Supporting Information

Bifunctional carbon dots as cocatalyst and reactor decorated organic photocatalyst for H₂ production from water-splitting in emulsion

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1. Supplementary Text

S1 Synthesis of p(DB) organic photocatalyst and x% CDs/p(DB)

For p(DB), A mixture of 5,11-dihydroindolo[3,2-b] carbazole (1.02 g, 4 mmol), NaH (288 mg, 12 mmol), and degassed o-xylene (30mL) was stirred at 120 ℃ for 1 h. Then, 1, 2-bis(4-bromophenyl) ethane (2.72 g, 8 mmol) was added into this mixture. The resultant mixture was transferred to a flask and immersed in a preheated oil bath, which was maintained at 140 ℃ for 48 h under constant stirring. The polymerization was quenched by adding 15 mL methanol. After cooling to room temperature, the mixture was filtered using deionized water and the residue was further washed by deionized water for several times. A brown product ploy(5,11-dihydroindolo[3,2-b] carbazole-1, 2-bis(4-bromophenyl) ethane) was obtained by vacuum drying and the sample was named p(DB).

For x% CDs/p(DB), different mass ratio of p(DB) and CDs (100:1, 100:3, 100:5 and 100:7) were added to 100 mL ethanol, then ultrasonic treated for 10 min to mix them evenly. After that, the solution was stirred at 65 ℃ for 5 h. Finally, the yellowish green powder was dried at 60 ℃ after washed with deionized water. According to the mass ratio of CDs and p(DB), the samples are named with x% CDs/p(DB) (x = 1, 3, 5 and 7).

S2 The experimental method of transient photovoltage (TPV)

The TPV measurements were conducted under room temperature on platinum net covered with power sample (1 cm × 1 cm) as the working electrodes and Pt wire as the counter electrodes. The *in-situ* TPV measurements were carried out under room temperature with indium-tin oxide (ITO) glass (1 cm × 2 cm) as the working electrodes and Pt wire as the counter electrodes. The working electrodes were prepared by depositing samples (100 μL, 2 mg mL^{-1}, dispersion liquid: 79.5% water, 20% isopropanol and 0.5% Nafion solution(v/v), respectively) on ITO glass substrates. During the testing process, the working electrodes were kept wet with anhydrous acetonitrile (or adding H_2O, N_2 saturated). The samples were excited by a laser radiation pulse (λ = 355 nm, pulse width 5 ns) from a third-harmonic Nd: YAG laser (Polaris II, New Wave Research, Inc.). The photocurrent is the ratio of the photovoltage to the internal resistance of the test system.

S3 Photocatalytic reactions

In non-emulsion catalytic system, 10 mg p(DB), x% CDs/p(DB) or CDs was added into 20 mL ultra-pure water and the mixture was ultrasonic treated for 10 min, making the catalysts disperse uniformly. Then, the mixture was transferred to a 40 mL glass bottle. After being sealed, the bottle was irradiated under visible light (420 nm $\leq \lambda \leq$ 700 nm, light intensity = 86.17 mW/cm^2).

In emulsion catalytic system, for p(DB), 10 mg p(DB) was mixed with 2.5 mL o-xylene and treated with ultrasonic to form a uniform solution. After that, 20 mL ultra-pure water and different mass of SDS (0, 10, 25, 50, 75, or 100 mg) were added into the solution. For x% CDs/p(DB), 10 mg x% CDs/p(DB) was mixed with 2.5 mL o-xylene and treated with ultrasonic to form a uniform solution. After that, 20 mL ultra-pure water was added into the solution. Then, the mixture was treated with ultrasonic and stirred for 10 min to form the emulsion. Afterwards, the emulsion was transferred to a 40 mL glass bottle. After being sealed, the bottle was irradiated under the same condition mentioned above. For CDs, 10 mg p(DB) was mixed with 2.5 mL o-xylene and treated with ultrasonic. After that, 20 mL ultra-pure water were added into the solution. Then, the mixture was treated with ultrasonic and stirred for 10 min and transferred to a 40 mL glass bottle. After being sealed, the bottle was irradiated under the same condition mentioned above.

S4 Material Characterization

Powder X-ray diffractometer (Empyrean, Holland Panalytical) and Cu K radiation (40 mA, 40 kV) were used to obtain the powder X-ray diffractometer and analyze the crystal structure of the material. The Zeiss Gemini 500 field emission scanning electron microscope (SEM) was used to record the surface morphology of the material. TEM images and HRTEM images were collected using an FEI-Titan G2 80-200 Chemi scanning transmission electron microscope with an accelerating voltage of 200 kV. Fourier transform infrared (FTIR) spectrum of the sample was collected by a Hyperion spectrophotometer (Bruker). X-ray photoelectron spectroscopy (XPS) measurement uses monochromatic Mg Kα rays to emit x-rays (*hv* = 1,253.6 eV). Ultraviolet/visible/near-infrared spectrophotometer (750, Perkinelmer) was used to measure the ultraviolet-visible absorption spectrum in the wavelength range of 200-800 nm. All electrochemical tests are performed on a CHI 760E

electrochemical workstation (CH Instruments, Shanghai, China), using a standard three-electrode system, in which a saturated calomel electrode (SCE) is used as the reference electrode, a glassy carbon (GC) electrode as the working electrode and the carbon electrode is used as the counter electrode. Dynamic light scattering (DLS) measurements were performed on a ζ potential instrument (Malvern, Nano ZS90). Contact angle (CA) was measured at the Contact Angle Meter (DataPhysics OCA).

S5 Electrochemical measurements for the determination of HOMO and LUMO

Cyclic voltammetry (CV) was operated using a standard three-electrode system with CHI 760E workstation (CH Instruments, Shanghai). A carbon electrode and a saturated calomel electrode (SCE) were used as the counter electrode and the reference electrode, respectively. A glassy carbon (GC) electrode (3 mm diameter) was used as the working electrode and was thoroughly cleaned by polishing to mirror finish, and dried before further use. 4 μL catalyst solution (2 mg mL^{-1}) and 5 μL of 0.5 wt % Nafion solution were dropped onto the working area of a cleaned GC electrode and put naturally to dry. The CV curves were measured in N_2-saturated 0.1M BMIMPF6 acetonitrile solution with a scan rate of 50 mV s^{-1}. Ferrocene was added into the above solution as an internal standard with a concentration of 1 mg mL^{-1}. The HOMO and LUMO energy levels were calculated from the onset oxidation (E_{onset}^{OX}) reduction (E_{onset}^{RED}) potential and the reference energy level for ferrocene (4.8 eV below the vacuum level) as determined by CV according to the equations:

$$E_{HOMO} = -\left(E_{onset}^{OX} - E_{Fc} + 4.8\right) eV \tag{1}$$

$$E_{LUMO} = -\left(E_{onset}^{RED} - E_{Fc} + 4.8\right) eV \tag{2}$$

Where E_{Fc} is the onset of the oxidation potential (vs. SCE) of ferrocene.

