Experimental Section

1.1 Materials

Sodium *n*-dodecyl sulfate (SDS; > 99%), titanium (IV) *n*-butoxide (TBT; 99%), cyclohexane (99.5%), triethanolamine (TEOA; ≥ 99%), silica (5-15 nm particle size), polystyrene (M_w ~192,000 g mol^{-1}), oleic acid (OA; 90%), tetrakis(triphenylphosphine)palladium(0), 99%) and Starks' catalyst were purchased from Sigma-Aldrich. Oleylamine (OLM; 80−90%) and 2,5-dibromobenzonitrile were acquired from Acros Organics and Fluorochem, respectively. 2,2'-(9,9-Di-*n*-octyl-9*H*-fluorene-2,7-diyl-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) was obtained from Ossila. Deionized water was obtained using a Milli-Q System (ρ = 15 MΩ). All chemicals were used as received without further purification.

1.2 Synthesis of the cyano-benzene-co-fluorene polymer (CSCP)

2,2'-(9,9-Di-*n*-octyl-9*H*-fluorene-2,7-diyl-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) 643 mg, 1.0 mmol), 2,5-dibromobenzonitrile (260.9 mg, 1.0 mmol), toluene (17.5 mL), Na_2CO_3 (7.5 mL, 2 M), Starks' catalyst (2 drops), and $[Pd(PPh_3)_4]$ (17.5 mg) were used in this reaction. After 2 days at 110 °C the solvent was evaporated and the product was washed with water. The crude polymer was then further purified by Soxhlet extraction with methanol, acetone, and ethyl acetate. The high molecular weight fraction of the polymer was recovered with chloroform. The chloroform was removed and the polymer redissolved in a minimal amount of chloroform, precipitated into a large access of methanol, filtered off and dried under reduced pressure giving the product as a brown solid in 73% yield (358 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ [ppm]: 8.12 (s, 1H), 8.11-7.42 (m, 8H), 2.11 (s, 4H), 1.44-0.93 (m, 20H), 0.93-0.38 (m, 10H). M_w = 223,600 g mol^{-1} (M_n = 61,700 g mol^{-1}; $Đ$ = 3.3.

1.3 Synthesis of Titanium dioxide dots (TDs)

Titanium dioxide dots was made using a modified literature procedure.[1] Under vigorous magnetic stirring, approximately 120 mg TBT, 3 mL oleic acid and 1 mL oleylamine were added to 10 mL cyclohexane. Then, the mixed solution was transferred into a 23 mL Teflon-lined stainless steel autoclave. After heating at 150 °C for 24 hours, a brown sol containing monodisperse TDs was obtained. TDs were precipitated by adding around 30 mL of ethanol and collected by centrifugation at 7830 rpm. After dispersing in 10 mL of cyclohexane, TDs were collected again by centrifugation after precipitation by adding 18 mL of ethanol. TDs were finally dispersed in 5 mL of cyclohexane (5.463 mg mL^{-1}).

1.4 Self-assembly of nanoparticles

5 mL of as-prepared TDs in cyclohexane (5.463 mg mL^{-1}) were washed with around 15 mL of ethanol. After centrifugation at 7830 rpm, TDs were re-dispersed in 2.73 mL of chloroform, serving as TDs stock solution (10 mg mL^{-1}). CSCP stock solution (10 mg mL^{-1}) was made by dissolving 30 mg of CSCP in 3 mL of chloroform. 1 mL of TDs or CSCP stock solution was diluted with additional 1 mL of chloroform. After sonication for 5 minutes, this solution was emulsified in 10 mL of SDS (3 mg mL^{-1}) aqueous solution using a Branson 550 W sonifier equipped with a 1/8″ tip at 40% amplitude. The emulsion was stirred at 250 rpm overnight in an open flask (50 mL) at 40 °C to completely evaporate the residual chloroform.

Synthesis 100% TDs NPs: 30 mg sodium dodecylsulfate (SDS) was first added in 10 mL of deionized water to form a clear solution. Then, 1 mL of TDs and 1 mL of chloroform were mixed together, followed by the injection of this solution into the SDS solution under ultrasonic treatment to form an oil-in-water emulsion. After evaporation of chloroform, the 100% TDs NPs aqueous solution was dialyzed and then diluted to 10 mL with water.

Synthesis 100% CSCP NPs: 30 mg sodium dodecylsulfate (SDS) was first added in 10 mL of deionized water to form a clear solution. Then, 1 mL of CSCP stock solution and 1 mL of chloroform were mixed together, followed by the injection of this solution into the SDS solution under ultrasonic treatment to form an oil-in-water emulsion. After evaporation of chloroform, the 100% CSCP NPs aqueous solution was dialyzed and then diluted to 10 mL with water.

1.5 Self-assembly of nanocomposites

TDs and CSCP stock solution (1 mL in total) was mixed together and then dilute with additional 1 mL of chloroform. After sonication for 5 minutes, this solution was emulsified in 10 mL of SDS (3 mg mL^{-1}) aqueous solution using a Branson 550 W sonifier equipped with a 1/8″ tip at 40% amplitude. The emulsion was stirred overnight at 250 rpm in an open flask (50 mL) at 40 °C to completely evaporate the residual chloroform, giving CSCP/TD nanocomposites aqueous solution.

