

Electronic Supplementary Information

Harnessing low energy photons (635 nm) for the production of H₂O₂ using upconversion nanohybrid photocatalysts

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Experimental section

Synthetic method of silica nanocapsules (SNCs)

Two chromophore stock solutions, sensitizer: palladium-tetraphenyltetrabenzoporphyrin (PdTPBP; 36 μM) and acceptor: 9,10-bis(phenylethynyl)anthracene (BPEA; 485 μM , perylene; 713 μM), were prepared into tetrahydrofuran (THF) and kept in dark prior to use. The mixture in oleic acid (OA) was prepared by combining two stock solutions, then stored at 70 $^{\circ}\text{C}$ oven for overnight to remove THF solvent. The final concentrations of PdTPBP and BPEA (perylene) in OA were 0.2 μM and 17 (25) μM . An aliquot (500 μL) of the mixture was emulsified in distilled water (28.8 mL) under sonication for 30 min followed by vigorous stirring (1100 rpm) for 30 min and then 1 mmol of (3-aminopropyl) triethoxysilane (ATES, 98 %; Aldrich) was added to obtain a micelle suspension. Six mmol of tetraethyl orthosilicate (TEOS, 98 %; Aldrich) was subsequently added at ATES mixture to yield TTA-UC nanocapsules. The mixture was left at room temperature for *ca.* 1 h, then placed in oven at 55 $^{\circ}\text{C}$ for 24 h. The final products were obtained after several washing steps with distilled water and ethanol. To attach the CdS nanoparticles (NPs), TTA-UC nanocapsules were firstly functionalized with amino groups using 0.98 mL (3-aminopropyl) trimethoxysilane (APMS; Aldrich) under gentle mixing (150 rpm) at 55 $^{\circ}\text{C}$ for 25-30 h. After washing with distilled water, the suspension of TTA-UC nanocapsules was mixed with 20 mL cadmium chloride (CdCl_2 ; Aldrich) solution (0.02 M) for 4 h. Residue was removed by washing with distilled water. The suspension was further treated with 20 mL thioacetamide (CH_3CSNH_2 ; Aldrich) solution (0.02 M) under gentle mixing at 30 $^{\circ}\text{C}$ for 24 h. The final product of CdS-NPs-loaded TTA-UC nanocapsules (CdS-SNCs) was washed with deionized water and collected.

Synthetic method of graphene oxide nanodisks (GONDs)

0.3 g of platelet graphite nanofiber (PGNF) was put into a concentrated H_2SO_4 solution (30 mL) containing 0.4g of NaNO_3 in water bath and then 1 g of KMnO_4 (333 wt% of PGNF) was slowly added to the above solution with vigorous stirring for 30 min to obtain complete mixing. The temperature of water bath was increased up to 35 °C and stirring continued for 7 h. Additional 1 g of KMnO_4 (333 wt% of PGNF) was added to the solution and stirring further continued for 12 h at the same temperature. The resulting mixture was cooled down in an ice bath, and 90 mL of H_2O_2 solution (85 mL water + 5 mL 30 wt% H_2O_2) was then added very slowly and stirred over an hour. The above solution was washed out by the filtration and centrifugation with deionized water. The obtained solid product was redispersed in water and dialyzed for more than two weeks with dialysis membrane (Cellu-Sep T3, MWCO: 12,000 - 14,000) to remove remaining acids and reactants. Oxidized PGNFs were obtained by the centrifugation (14,000 rpm for 1 h) of the dialyzed mixture and drying in oven (at 80 °C). A specific amount of oxidized PGNFs was added into water and finally ultrasonicated for 1 h to obtain fully exfoliated GONDs from fragments of oxidized PGNFs. The resulting product was used to prepare all of the sub-bandgap semiconductor hybrids.

Analysis of formaldehyde production (from methanol) accompanied by H_2O_2 production

The concentration of formaldehyde was analyzed using a high performance liquid chromatograph (HPLC Agilent 1100) with UV detection at 350 nm after forming 2,4-dinitrophenylhydrazine derivative. 2,4-dinitrophenylhydrazine ($\geq 99.0\%$, Aldrich) was further purified by recrystallizing three times from acetonitrile prior to use.

Quantum yield measurement

The internal quantum efficiency (IQE, $\Phi_{H_2O_2}$) of photocatalytic production of H_2O_2 on ternary nano hybrid photocatalyst was determined based on the equation S1. The number of photocatalytically produced H_2O_2 molecules ($n_{H_2O_2}$) was obtained from the data of Figure 8b. To estimate the number of photons absorbed by nano hybrids, we first measured the number of photons absorbed (I_a) by the OA core solution and then multiplied this value by the volume ratio (F) of OA core in nano hybrid suspension versus the OA core solution in which I_a was measured. The value of I_a for OA containing 0.2 μM PdTPBP placed in a 1-cm pass-length cuvette under red LED illumination (631 ± 15 nm, fwhm; 23 mW/cm^2) was determined to be 10.34 mW/cm^2 using a thermopile head (Newport 818P-001-12) connected to an optical power meter (Newport 1918-R). The volume fraction of the sample suspension, F , in the same 1-cm cuvette cell was estimated to be 0.06 by comparing the Stokes fluorescence at 600-850 nm under the identical laser excitation at 635 nm (1250 mW/cm^2). The value of 0.5 in the denominator of equation S1 accounts for the involvement of two low-energy photons for the production of one higher-energy photon through the UC process.