S6 Calculation of apparent quantum yield (AQY)

For apparent quantum yield (AQY) valuations, 10 mg 5% CDs/p(DB) was mixed with 2.5 mL o-xylene and treated with ultrasonic to form a uniform solution. Then, 20 mL ultra-pure water and a stir bar were added into the solutions. Afterwards, the system was sealed and the vials were set under constant stirring and irradiated by light-emitting diodes with different wavelengths (λ = 365, 420, 500, 590 or 630 nm) for 8 h. The yield of H_2 was determined by a gas chromatograph (EWAI, GC 4000-

A). The average intensity of irradiation was determined by an ILT 950 spectroradiometer (International Light Technologies) and the irradiation area was 11.2 cm^2. The number of incident photons (N) is calculated by Eq. (3)

$$N = {E\lambda}/{hc} \tag{3}$$

In Eq. (4), E is the average intensity of irradiation, λ stands for the wavelength of the irradiation, h represents the Planck constant and c is the speed of light.

The quantum efficiency is calculated from Eq. (4).

$$AQY = \frac{2 \times number\ of\ H_2\ molecules}{number\ of\ incident\ photons} \tag{4}$$

S7 Transient photocurrent responses (TPR) measurement

The TPR measurement was conducted with a three electrodes system. The test was performed at the open circuit potential with a 30-second light on/off cycle ($\lambda \geq 420$ nm). Typically, L-type glassy carbon electrodes were used as the working electrodes, which were loaded with p(DB) and x% CDs/p(DB) (100 μg cm^{-2}). The carbon rod was treated as the counter electrode and the saturated calomel electrode (SCE) was used as the reference electrode.

S8 Electrochemical impedance spectroscopy (EIS) measurement

The EIS was measured in a water solution with a three electrodes system at the open circuit potential. The glassy carbon electrode (GCE) coated with different catalysts (100 μg·cm^{-2}) was used as the working electrode. The carbon rod and saturated calomel electrode (SCE) were served as the counter electrode and the reference electrode, respectively. High frequency: 10^6 Hz, low frequency: 0.01 Hz.

S9 The electron transfer number measurements

The electron transfer number of water oxidation reaction was characterized by rotating disk-ring electrodes (RRDE) testing system (RRDE-3A, ALS Co., Ltd). In N$_2$-saturated 0.1 M Na$_2$SO$_4$ solution, the *i-t* curve was tested at the scan rate of 10 mV s^{-1} with the rotating speed of 1600 rpm. The disk potential was set at OCP to avoid water oxidation during photochemical and electrochemical catalysis

process. The ring potential was kept at 0.9 V *vs*. SCE, which can oxidize the generated H_2O_2 from the disk into O_2. Finally, n is obtained by the following formula:

$$n = \frac{4\Delta I_d}{\Delta I_d + \dfrac{\Delta I_r}{N}} \tag{5}$$

Here, I_d represents the disk current and I_r represents the ring current, while N is the RRDE collection efficiency determined to be 0.40.
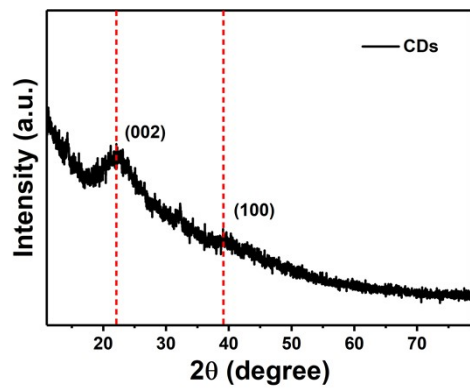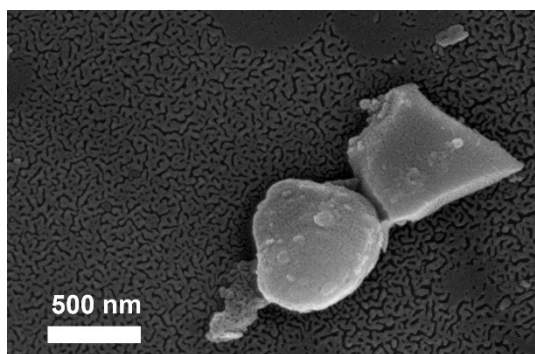
2. Supplementary Figures
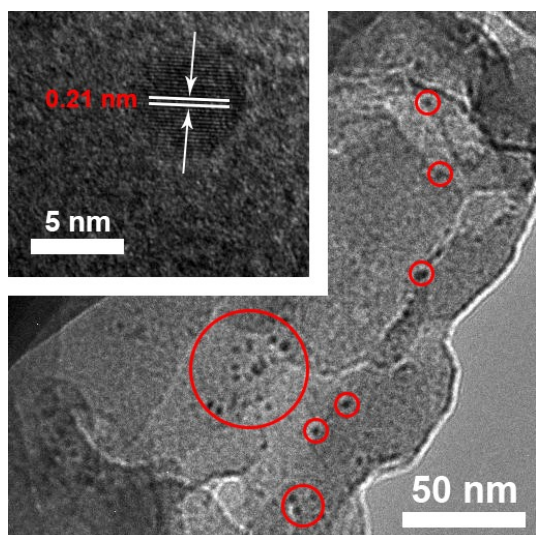

Figure S1. XRD patterns of CDs.

Figure S2. SEM image of p(DB).