In a typical synthesis experiment of NC10%, 30 mg sodium dodecylsulfate (SDS) was first added in 10 mL of deionized water to form a clear solution. Then, a mixture of 0.9 mL of TDs and 0.1 mL of CSCP stock solution (10 mg mL^{-1}) were mixed together and diluted to 2 mL using chloroform, followed by the injection of this solution into the SDS solution under ultrasonic treatment to form an oil-in-water emulsion. After evaporation of chloroform, the NC10% aqueous solution was dialyzed and then diluted to 10 mL. For the preparation of NC50%, all the procedures are the same except that a mixture of 0.5 mL of TDs and 0.5 mL of CSCP stock solution was applied. CSCP/TD NCs with different CSCP to TDs ration were obtained by simply changing the volume ratio of TDs to CSCP stock solution in synthesis procedure.

To minimize the difference in surfactant content, NPs and NCs aqueous solution was simultaneous dialyzed in one large beaker (2 L) for 3 days by using dialysis membrane tubing (3500 Da cut-off; the deionized water was replaced 3-4 times a day). Finally, these solutions were diluted to 10 mL with deionized water to give a constant concentration of 1 mg mL^{-1}.

1.6 Materials characterization

Scanning electron microscope (SEM) measurements were performed on Hitachi S-4800 cold field emission scanning electron microscope (FE-SEM) and imaging was conducted at a working voltage of 3 kV and a working distance of 8 mm using a combination of upper and lower secondary electron detectors. High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) and bright field transmission electron microscopy (BF-STEM) images were obtained and electron energy loss spectroscopy (EELS) was recorded on a JEOL 2100FCs microscopy at an accelerating voltage of 200 kV. Fast Fourier transform (FTT) was obtained on Gatan Digital Micrograph by converting a signal from its original domain to a representation in the frequency domain. Powder X-ray diffraction (PXRD) measurements were performed on a PANalytical X'Pert PRO MPD, with a Cu X-ray source, used in high throughput transmission mode with Kα focusing mirror and PIXCEL 1D detector. ^1H NMR spectra were recorded using a Bruker Avance 400 NMR spectrometer. Fourier-transform infrared spectroscopy (FT-IR) were measured on a Bruker Tensor 27 FT-IR spectrometer using bulk sample and an ATR attachment (16 scans). Single detection gel permeation chromatography (GPC) was calibrated against polystyrene standards (Agilent EasiCal PS-2 standards), and performed using an Agilent 1260 Infinity II GPC/SEC system (Agilent, UK), two PLgel 5 µm MIXED-D columns and a PL gel 5 µm guard column, with samples detected by refractive index (RI). Dynamic light scattering (DLS) measurements were performed on a Malvern Zetasizer Nano Particle Sizer, at 25 °C, in aqueous solutions. Inductively coupled plasma optical emission spectrometry (ICP-OES) analysis was performed on an ICP-OES Agilent 5110 after a microwave digest of the materials in nitric acid (67-69%, trace metal analysis grade) to determine the palladium content. The UV-visible absorption spectra were recorded on a Shimadzu UV-2550 UV-Vis spectrometer. The 50 µL of nanoparticles and nanocomposites (1 mg mL^{-1}) aqueous solution were diluted with 3 mL of distilled water. Steady-state photoluminescence spectra and time-correlated single photon counting (TCSPC) measurements were performed on an Edinburgh Instruments LS980-D2S2-STM spectrometer equipped with picosecond pulsed LED excitation sources and a R928 detector, with a stop count of 10000. An EPL-375 diode ($\lambda = 370.5$ nm, instrument response 100 ps, fwhm) for emission detection was used. Long pass filter (395 nm) with a cutoff wavelength greater than the laser wavelength (370.5 nm) was employed to prevent light scattering. The instrument response (IRF) was measured with colloidal silica (LUDOX HS-40, Sigma-Aldrich). Decay times were fitted in the FAST software using suggested lifetime estimates. Samples for these measurements were prepared by adding 50 µL of nanoparticles and nanocomposites (1 mg mL^{-1}) aqueous solution into 3 mL of 10% (v/v) TEOA aqueous solution.

1.7 Photocatalytic activity measurements

For high throughput solar simulator measurements, 1 mL of NPs and NCs aqueous solutions (1 mg mL^{-1}) were added into sample vials (V = 12.5 mL) and purged with nitrogen in a Sweigher Chemspeed Technologies robot for 3 hours. 4.2 mL of TEOA aqueous solution (12.3% v/v) was added into each vial via the liquid handling system under inert conditions. Then, all sample vials were irradiated under a solar simulator (AM1.5G, Class AAA, IEC/JIS/ASTM, 1440 W xenon, 12 × 12 in., MODEL:94123A) equipped with a rocker/roller device. Gaseous products were analyzed on a Shimadzu GC-2010 equipped with Shimadzu HS-20 injecting a sample from the headspace sampler via a transfer line (temperature 150 °C) onto a Rt-Msieve 5 Å column with He as the carrier gas at a flow rate of 30 mL min^{-1}. Hydrogen was detected with a barrier discharge ionization detector referencing against standard gas with a known concentration of hydrogen.

Kinetic measurements were conducted in a 67 mL quartz flask. 2 mL of NPs or NCs aqueous solutions (10 mg mL^{-1}) and 2 mL of TEOA were dispersed into 16 mL of water to give a 10% (v/v) TEOA aqueous solution, then this solution was purged with N_2 for 30 minutes. The reaction mixture was illuminated with a 300 W Newport Xe light source (Model: 6258, Ozone free) using a $\lambda > 295$ nm cut-off filter. The light source was cooled by water circulating through a metal jacket. Gas samples were taken with a gas-tight syringe and run on a Bruker 450-GC gas chromatograph. Hydrogen was detected with a thermal conductivity detector referencing against standard gas with a known concentration of hydrogen.

