Supplementary Materials

Core-shell nanostructures of graphene-wrapped CdS nanoparticles and TiO_2 (CdS@G@TiO_2): The role of graphene in enhanced photocatalytic H_2 generation

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S1. Calculation steps for Apparent Quantum Efficiency (AQE):

Following well-known equations are used to calculate the AQE.

$$AQE = \frac{Number\ of\ reacted\ electrons}{Total\ umber\ of\ photons\ absorbed} \times 100 \quad (1)$$

$$Number\ of\ reacted\ electrons = 2\ x\ [H_2]\ x\ N_A \quad (2)$$

$$Total\ number\ of\ photons\ absorbed = \frac{Light\ absorbed\ by\ the\ photocatalyst}{The\ energy\ of\ the\ photon} \times t \quad (3)$$

$$Light\ absorbed\ by\ the\ photocatalyst = H \times A \quad (4)$$

$$Energy\ of\ the\ photon = hc/\lambda \quad (5)$$

- $[H_2]$ = 1510 µmol (by most active sample, i.e. CdS@50G@TiO_2)
- $N_A = 6.022 \times 10^{23}\ mol^{-1}$
- H = 1000 W m^{-1} (intensity of 150W solar simulator at AM 1.5G conditions)
- A = 0.0044 m^{-2} (linear surface area of the photoreactor illuminated during photocatalytic reaction)
- h = 6.626 x 10^{-34} J (Planck's constant)
- c = 3 x 10^8 m s^{-1} (speed of light)
- λ = 393 nm (average wavelength of broadband light source which is estimated with reference to the band gap of CdS (2.31 eV). The photons having less energy than the band gap of CdS will not excite the electron to the conduction band of CdS. Hence, the average wavelength of 250-536 nm is selected for AQE calculations [1–4].

By combining the equations 1, 2, 3, 4 and 5, we obtained the values of AQE which are tabulated in Table S1.

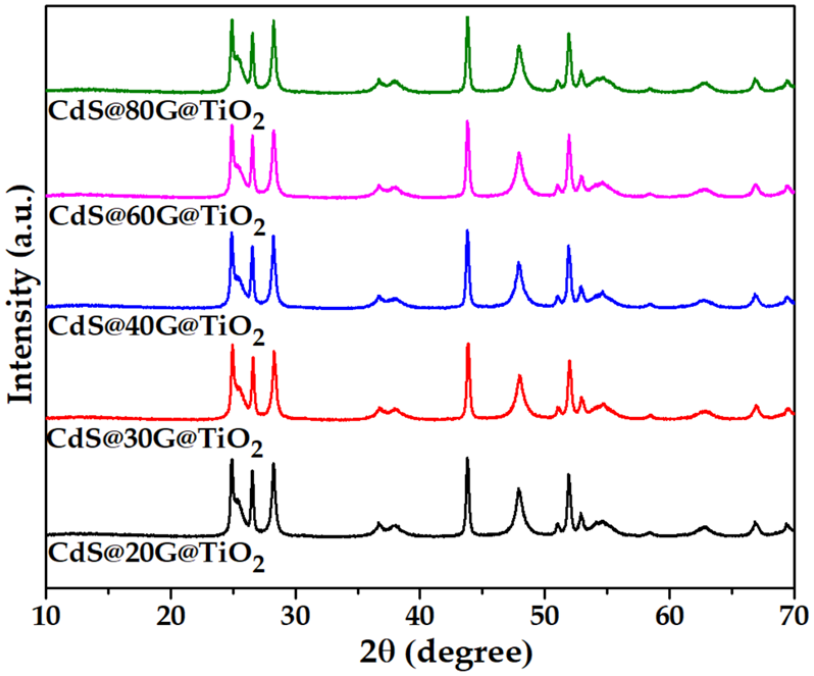

Figure S1. XRD pattern of CdS@xG@TiO_2 (x = 20, 30, 40, 50, 60, 80 µl of GQD solution with concentration of ~100 mg mL^{-1} were used in the synthesis).