Figure S3. TEM image of 5% CDs/p(DB) (inset: HRTEM image of the CDs on the surface of p(DB)).
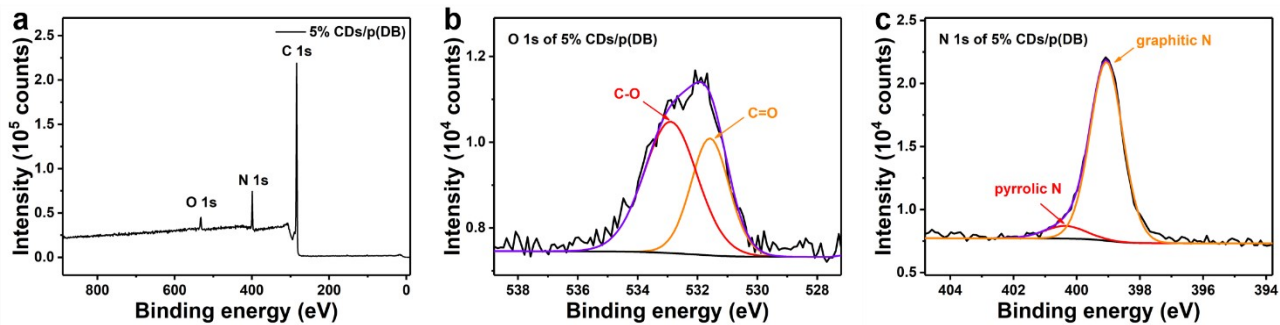
Figure S4. The XPS survey spectra of 5% CDs/p(DB). (a) The full XPS spectrum. (b) The O 1s spectra. And (c) The N 1s spectra.
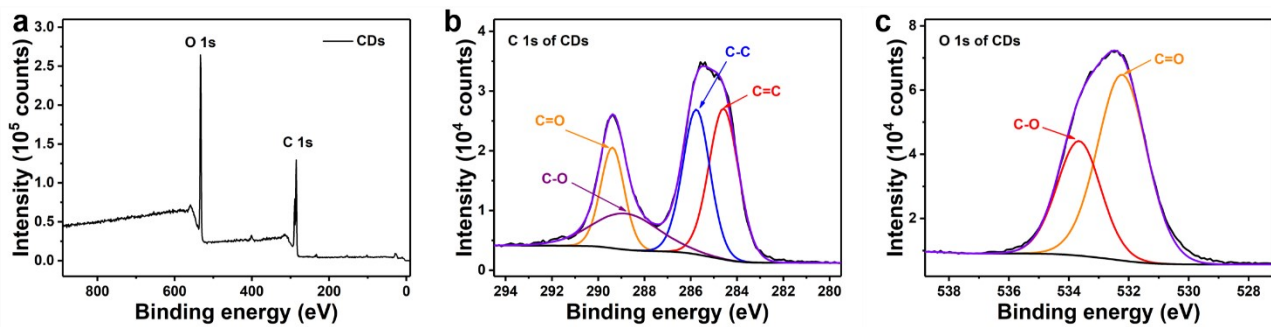
Figure S5. The XPS survey spectra of CDs. (a) The full XPS spectrum. (b) The C 1s spectra. And (c) The O 1s spectra.
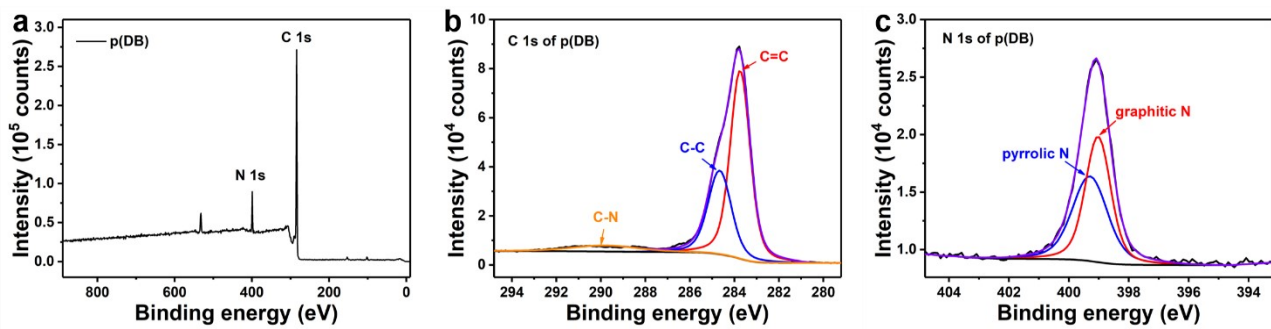
Figure S6. The XPS survey spectra of p(DB). (a) The full XPS spectrum. (b) The C 1s spectra. And (c) The N 1s spectra.
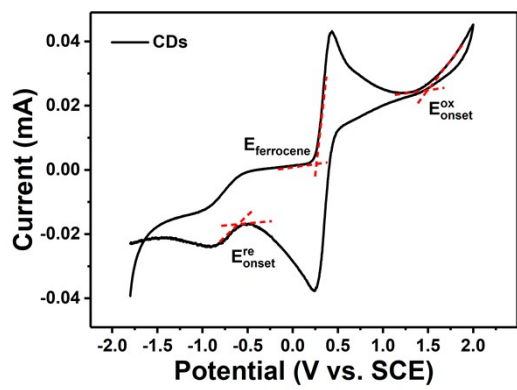
Figure S7. The CV curves of CDs.
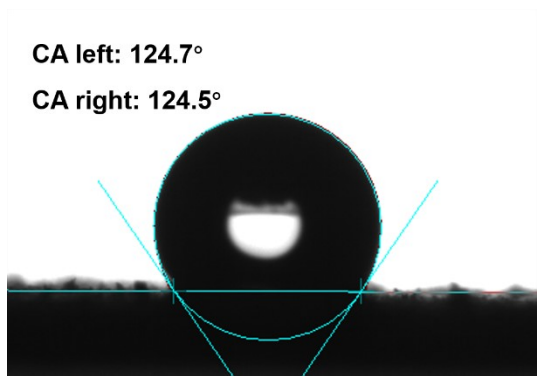
Figure S8. The CA of p(DB) with water.