1.8 Calculation of half-reactions for free electrons/holes (CSCP)

Standard reduction potentials of half-reactions for free electrons/holes and excitons were calculated using DFT and time-dependent DFT (TD-DFT). The B3LYP density functional was used for all DFT and TD-DFT calculations, together with the Def2-SVP basis set, using Gaussian 16 software. The effect of solvation by water was accounted for using the SMD solvation model (See results in Figure S14).

1.9 Cyclic voltammetry methods

The CV measurement was performed on the Bio-logic SP200 workstation with 0.1 M $TBAPF_6$ in CH_3CN solution, which used a standard three-electrode cell (Ag/AgCl electrode as the reference electrode, Pt wire as the counter electrode, and glassy carbon electrode as the working electrode). The film was casted onto the electrode from chloroform solution and dried before the measurement. The ferrocenium/ferrocene couple was used as the internal standard. (See results in Figure S15).

2.0 Apparent quantum yield measurements

The apparent quantum yield for the photocatalytic H_2 evolution was measured using a λ = 340 nm LED (28.6 mW), λ = 395 nm LED (69.1 mW) and λ = 420 nm LED (101.0 mW) controlled by an IsoTech IPS303DD power supply. For the measurement, 10 mg of NC10% were add to 25 mL with TEOA aqueous solution (10% v/v) before illuminating with LED. The light intensity was measured with a ThorLabs S120VC photodiode power sensor controlled by a ThorLabs PM100D Power and Energy Meter Console and the apparent quantum yield was estimated using the equation below:

$$AQY = 2 \times \frac{moles\ of\ hygrogen\ evolved}{moles\ of\ incidentphotons} \times 100\%$$

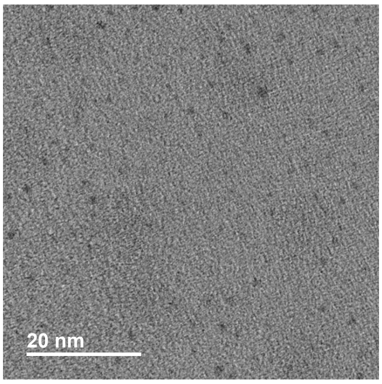

Figure S1. HR-TEM image of TiO_2 quantum dots.

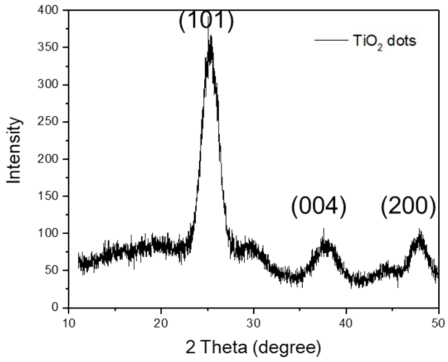

Figure S2. PXRD Pattern of anatase TiO_2 dots.

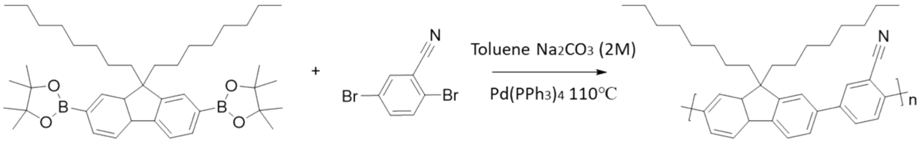

Figure S3. Synthesis of CSCP.

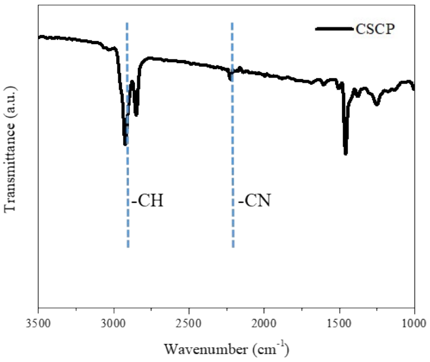

Figure S4. FT-IR of CSCP measured in the solid state using ATR.

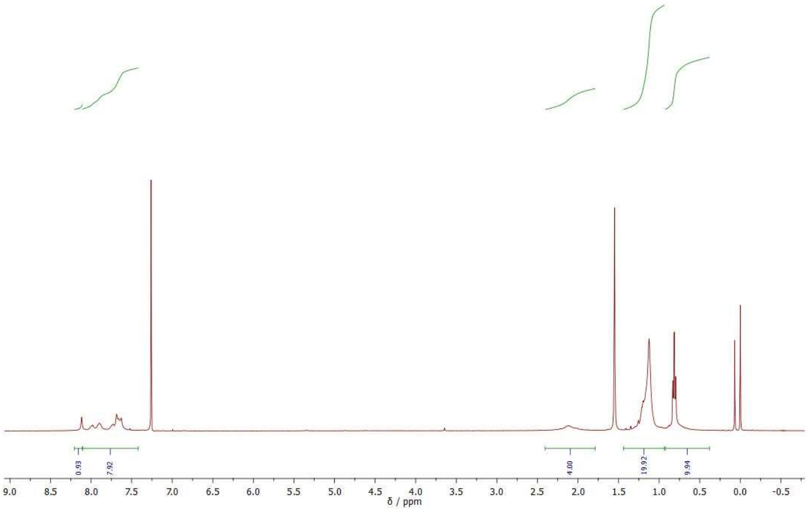

Figure S5. ^1H NMR spectra of CSCP in $CDCl_3$.