$$\Phi_{H_2O_2} = \frac{2 \cdot n_{H_2O_2}}{I_a \cdot F \cdot \Phi_{UC} \cdot 0.5} \quad (S1)$$

The IQE of the core solution UC (Φ_{UC}) was estimated to be *ca.* 4.3% following the previously established procedure¹ and according to equation S2 where A_{uc} , I_{uc} , and η_{uc} represent absorbance at 635 nm, integrated photoluminescence intensity, and refractive index of the upconversion medium (1.459 for OA and 1.329 for methanol, respectively).² The subscript “*std*” refer to the same terms for a reference, methylene blue in methanol, under identical excitation at 635 nm. We adopted 0.03 as the fluorescence QY of methylene blue in methanol.³ The Stokes fluorescence of the standard solution and the anti-Stokes fluorescence of the TTA-UC solution were measured at various laser power densities and integrated over 600-850 nm for methylene blue and 440-600 nm for BPEA to calculate QY.

$$\Phi_{UC} = 2\Phi_{std} \left(\frac{A_{std}}{A_{UC}} \right) \left(\frac{I_{UC}}{I_{std}} \right) \left(\frac{\eta_{UC}}{\eta_{std}} \right)^2 \quad (S2)$$

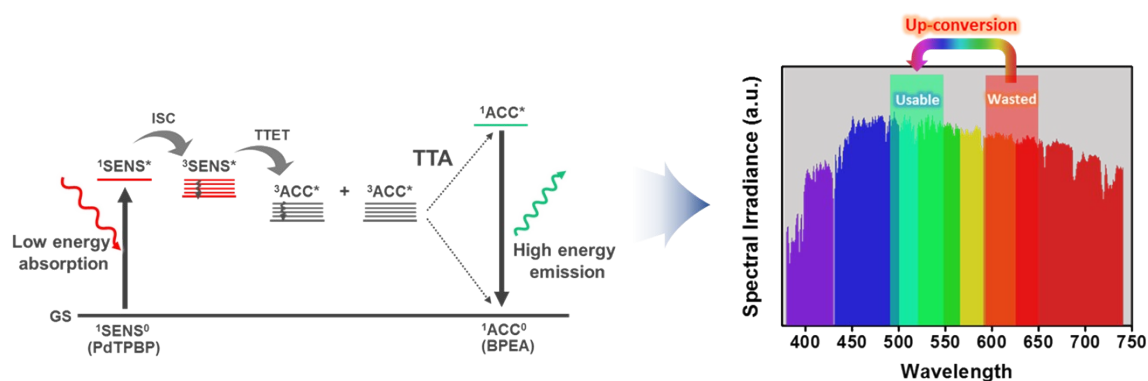


Fig. S1. Schematic illustration of TTA-UC process. Red to green UC occurs between PdTPBP (SENS) and BPEA (ACC) to obtain the singlet fluorescence of BPEA ($^1\text{ACC}^*$). To emit a higher-energy photon ($^1\text{ACC}^*$) from a lower-energy one ($^3\text{SENS}^*$), two TTET processes from $^3\text{SENS}^*$ should be required to form two $^3\text{ACC}^*$ which then undergo TTA process.