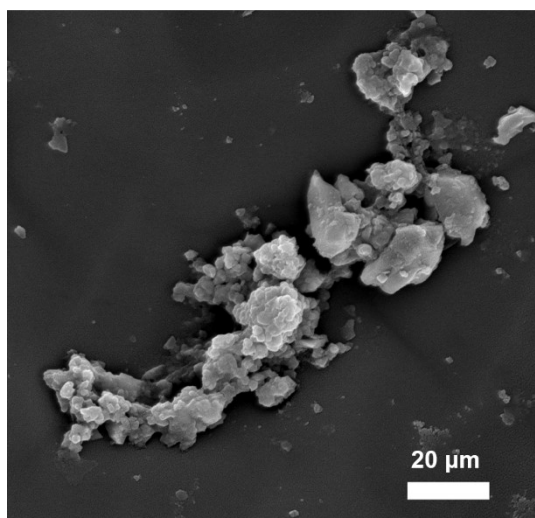
Figure S9. SEM image of p(DB) after dispersing it in water and drying.
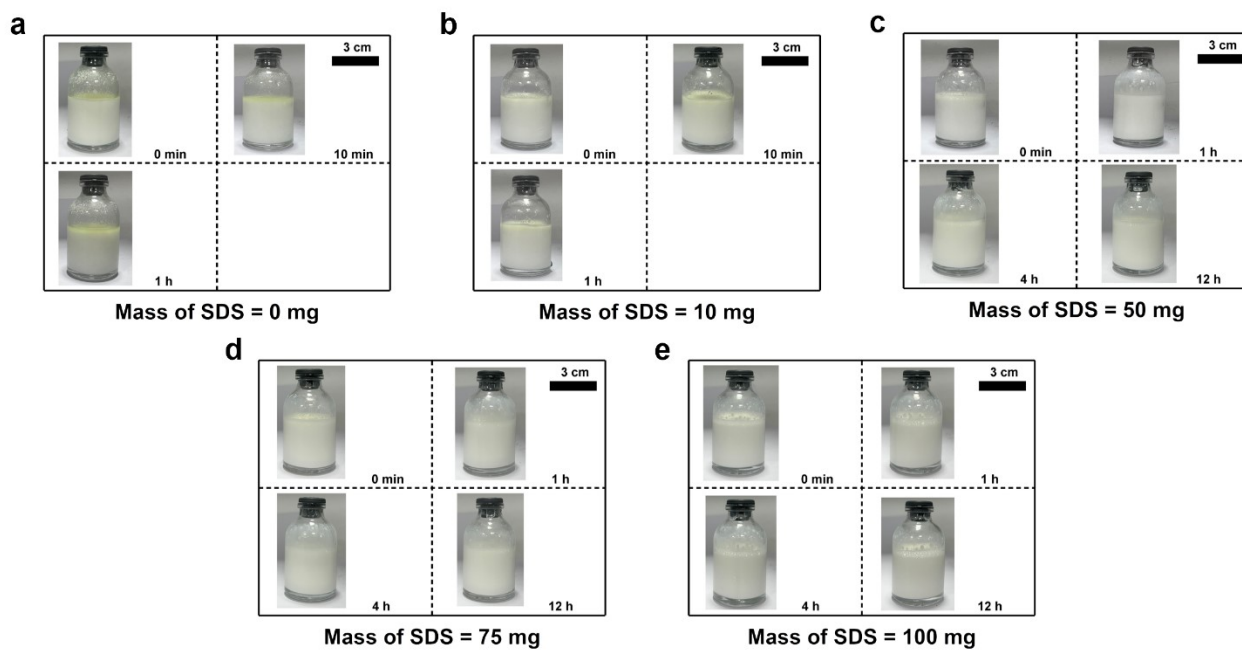
Figure S10. The photographs of p(DB) in o-xylene-in-water emulsion with different times when adding with different masses of SDS. (a) 0 mg, (b) 10 mg, (c) 75 mg, and (d) 100 mg. (The emulsions were continuously stirred at 180 rpm.)
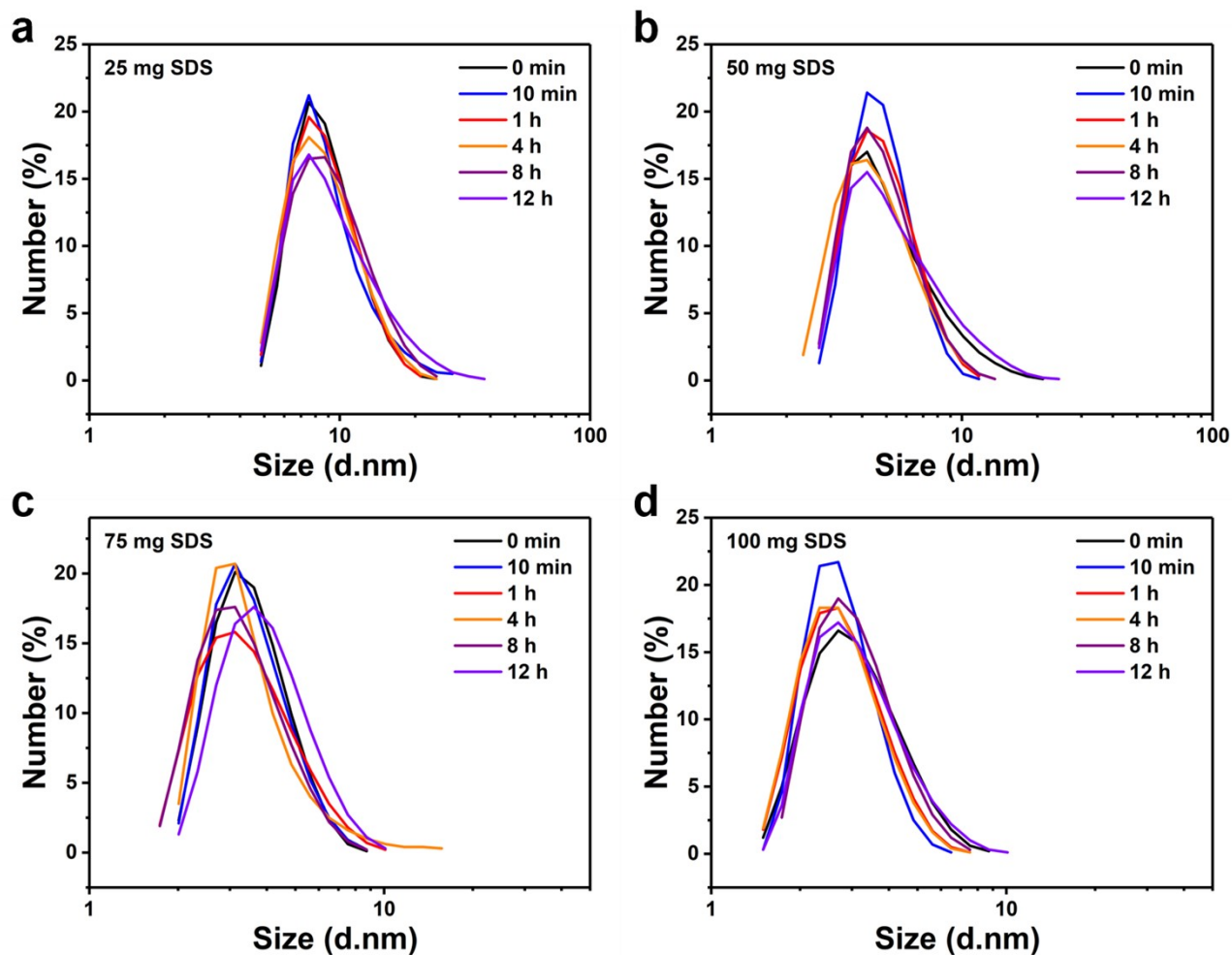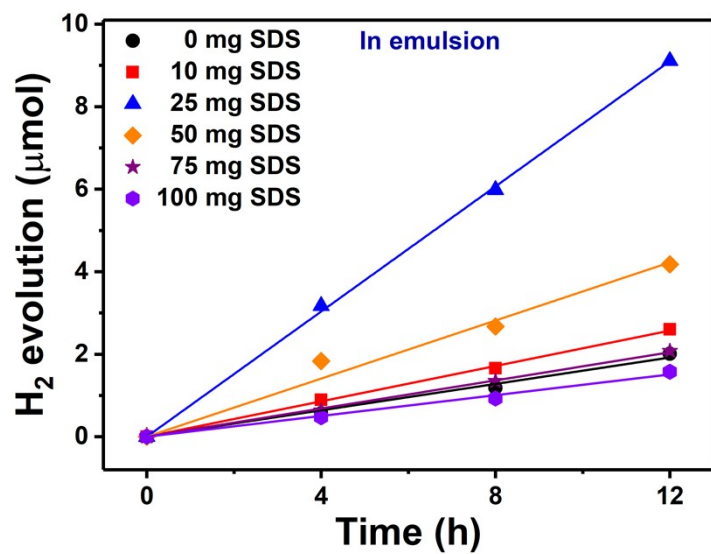
Figure S11. The droplet sizes of p(DB) in o-xylene-in-water emulsion with different times when adding different masses of SDS. (a) 25 mg, (b) 50 mg, (c) 75 mg, and (d) 100 mg. (The emulsions were continuously stirred at 180 rpm.)