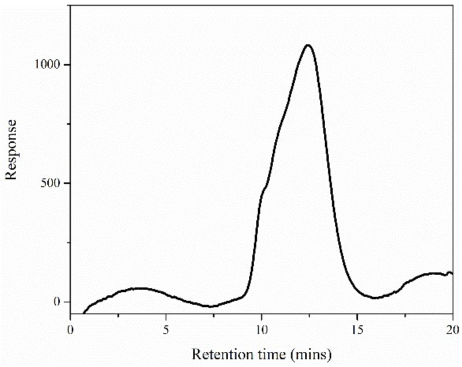

Figure S6. Gel permeation chromatogram of CSCP (chloroform was used as the mobile phase with a flow-rate of 1 mL min^{-1}; GPC was calibrated against poly(styrene) standards).

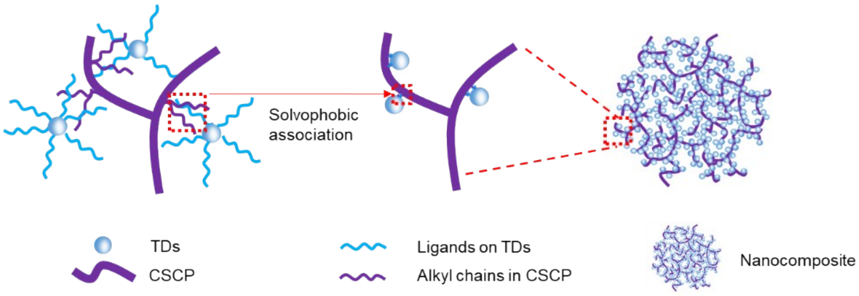

Figure S7. Diagram of proposed nanocomposite assembly mechanism.

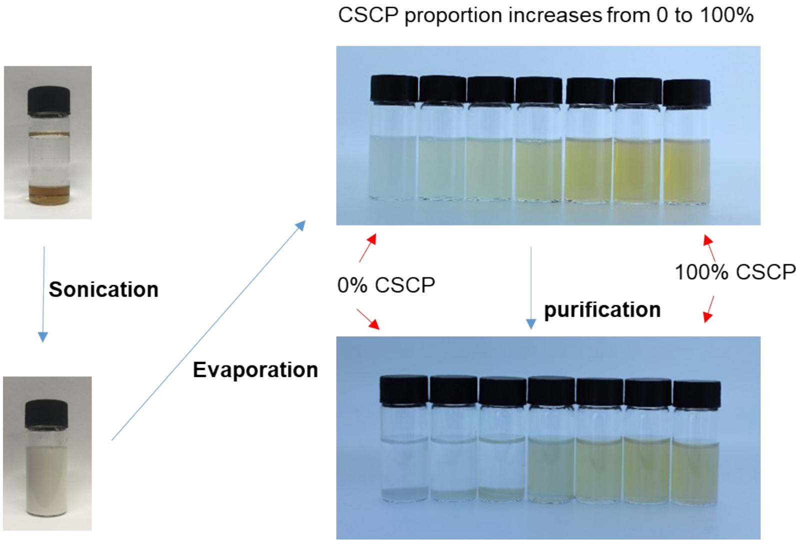

Figure S8. Pictures on left side show evaporation induced self-assembly procedure and pictures on right side show nanoparticles and nanocomposites aqueous solution with different CSCP proportion before and after purification (CSCP proportion is 0, 10, 25, 50, 75, 90, 100% from left to right).

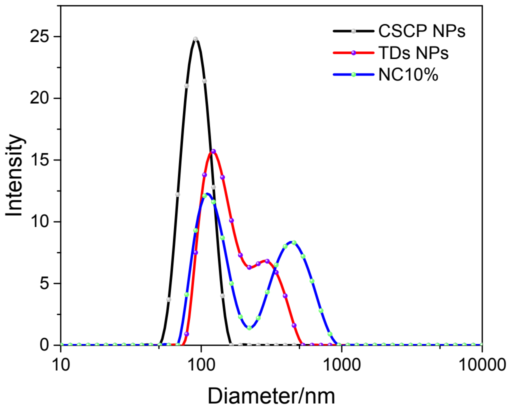

Figure S9. Size distribution measured by DLS.