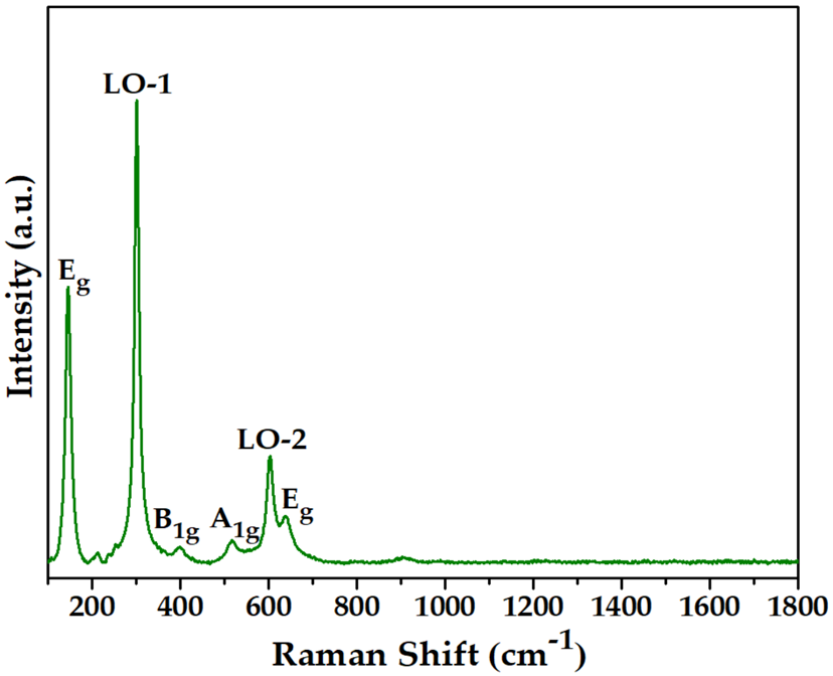

Figure S2. Raman spectrum of the CdS@50G@TiO_2 sample.