Figure S12. The production of H$_2$ *verse* time of p(DB) in water-in-o-xylene emulsion with the change of the mass of SDS.
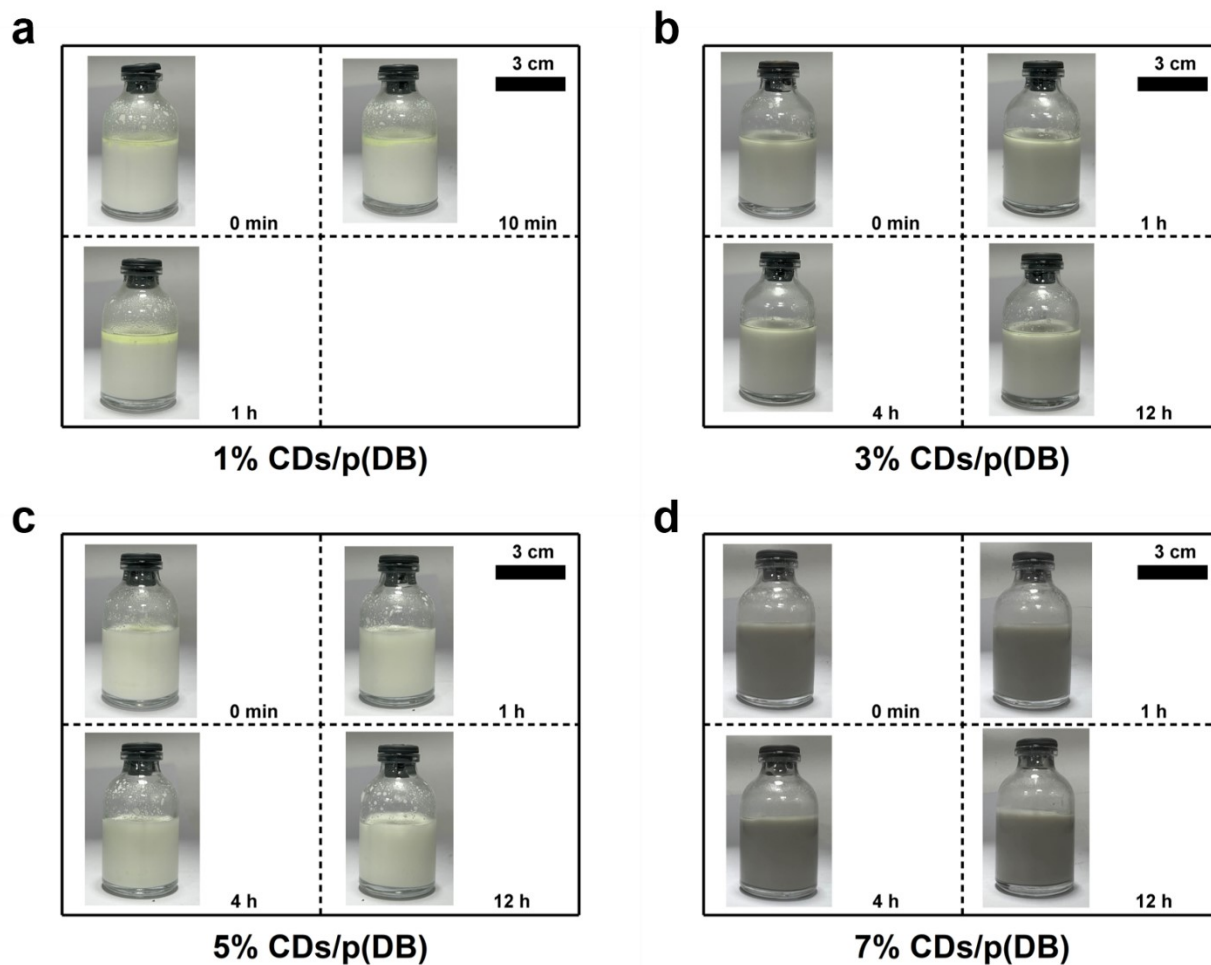
Figure S13. The photographs of x% CDs/p(DB) in o-xylene-in-water emulsion with different times. (a) 1%, (b) 3%, (c) 5%, and (d) 7%. (The emulsions were continuously stirred at 180 rpm.)
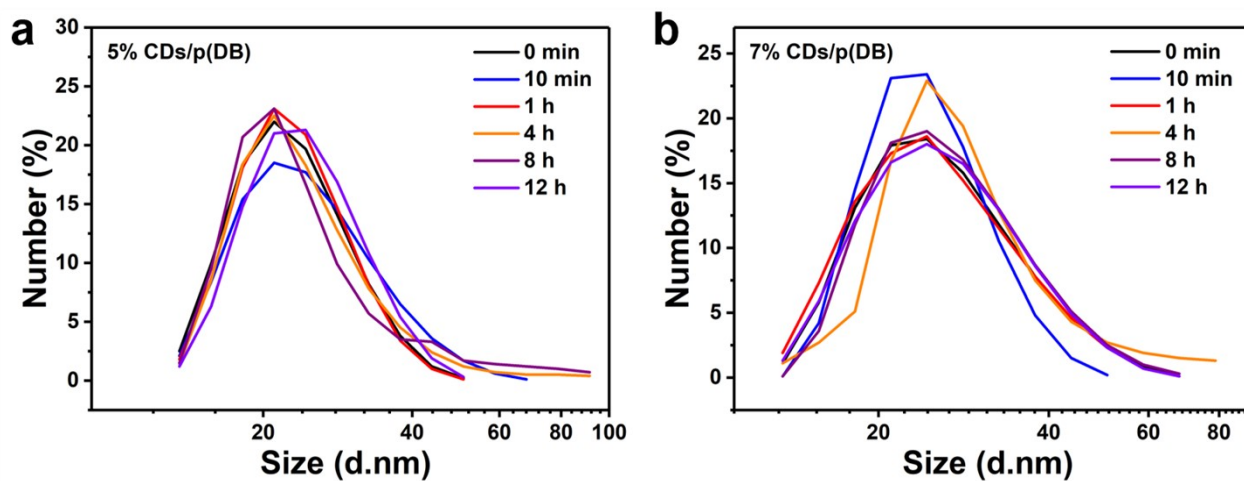
Figure S14. The droplet sizes of x% CDs/p(DB) in o-xylene-in-water emulsion with different times. (a) 5%, and (b) 7%. (The emulsions were continuously stirred at 180 rpm.)