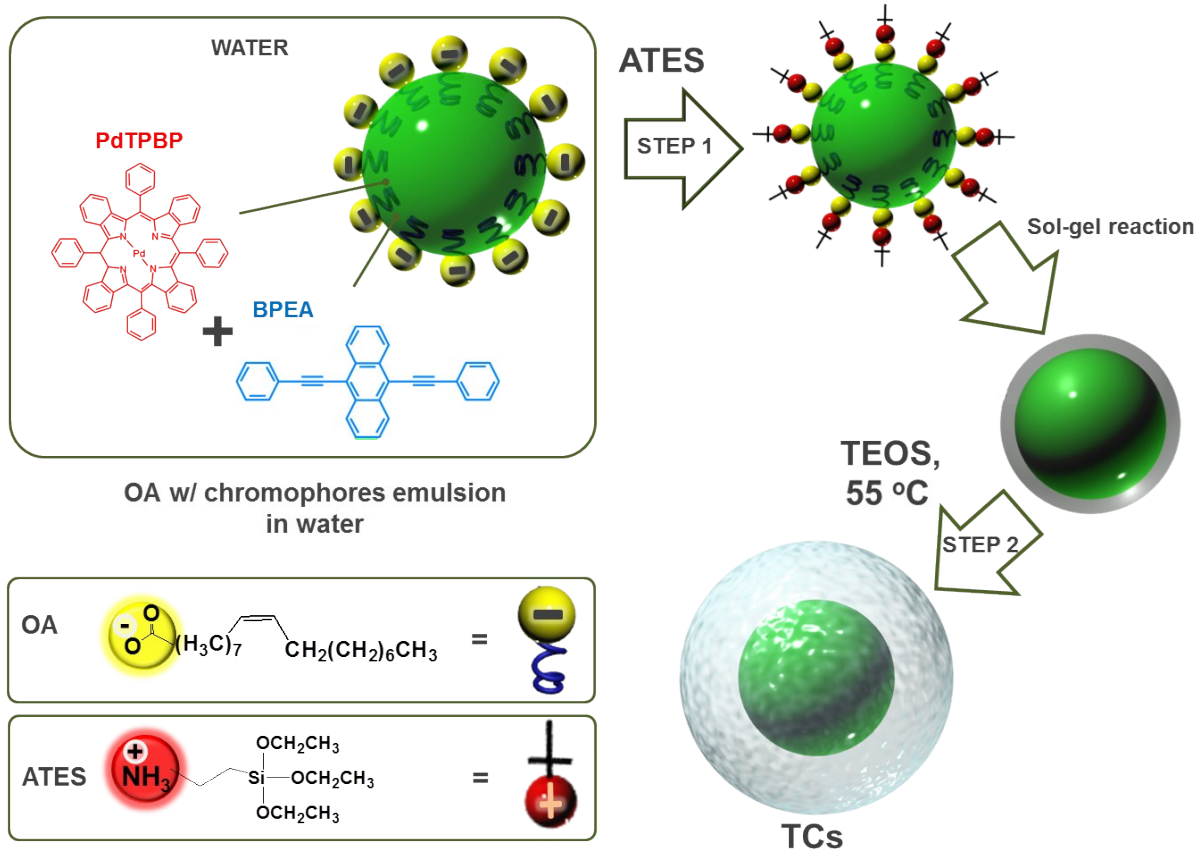


Fig. S2. Schematic illustration of the fabrication process for TTA-UC silica capsule (SNC) based on an emulsion self-assembly.

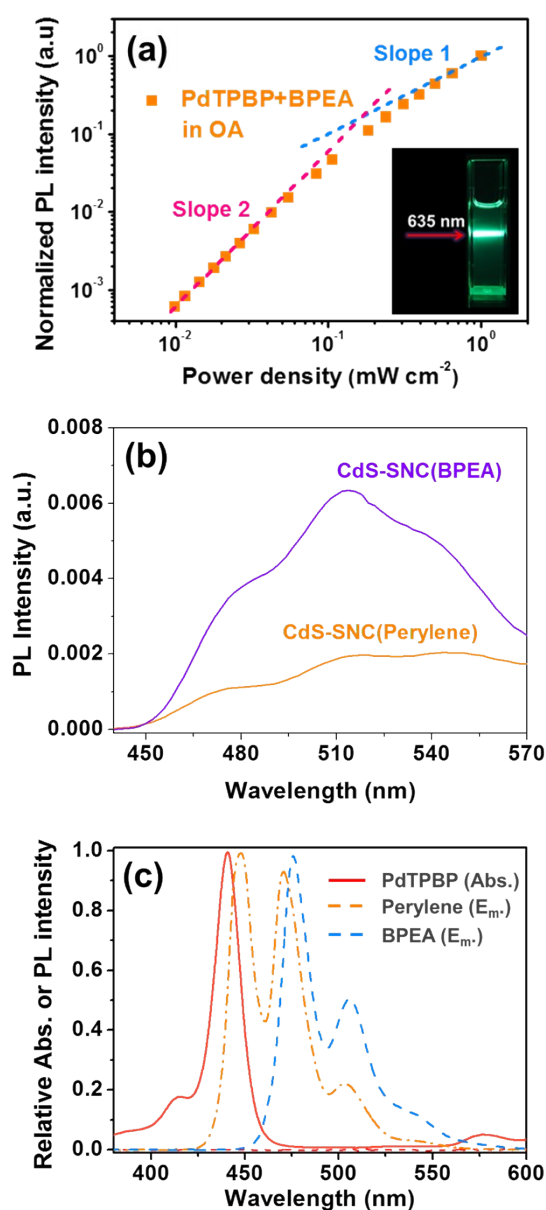


Fig. S3. (a) Log-log plot of normalized integrated UC emission intensities from the liquid-state TTA-UC solution in OA as a function of the incident laser power density ($\lambda_{\text{Ex}} = 635 \text{ nm}$). An inset photo image shows TTA-UC in OA which was taken through a 600 nm short-pass filter upon excitation at 635 nm. The dashed lines are linear fits with slopes of 1.0 (cyan, linear) and 2.0 (magenta, quadratic). (b) Comparison of emission spectra between CdS-SNCs with PdTPBP/BPEA and PdTPBP/perylene pairs under excitation at 635 nm (292 mW cm^{-2}). (c) Normalized absorption and emission spectra of PdTPBP, perylene, and BPEA in OA at room temperature (red solid line: absorption peaks of PdTPBP, orange and cyan dashed lines: emission peaks of perylene and BPEA, respectively).