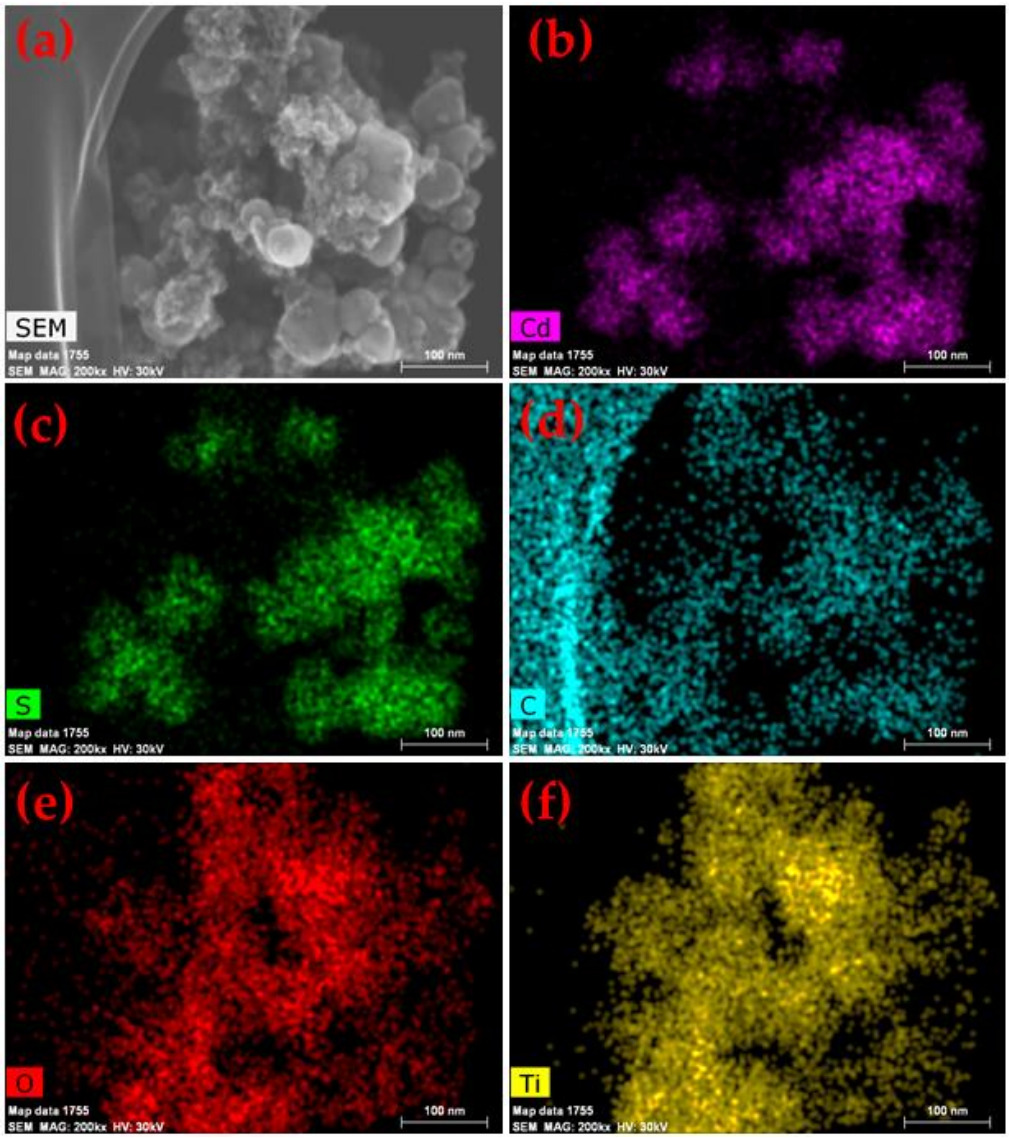

Figure S3. EDX elemental mapping images of the CdS@50G@TiO_2 sample which shows the presence of Cd, S, C, O and Ti in the sample.

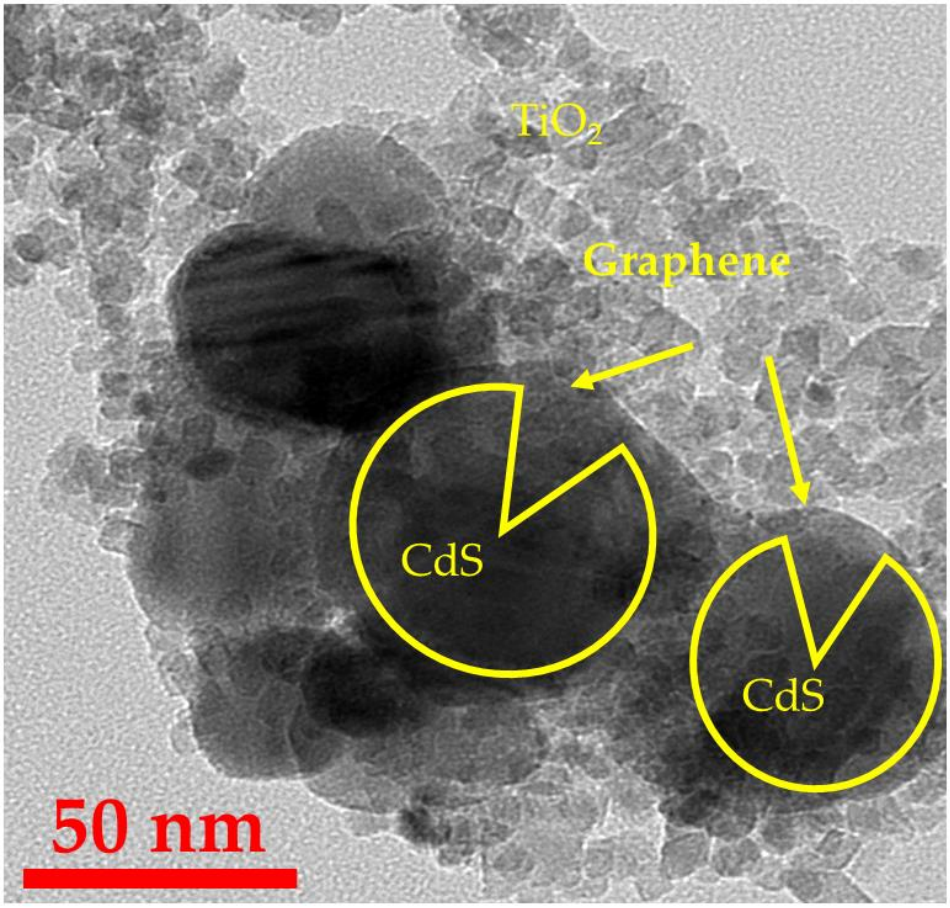

Figure S4. TEM image of the CdS@50G@TiO_2 sample.