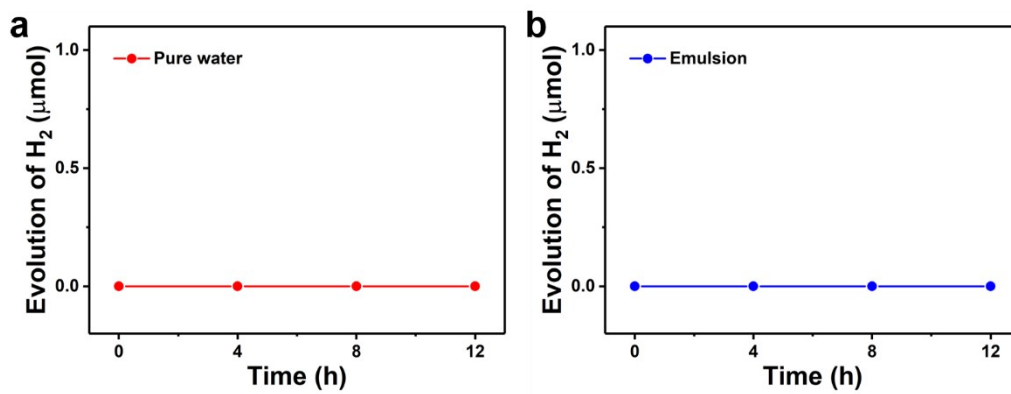
Figure S15. (a) The H_2 production of CDs *verse* time in pure water and (b) The H_2 production of CDs *verse* time in emulsion.
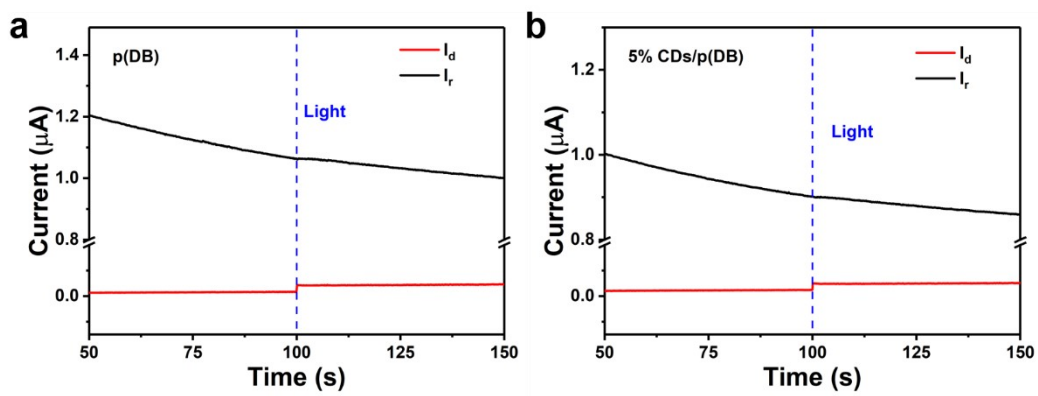
Figure S16. (a) The RRDE collection of p(DB). (b) The RRDE collection of 5% CDs/p(DB).
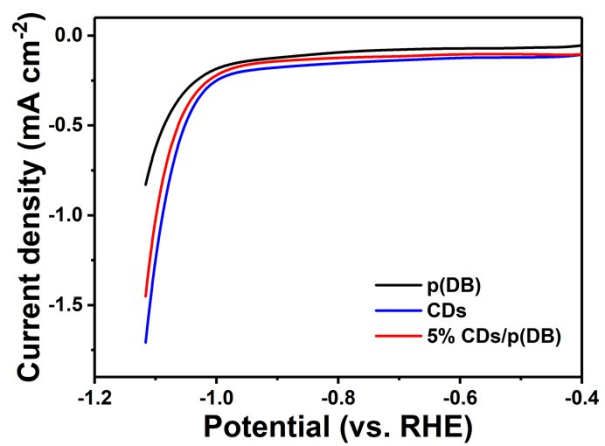
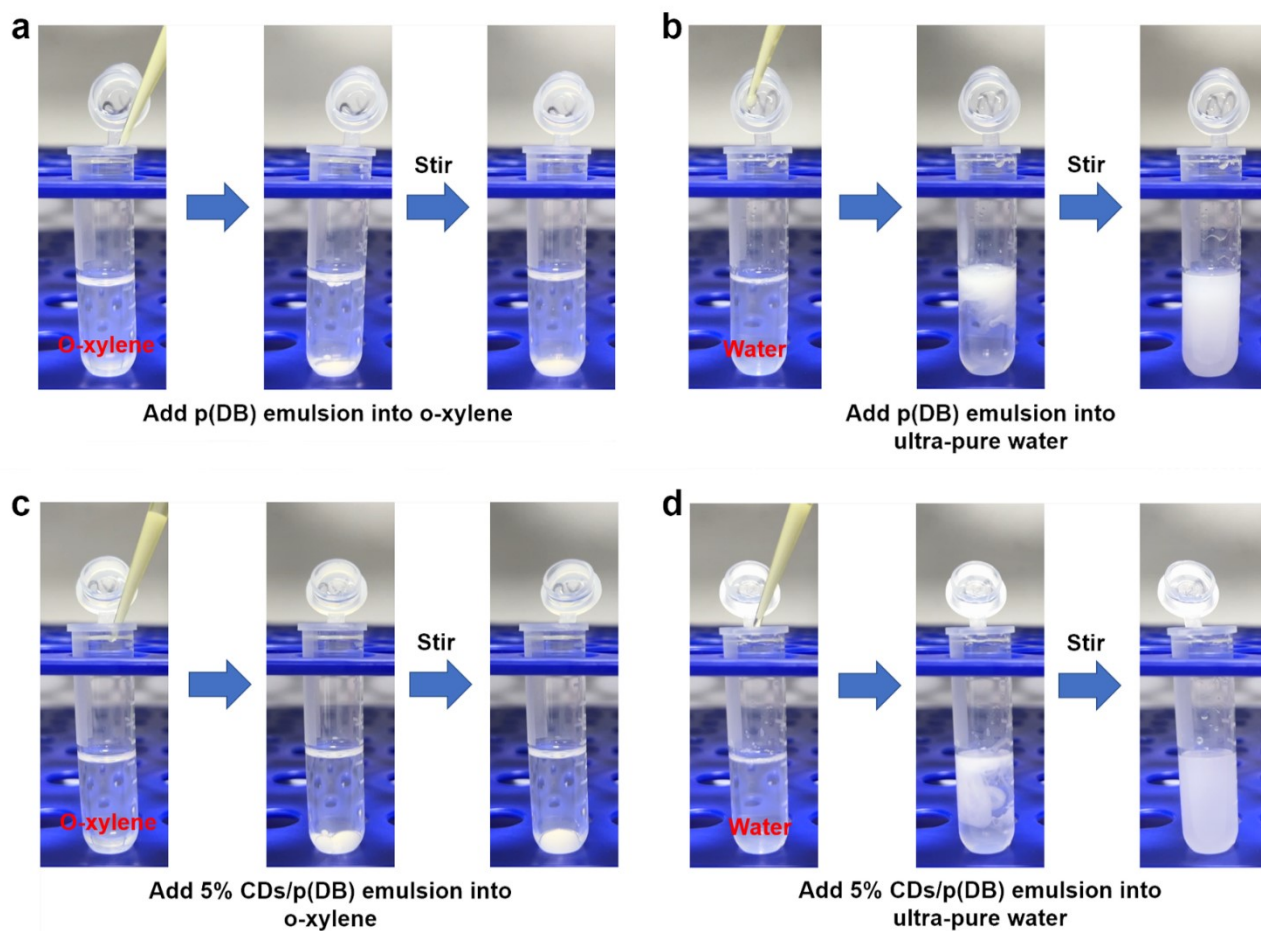**Figure S17**. LSV curves of p(DB), CDs and 5% CDs/p(DB).