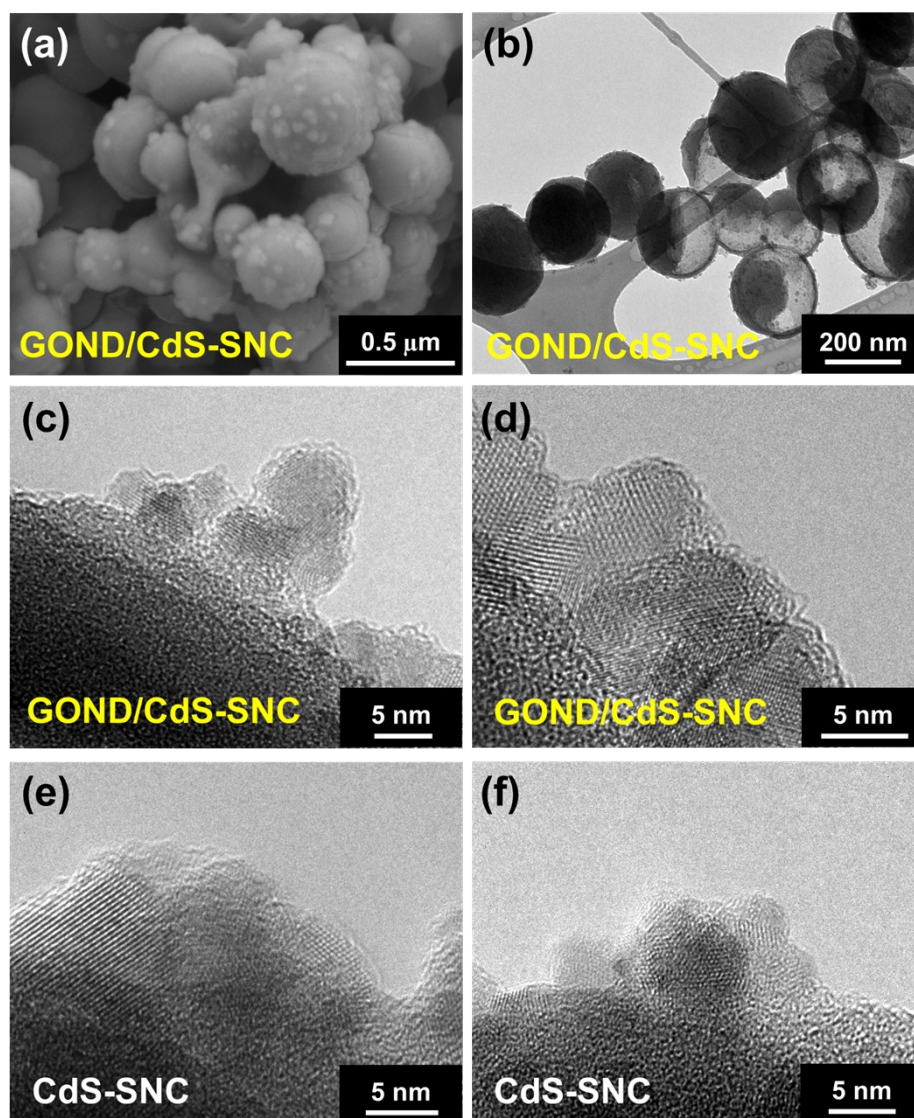


Fig. S4. (a) FE-SEM image of GOND (3 wt%)/CdS-SNC. TEM and HR-TEM images of (b-d) GOND (3 wt%)/CdS-SNC and (e,f) CdS-SNC.