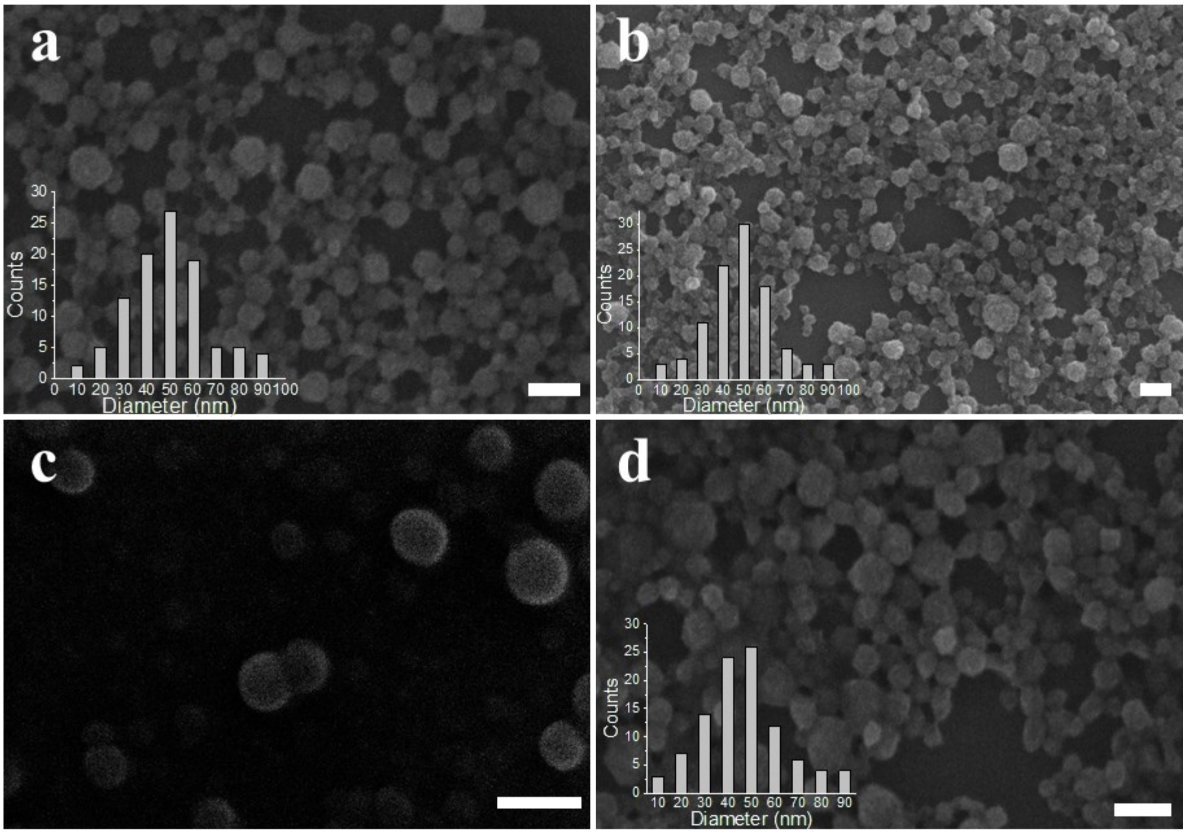

Figure S10. High resolution FE-SEM images of (a) TDs NPs, (b) NC10%, (c) CSCP NPs and (d) 10% polystyrene/90% TDs NCs. Inset figures show the size distribution. Scale bars: 100 nm.

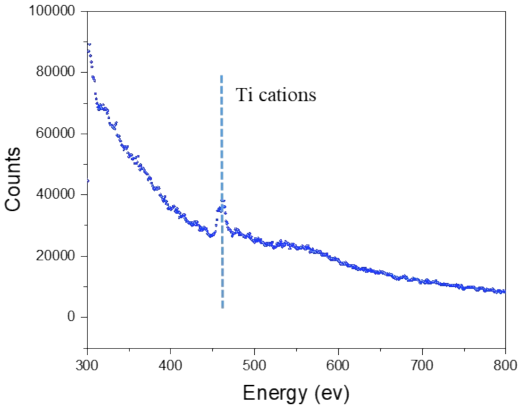

Figure S11. Electron energy loss spectroscopy of TDs NPs.

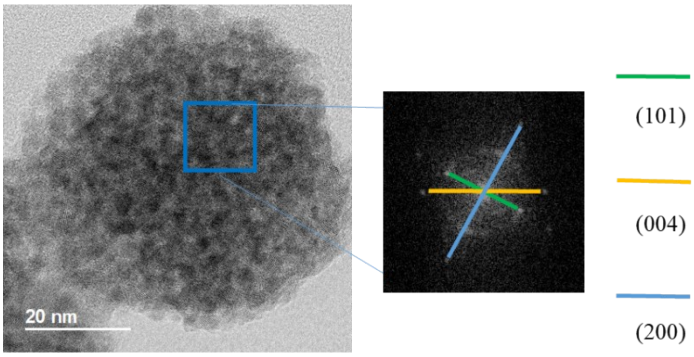

Figure S12. Lattice fringe d-spacing of TDs NPs as calculated by fast Fourier transform (FTT).

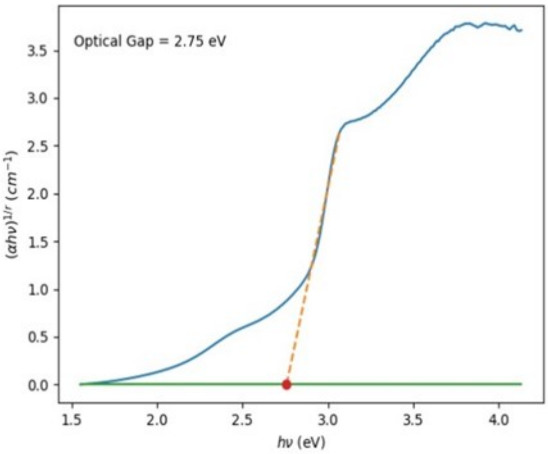

Figure S13. Band gap of CSCP determined using the Tauc method.