Figure S18. Verification of the types of the emulsions. (a, b) Add p(DB) emulsion into o-xylene and ultra-pure water, respectively. (c, d) Add 5% CDs/p(DB) emulsion into o-xylene and ultra-pure water, respectively.
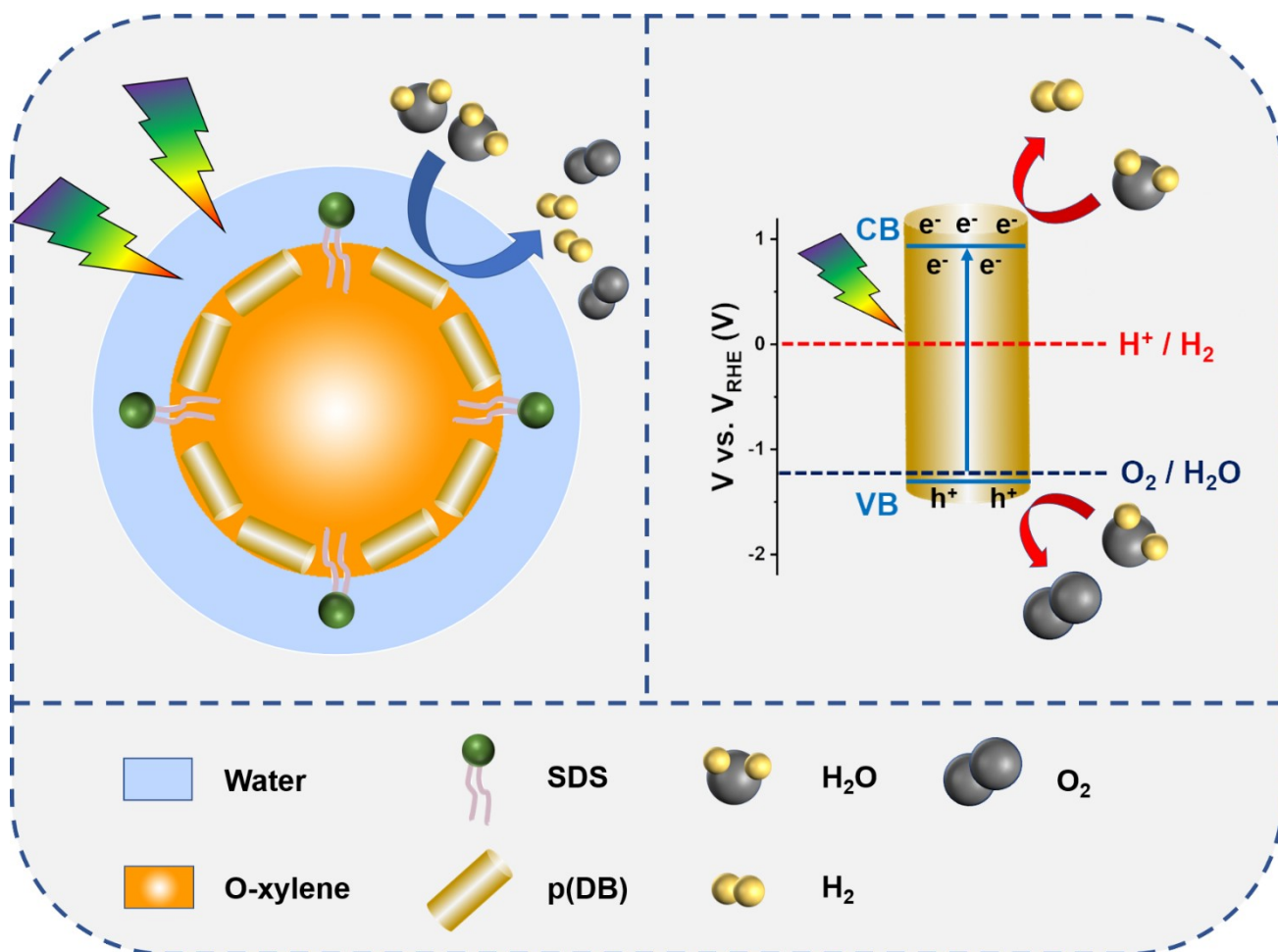
Figure S19. Schematic diagram of mechanisms of p(DB) mediated photocatalytic water-splitting in emulsion.