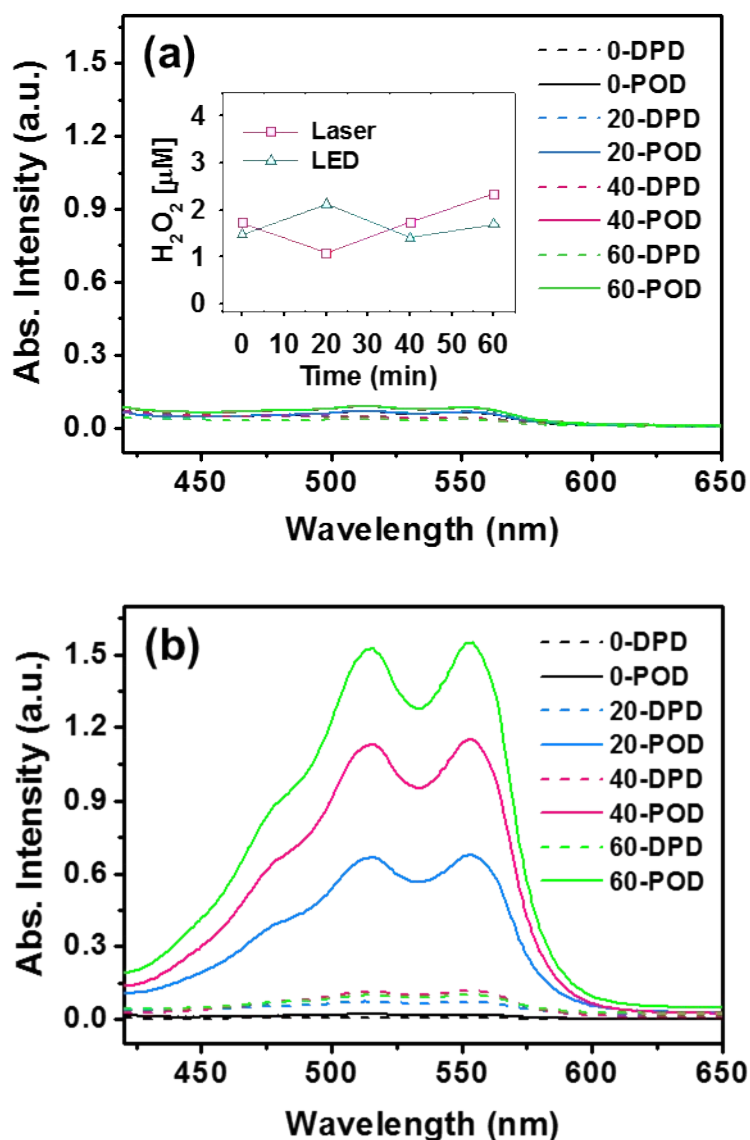


Fig. S5. Time-dependent profiles of DPD and POD absorption spectra of (a) GOND and (b) GOND (3 wt%)/CdS-SNC solution under excitation with a commercial diode laser ($\lambda_{Ex} = 635$ nm) after filtration with $0.45 \mu m$ syringe filter. The experimental conditions were as follows: $[GOND] = 0.05 \text{ g L}^{-1}$, $[GOND/CdS-SNC] = 0.5 \text{ g L}^{-1}$ (GOND/CdS component only), $[MeOH]_0 = 5 \text{ vol\%}$, $pH_i = 4.0$, and O_2 -saturated). Inset in (a) represents the amount of H_2O_2 generation over the GOND suspension under excitation with a commercial diode laser ($\lambda_{Ex} = 635$ nm, corresponding to (a)) and a green LED ($\lambda_{Max} = 533$ nm). All DPD and POD spectra of GOND were obtained with an additional centrifugation (13000 rpm for 30 min).