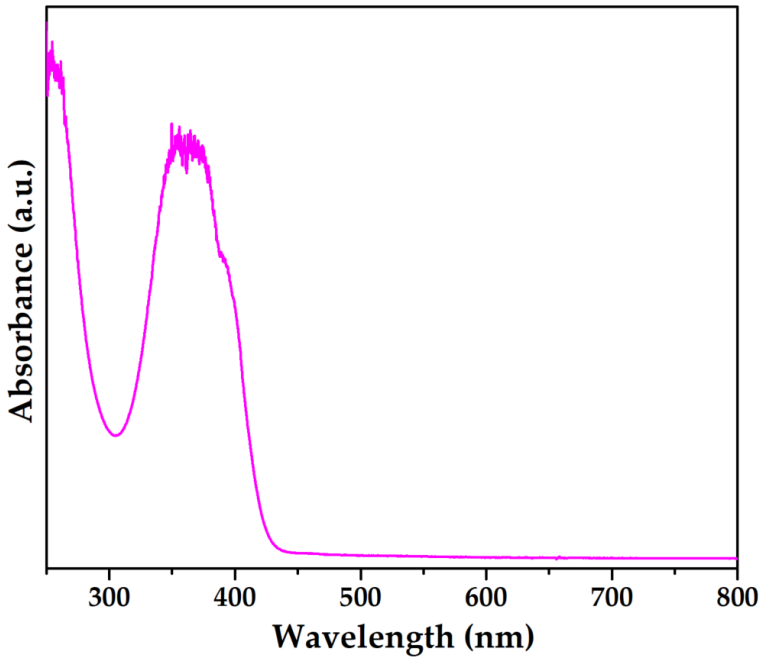

Figure S5. UV-vis spectrum of pure graphene quantum dots (GQD)

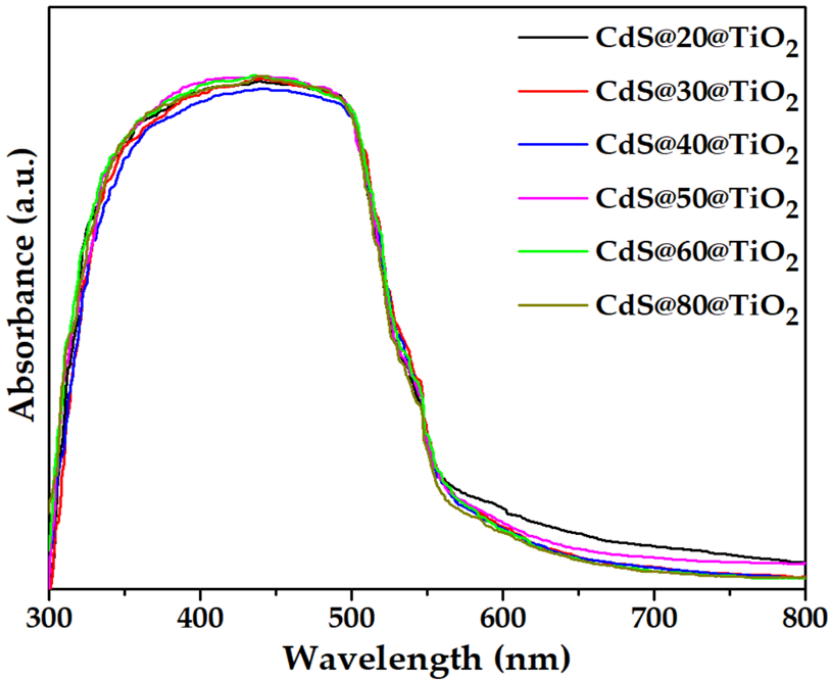

Figure S6. UV-vis DRS spectra of CdS@xG@TiO_2 samples.