4. Supplementary Table

Table S1. The detailed information on H_2 evolution for p(DB) and x% CDs/p(DB) in pure water *verse* time.

Samples	4 h (μmol)	8 h (μmol)	12 h (μmol)	Average rate of H_2 evolution (μmol g^{-1} h^{-1})
p(DB)	0.90	2.01	2.64	22.91
1% CDs/p(DB)	2.17	3.99	5.78	49.12
3% CDs/p(DB)	1.00	2.03	3.04	25.27
5% CDs/p(DB)	1.11	2.19	3.33	27.63
7% CDs/p(DB)	0.85	1.57	2.47	20.34

Table S2. The standard error of H_2 evolution for p(DB) and x% CDs/p(DB) in pure water.

Samples	4 h	8 h	12 h
p(DB)	0.11	0.20	0.14
1% CDs/p(DB)	0.45	0.33	0.34
3% CDs/p(DB)	0.21	0.15	0.46
5% CDs/p(DB)	0.17	0.25	0.35
7% CDs/p(DB)	0.90	0.16	0.22

Table S3. The detailed information on H_2 evolution for p(DB) in emulsion with the change of the mass of SDS *verse* time.

The mass of SDS (mg)	4 h (μmol)	8 h (μmol)	12 h (μmol)	Average rate of H_2 evolution (μmol g^{-1} h^{-1})
0	0.57	1.18	2.01	16.00
10	0.89	1.66	2.60	21.42
25	3.17	5.98	9.11	75.83
50	1.83	2.67	4.18	35.20
75	0.63	1.34	2.08	17.05
100	0.47	0.92	1.58	12.58

Table S4. The standard error of H_2 evolution for p(DB) in emulsion with the change of the mass of SDS.

The mass of SDS (mg)	4 h	8 h	12 h
0	0.09	0.17	0.16
10	0.20	0.22	0.25
25	0.21	0.28	0.34
50	0.22	0.17	0.40
75	0.09	0.16	0.08
100	0.12	0.19	0.12

Table S5. The detailed information on H_2 evolution for p(DB) and x% CDs/p(DB) in emulsion *verse* time.

Samples	4 h (μmol)	8 h (μmol)	12 h (μmol)	Average rate of H_2 evolution (μmol g^{-1} h^{-1})
p(DB)	0.57	1.18	2.01	16.00
1% CDs/p(DB)	2.00	3.90	5.53	47.14
3% CDs/p(DB)	3.87	8.08	11.89	99.46
5% CDs/p(DB)	5.59	10.73	17.28	140.88
7% CDs/p(DB)	4.60	8.97	13.72	113.77

Table S6. The standard error of H_2 evolution for p(DB) and x% CDs/p(DB) in emulsion.

Samples	4 h	8 h	12 h
p(DB)	0.09	0.17	0.16
1% CDs/p(DB)	0.14	0.07	0.63
3% CDs/p(DB)	0.13	0.29	1.13
5% CDs/p(DB)	0.43	0.49	0.62
7% CDs/p(DB)	0.18	0.16	1.19

Table S7. The AQE values of 5% CDs/p(DB) with different incident light wavelengths.

Wavelength (nm)	Light intensity (mW cm^{-2})	n_{H_2} (μmol)	AQE (%)
365.0	57.0	1.75	0.63
420.0	66.0	2.22	0.59
500.0	40.0	1.19	0.44
590.0	48.0	1.34	0.35
660.0	134.0	0.83	0.070