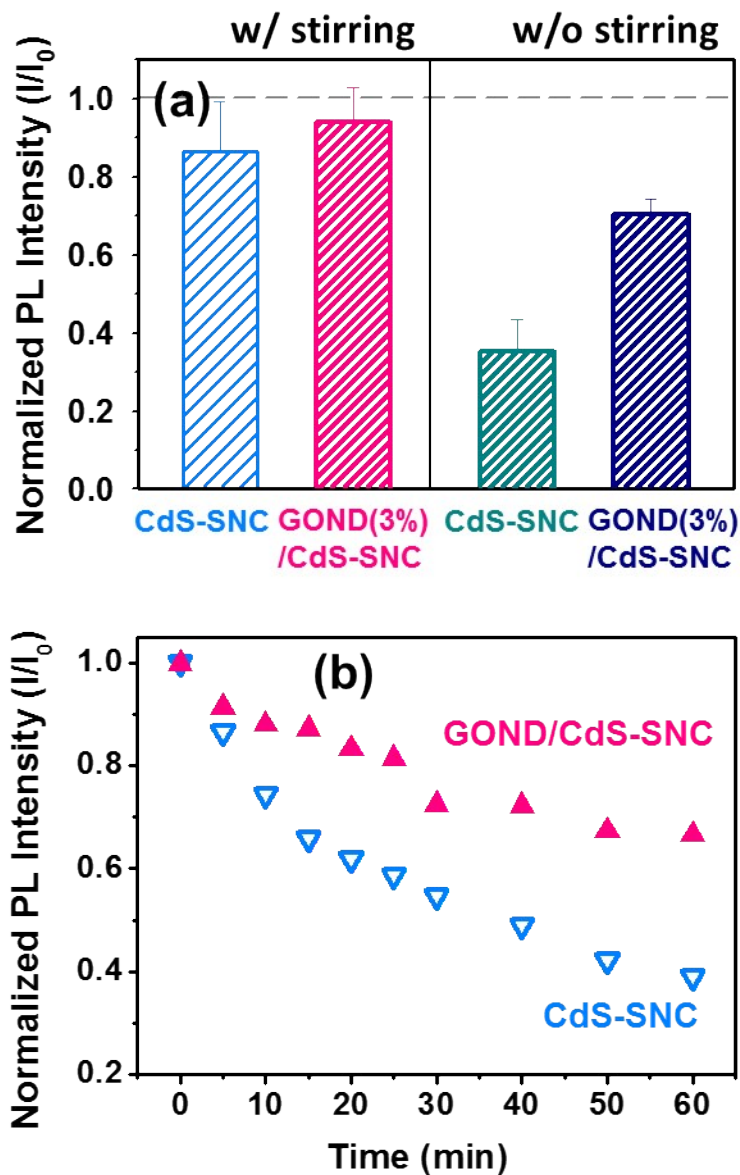


Fig. S6. (a) Normalized emission intensities at 513 nm (as max. PL peak of CdS) of CdS-SNC and GOND (3 wt%)/CdS-SNC in aqueous solution under 1 h excitation at 635 nm (254 mW cm^{-2}) with (left panel) and without stirring (right panel). (b) Time-profiles of normalized emission intensities at 513 nm (as max. PL peak of CdS) of CdS-SNC and GOND (3 wt%)/CdS-SNC in aqueous solution under excitation at 635 nm (254 mW cm^{-2}) without stirring. The PL intensities (I) were normalized by the initial intensity (I_0).

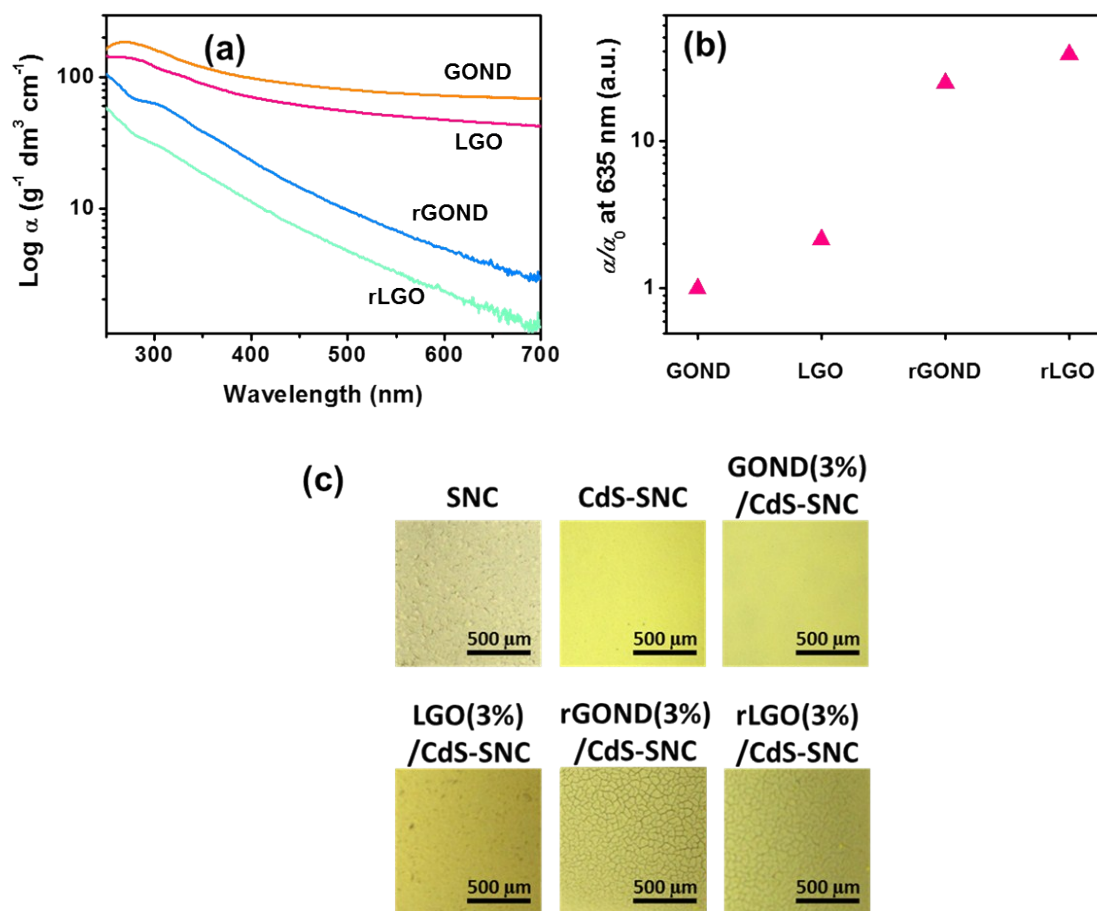


Fig. S7. (a) Absorption coefficient (α) spectra and (b) relative absorption coefficient change (vs. GOND) at 635 nm (as a wavelength of laser excitation) over GOND, LGO, rGOND, and rLGO aqueous solution (0.01 g L^{-1}). (c) Digital photographs of SNC, CdS-SNC, GOND (3 wt%)/CdS-SNC, LGO (3 wt%)/CdS-SNC, rGOND (3 wt%)/CdS-SNC, and rLGO (3 wt%)/CdS-SNC films on slide glasses.

