, C@P15@Co7 and C@P15@Cu7.

Element	C@P15@NiSe <sub>2</sub> 7	C@P15@CoSe27	C@P15@CuSe7	Chemical Bond
				Species
C 1s A	284.8	284.8	284.8	C-C <sup>26</sup>
C 1s B	286.2	286.25	286.3	C-O <sup>26</sup>
Cd 3d <sub>5/2</sub>	404.94	404.93	404.79	Cd <sup>2+ 27</sup>
Cd 3d <sub>3/2</sub>	411.70	411.68	411.56	Cd <sup>2+ 27</sup>
S 2p <sub>3/2</sub>	161.44	161.39	161.30	S <sup>2-28</sup>
S 2p <sub>1/2</sub>	162.55	162.53	162.41	S <sup>2-28</sup>
Ni 2p <sub>3/2</sub>	855.54	N.D.	N.D.	Ni <sup>2+ 9</sup>
Ni 2p <sub>1/2</sub>	873.28	N.D.	N.D.	Ni <sup>2+ 9</sup>
Co 2p <sub>3/2</sub>	N.D.	778.46	N.D.	Co <sup>2+ 14</sup>
Co 2p <sub>1/2</sub>	N.D.	796.27	N.D.	Co <sup>2+ 14</sup>
Cu 2p <sub>3/2</sub>	N.D.	N.D.	934.10	Cu <sup>2+ 15</sup>
Cu 2p1/2	N.D.	N.D.	953.97	Cu <sup>2+ 15</sup>
Se 3d5/2	54.20	54.20	54.20	Se-M <sup>13-15</sup>
Se 3d <sub>3/2</sub>	54.90	55.0	55.0	Se-M <sup>13-15</sup>
SeOx	59.13	59.13	N.D.	Se-O <sup>14</sup>
Cl 2p <sub>3/2</sub>	198.25	198.35	198.10	Cl <sup>- 29</sup>
Cl 2p <sub>1/2</sub>	200.0	200.0	199.97	Cl <sup>- 29</sup>

Table S6. Chemical bond species vs. B.E. for C@P15@NiSe<sub>2</sub>7, C@P15@CoSe<sub>2</sub>7 and C@P15@CuSe7.

Samples	Wavelength (nm)	Activity (µmol·g <sup>-1</sup> h <sup>-1</sup> )	A.Q.Y(%)
	400	5.846	9.743
	420	13.556	26.241
	450	12.717	26.914
C@P15@Au7	500	22.910	26.795
	520	1.675	1.760
	550	0	0
	600	0	0
	650	0	0
	700	0	0

Table S7. A.Q.Y results of C@P15@Au7.

Table S8. Fitted EIS results of different samples under visible light irradiation based on the equivalent circuit.

Samples	R <sub>s</sub> /ohm	R <sub>ct</sub> /ohm	CPE /(F·cm <sup>-2</sup> )
C@Au7	22.45	4698	1.951E-5
C@P15@Au7	21.85	3158	3.325E-5

Note: As shown in Table S8,  $R_{ct}$  values were obtained by fitting the EIS results according to a simple equivalent circuit composed of a series of resistance (Figure 6b, inset). Apparently, C@P15@Au7 demonstrates the smallest  $R_{ct}$  value in comparison with other counterparts, indicative its lowest interfacial charge transfer resistance.

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