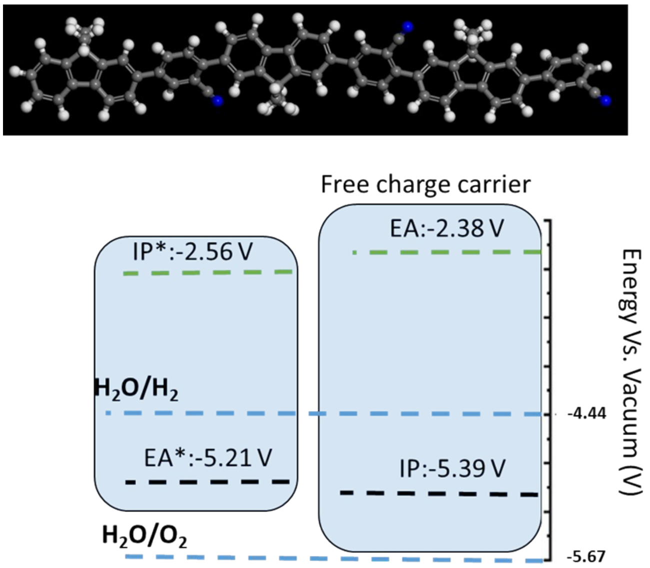

Figure S14. DFT calculation results from model compound of CSCP (n=3).

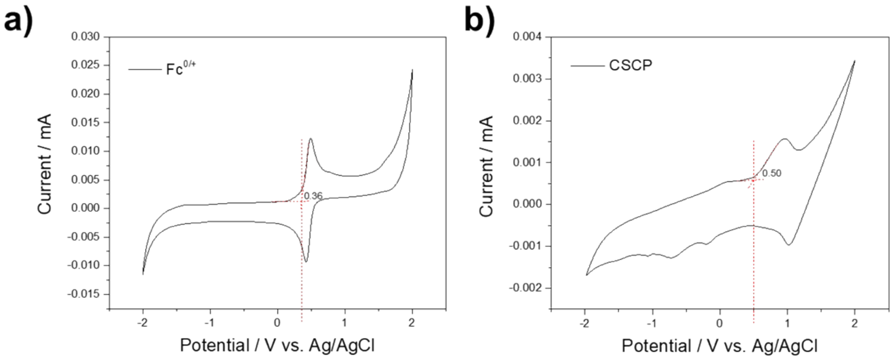

Figure S15. (a) Cyclic voltammograms curves of ferrocene/ferrocenium ($F_c^{0/+}$) redox couple. (b) Oxidative half cyclic voltammograms to determine the HOMO positions of the polymers. Measurement was performed on the Bio-logic SP200 workstation with 0.1 M TBAPF$_6$ in CH$_3$CN solution. The HOMO positions are determined as follows: E_{HOMO} (eV) = -4.8-(E_{ox}-E(F_c/F_c^+)) = -(0.5-0.36+4.8) eV= -4.94 eV.

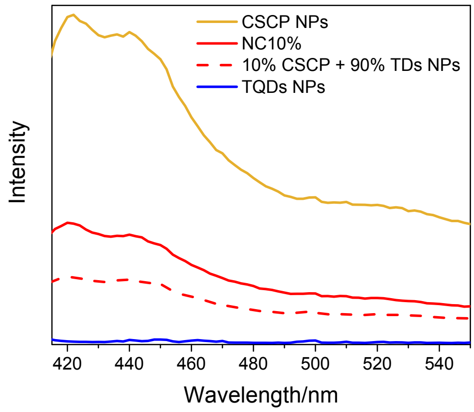

Figure S16. Fluorescence intensity of TDs NPs, CSCP NPs, CSCP + TDs NPs mixtures and CSCP/TD NCs aqueous solution (λ_{exc} = 400 nm) measured at room temperature.

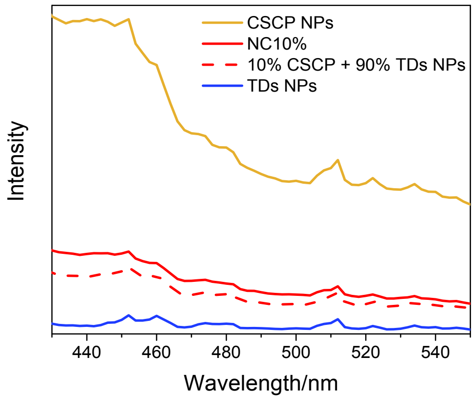

Figure S17. Fluorescence intensity of TDs NPs, CSCP NPs, CSCP + TDs NPs mixtures and CSCP/TD NCs aqueous solution (λ_{exc} = 410 nm) measured at room temperature.

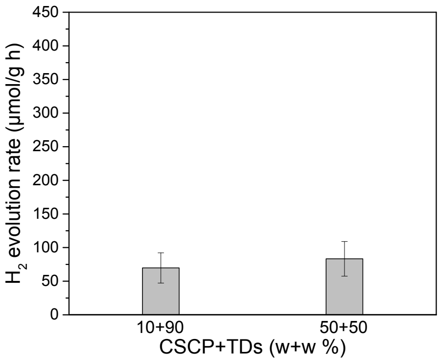

Figure S18. Photocatalytic hydrogen production activities for the CSCP + TDs NPs. Conditions: catalyst 192.3 μg mL^{-1} (1 mg of CSCP and TDs NPs in 5.2 mL solution), TEOA (10 vol.% in water), AM1.5g ABA certified solar simulator (1 sun), 5 hours irradiation.