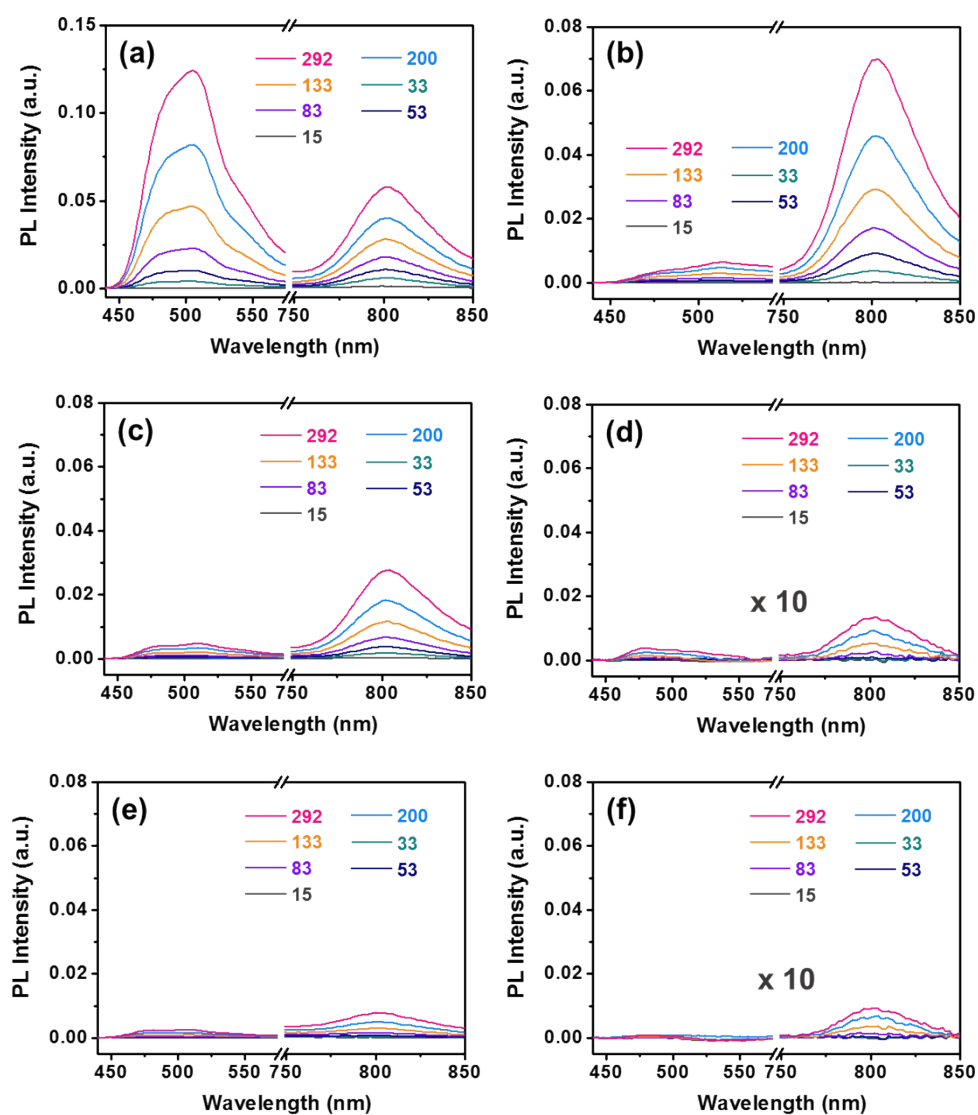


Fig. S8. Transition Emission profiles of (a) SNC, (b) CdS-SNC, (c) GOND (3 wt%)/CdS-SNC, (d) rGOND (3 wt%)/CdS-SNC, (e) LGO (3 wt%)/CdS-SNC, and (f) rLGO (3 wt%)/CdS-SNC in aqueous solution as a function of the incident laser power density (mW cm⁻²) under excitation at 635 nm.