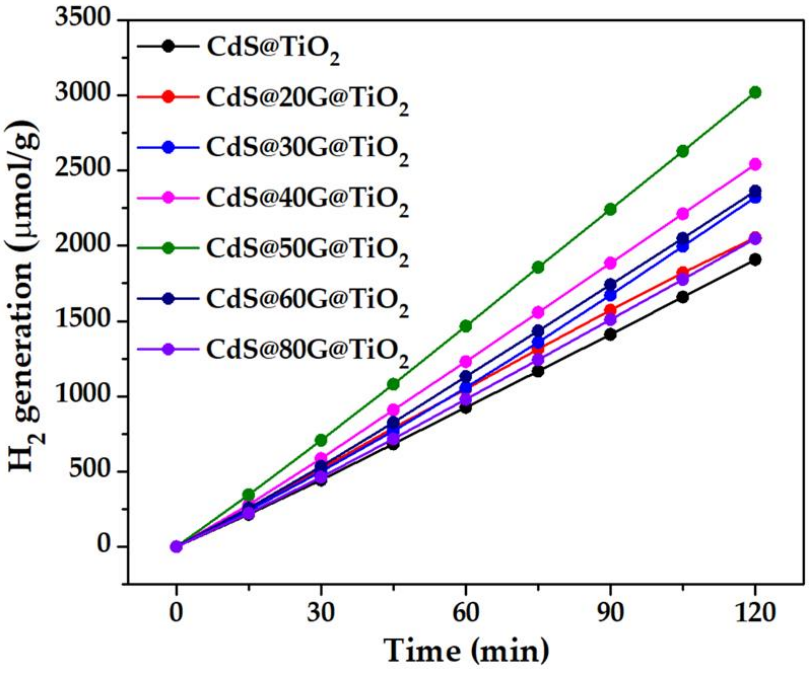

Figure S7. Photocatalytic H_2 generation from water employing $CdS@TiO_2$ and $CdS@xG@TiO_2$ samples under simulated solar light with 1.5 AM filter.

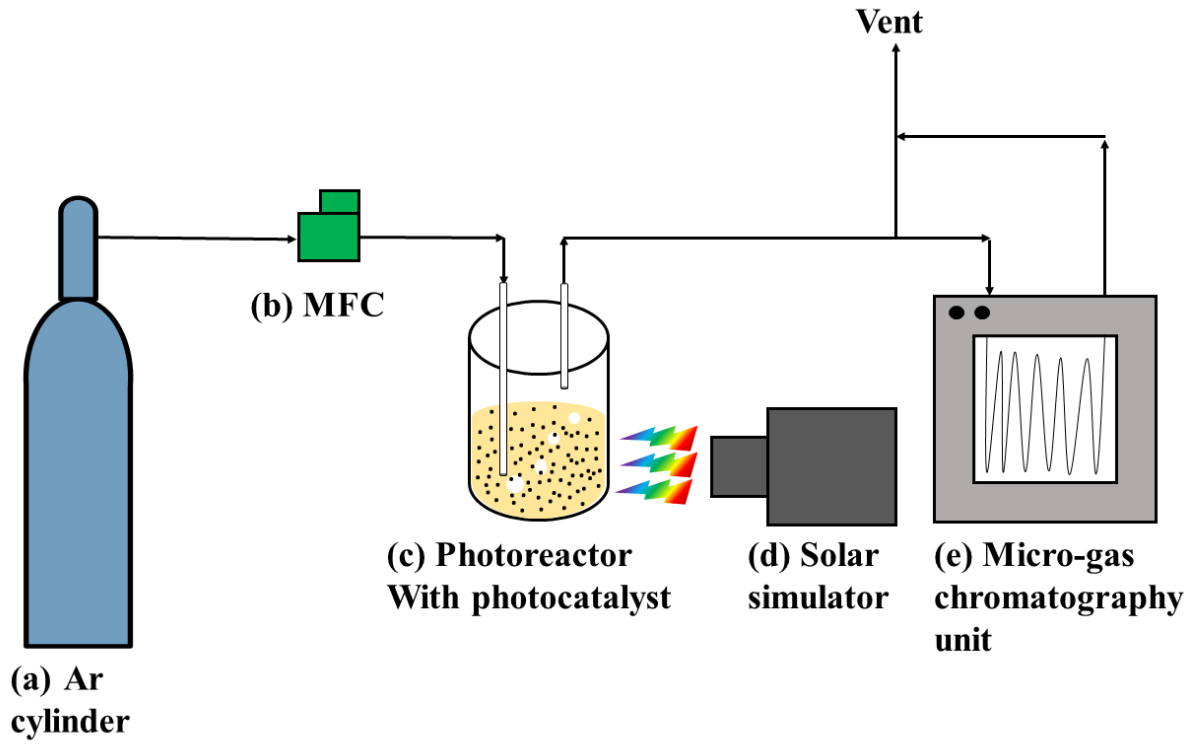

Figure S8. Schematic diagram of photocatalytic H_2 generation setup in which Ar gas (a) was bubbled through mass flow controller (b) from the photoreactor (c) (V = 1.2 L) filled with a uniform reaction mixture consisting of 40 mg photocatalyst in aqueous 0.125 M Na_2S and 0.175 M Na_2SO_3 solution. The photoreactor is illuminated with a solar simulator (d) equipped with AM 1.5 G filter and the effluent of the photoreactor is analyzed by a micro-gas chromatography unit (e).