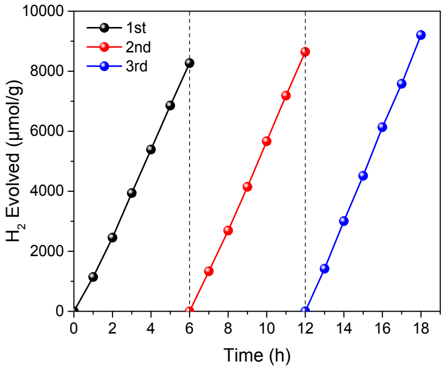

Figure S19. Time course of hydrogen production for NC10%, irradiated for 18 hours (degassed after every 6 hours) by 300 W Xe light source fitted with a λ > 295 nm filter using 2 mg of the catalyst in 20 mL of aqueous TEOA solution (10 vol.% in water).

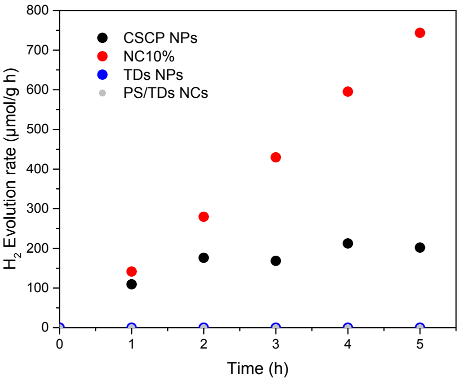

Figure S20. Time course of hydrogen production under broadband illumination of TDs NPs, CSCP NPs, PS/TDs NCs (10% wt.% of PS) and NC10%. Conditions: catalyst 2 mg in 20 mL of aqueous TEOA (10 vol. %), 5 hours irradiation with a 300 W Xe light source fitted with a λ > 395 nm filter.

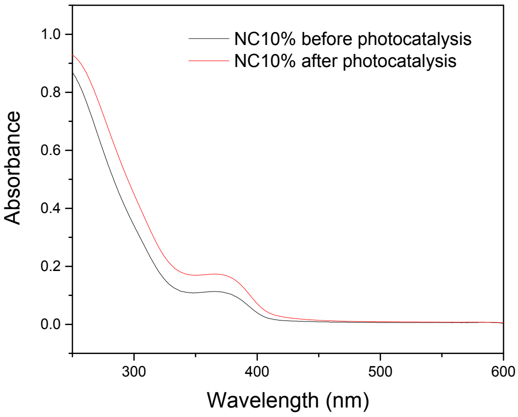

Figure S21. UV-Vis absorption spectra of NC10% before and after photocatalysis.

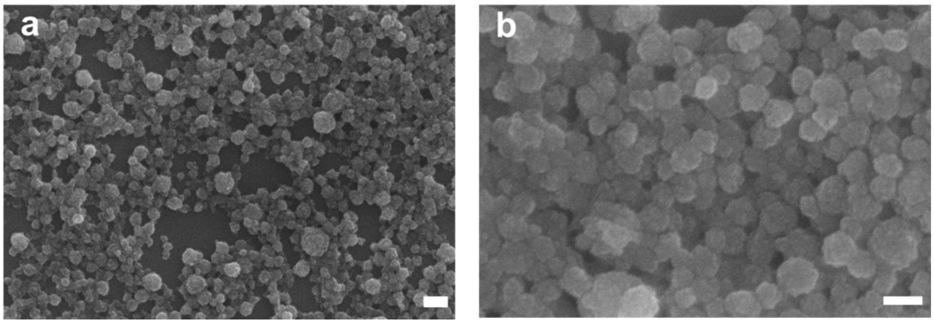

Figure S22. SEM images of NC10% before and after photocatalysis. Scale bars: 100 nm.

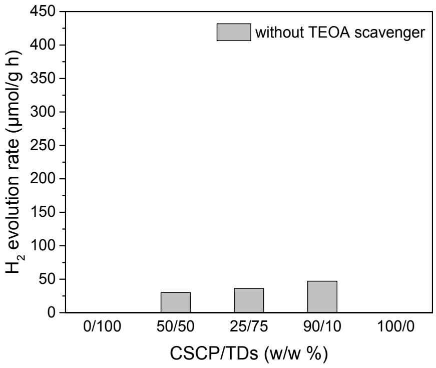

Figure S23. Photocatalytic hydrogen production activities for the CSCP/TD NCs without TEOA scavenger. Conditions: Catalyst 192.3 μg mL^{-1} (1 mg of CSCP/TD NCs in 5.2 mL solution), no scavenger, AM1.5g ABA certified solar simulator (1 sun), 5 hours irradiation.

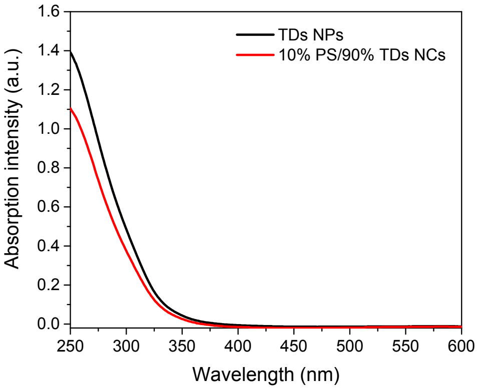

Figure S24. Absorption spectrum of photo-inactive PS/TD NCs.