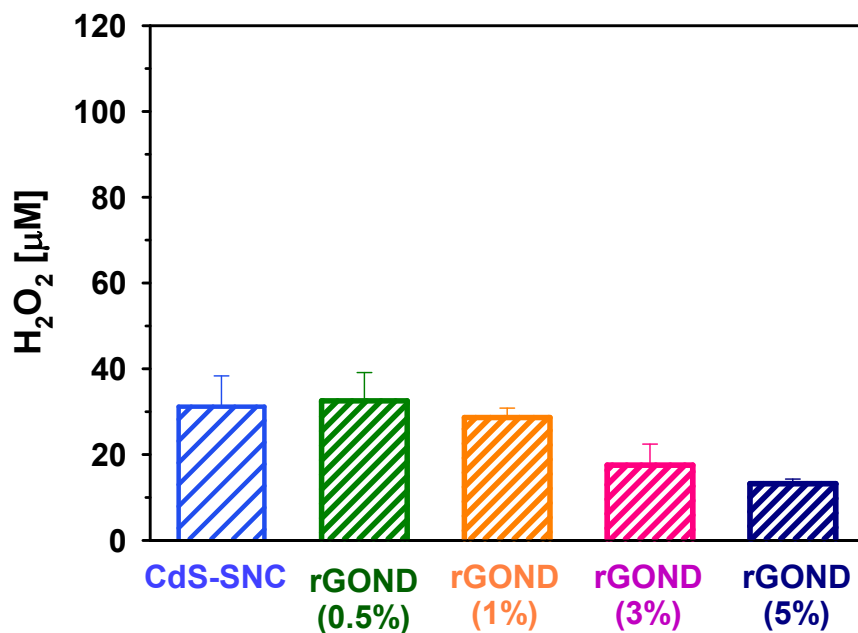


Fig. S9. The amount of H_2O_2 production as a function of the rGOND content (wt%) in rGOND/CdS-SNC hybrids (after 1 h reaction). The experimental conditions were as follows: [catalyst] = 0.5 g L^{-1} of rGOND/CdS component only or 4.0 g L^{-1} overall hybrid of rGOND/CdS-SNC, $[\text{MeOH}]_0 = 5 \text{ vol}\%$, $\text{pH}_i = 4.0$, $\lambda_{\text{Ex}} = 635 \text{ nm}$, and O_2 -equilibrated.

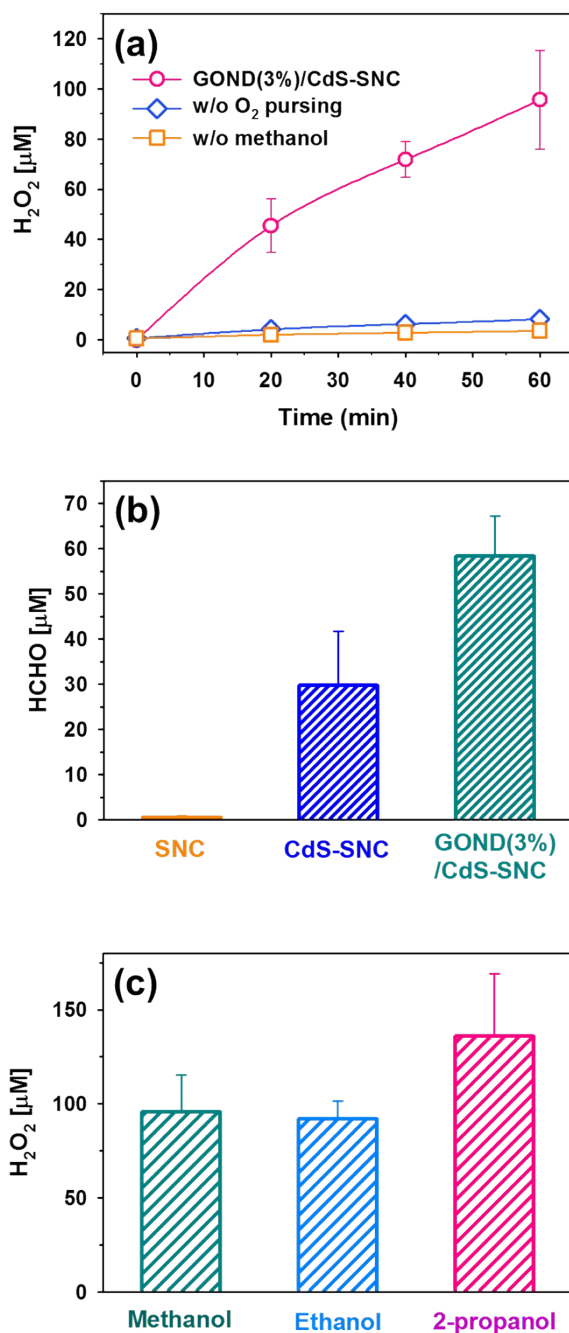


Fig. S10. (a) Time-profiles of H_2O_2 production on GOND (3 wt%)/CdS-SNC with O_2 purging/methanol (5 vol%), with only O_2 purging (without methanol), and only methanol (without O_2 purging, under air-equilibrated condition). (b) The amount of HCHO production on SNC, CdS-SNC, and GOND (3 wt%)/CdS-SNC in methanol (5 vol%) solution (after 1 h reaction). (c) The amount of H_2O_2 production on GOND (3 wt%)/CdS-SNC with different electron donors (after 1 h reaction). The experimental conditions were as follows: [catalyst] = 0.5 g L^{-1} of GOND/CdS component only or 4.0 g L^{-1} overall hybrid of GOND/CdS-SNC, [Electron donor] $_0$ = 5 vol%, pH_i = 4.0, O_2 -equilibrated (except a), and red laser excitation (2400 mW cm^{-2}) for a, c and red LED excitation (23 mW cm^{-2}) for b.

References

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2. R. S. Khnayzer, J. Blumhoff, J. A. Harrington, A. Haeefele, F. Deng and F. N. Castellano, *Chem. Commun.*, 2012, **48**, 209-211
3. J. Olmsted, *J. Phys. Chem.*, 1979, **83**, 2581-2584.