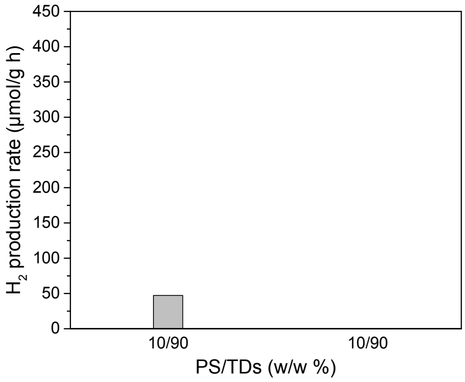

Figure S25. Photocatalytic hydrogen production activities for the 10% PS/90% TD NCs with TEOA (left) and without TEOA (right). Conditions: catalyst 192.3 μg mL^{-1} (1 mg of 10% PS/90% TD NCs in 5.2 mL solution), TEOA (10 vol.% in water), AM1.5g ABA certified solar simulator (1 sun), 5 hours irradiation.

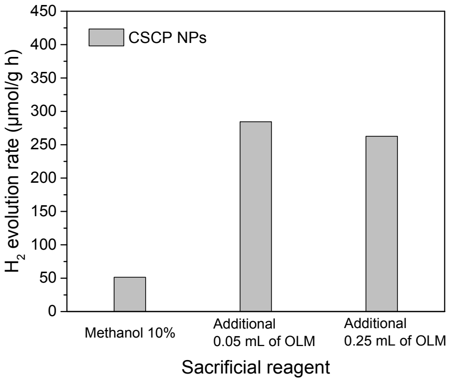

Figure S26. Effect of oleylamine (OLM) on photocatalytic hydrogen production activities of the CSCP NPs. Conditions: Catalyst 96.2 μg mL^{-1} (0.5 mg of CSCP in 5.2 mL solution), methanol (10 vol.% in water), AM1.5g ABA certified solar simulator (1 sun), 5 hours irradiation.

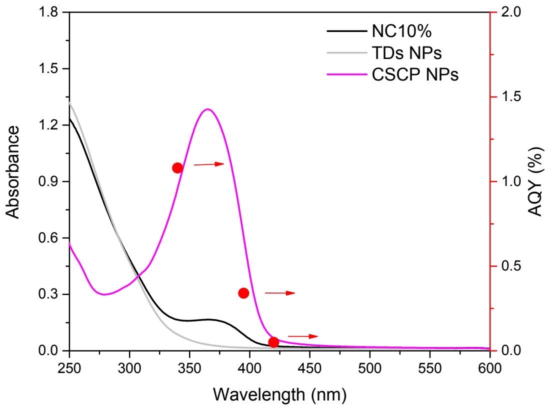

Figure S27. UV-vis spectra and AQY of NC10% measured with monochromatic LED light at 340. 395 and 420 nm, respectively. UV-vis spectrum of CSCP and TDs nanoparticles are also plotted (Intensity rescaled for clarity).

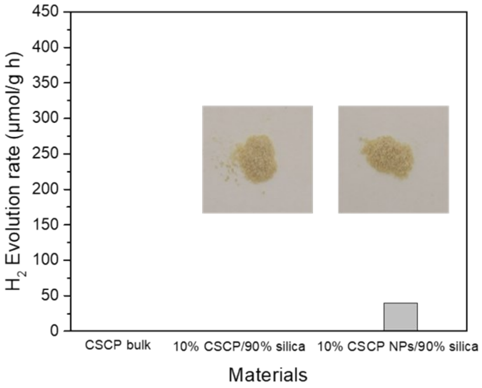

Figure S28. Photocatalytic hydrogen production activities for bulk polymer, 10%CSCP/90% SiO_2 and 10%CSCP NPs/90% SiO_2 normal composites. Inset shows pictures of 10%CSCP/90% SiO_2 (left) and 10%CSCP NPs/90% SiO_2 (right). Conditions: catalyst 192.3 μg mL^{-1} (1 mg of catalysts in 5.2 mL solution), TEOA (10 vol.% in water), AM1.5g ABA certified solar simulator (1 sun), 5 hours irradiation.

Table S1. Fitting parameters for time correlated fluorescence lifetime experiments for NCs and NPs (λ_{exc} = 370.5 nm and λ_{em} = 480 nm).

Sample	τ_1 (ns)	τ_2 (ns)	τ_3 (ns)	τ_4 (ns)	A_1	A_2	A_3	A_4	τ (ns) [a]
CSCP NPs	0.217	1.325	5.285	-	65.217	23.937	10.846	-	3.372
NC10%	0.322	1.671	6.836	-	59.84	28.171	11.989	-	4.350
10% CSCP + 90% TDs NPs	0.23	1.358	5.343	-	64.959	24.254	10.787	-	3.375
TDs NPs	0.25	1.108	4.611	12.828	40.723	28.596	22.081	8.6	7.568

[a] τ is the average PL lifetime calculated from the following equation: $\tau = \sum_{i=1}^{4}(A_i\tau_i^2)/\sum_{i=1}^{4}(A_i\tau_i)$

References

1 X. Xu, Z. Gao, Z. Cui, Y. Liang, Z. Li, S. Zhu, X. Yang, J. Ma, *ACS Appl Mater Interfaces* 2016, **8**, 91-101.