Table S1. BET surface areas, H_2 production rates and apparent quantum efficiencies (AQE) of all the photocatalytic samples.

Sample	BET surface area $m^2 g^{-1}$	Hydrogen production $\mu mol\ g^{-1} h^{-1}$	Apparent quantum efficiency %
Pure TiO_2	375	565	2.16
Pure CdS	18	673	2.57
CdS@TiO_2	110	954	3.65
CdS@20G@TiO_2	97	1027	3.93
CdS@30G@TiO_2	102	1160	4.45
CdS@40G@TiO_2	107	1270	4.87
CdS@50G@TiO_2	107	1510	5.78
CdS@60G@TiO_2	110	1181	4.52
CdS@80G@TiO_2	96	1024	3.92

Table S2. Comparison of various CdS-TiO_2 with carbon and noble metal based photocatalysts reported for photocatalytic H_2 generation from water.

Sr. Number	Photocatalyst sample	Light source	Reaction conditions	H_2 generation	AQE
1	Pt/CdS/TiO_2 [5]	Osram XBO 450W	Na_2S = 4.8 mM Na_2SO_3 = 7.0 mM Mass of catalysts = 80 mg	0.9 μmol min^{-1}	Not reported
2	Au@TiO_2−CdS [6]	300 W Xenon Lamp (λ > 420 nm)	Na_2S = 0.25 M Na_2SO_3 = 0.35 M Mass of catalysts = 2 mg	3.94 μmol h^{-1}	Not reported
3	C_{60}-Decorated CdS/TiO_2 [7]	4 UV-LEDs (3 W, 420 nm)	Na_2S = 0.25 M Na_2SO_3 = 0.25 M Mass of catalysts = 50 mg	6.03 μmol h^{-1}	2 %
4	Au@CdS/TiO_2 [8]	300 W xenon arc lamp with a UV cutoff filter	[Na_2S]:[Na_2SO_3] = 0.1M Concentration of photocatalysts = 1g L^{-1}	6.03 μmol After 3 hrs	Not reported
5	CdS–TiO_2 [9]	500 W Tungsten filament bulb (λ ≤ 420 nm)	Na_2S = 0.02 M Na_2SO_3 = 0.1 M Mass of catalysts = 50 mg	0.86 mmol h^{-1} g^{-1}	25.42 %
6	CdS–TiO_2 3DOM TiO_2-Au-CdS [10]	PLS-SXE-300C lamp	Na_2S = 0.1 M Na_2SO_3 = 0.1 M Mass of catalysts = 0.1 g	0.18 mmol $h^{-1}g^{-1}$ 1.81 mmol $h^{-1}g^{-1}$	Not reported
7	1 wt% Pt-CdS-TiO_2 [11]	450 W Hg-arc lamp	Na_2S = 0.1 M Na_2SO_3 = 0.02 M Mass of catalysts = 0.1 g	3.94 μmol h^{-1}	Not reported
8	Core-shell TiO_2-CdS [Our previous work] [4]	150 W Xenon solar simulator	Na_2S = 0.125 M Na_2SO_3 = 0.175 M Mass of catalysts = 40 mg	954 μmol h^{-1} g^{-1}	3.53%
9	CdS@G@TiO_2 [current work]	150 W Xenon solar simulator	Na_2S = 0.125 M Na_2SO_3 = 0.175 M Mass of catalysts = 40 mg	1510 μmol h^{-1} g^{-1}	5.78%

Table S3. Comparison of various photocatalysts recently reported for photocatalytic H_2 generation from water.

Sr. Number	Photocatalyst sample	Light source	Reaction conditions	H_2 generation	AQE
1	High crystalline 3% Pt-g-C_3N_4 [12]	300W Xenon arc lamp	10 vol% triethanolamine Mass of catalysts = 50 mg	339 μmol h^{-1} g^{-1}	Not reported
2	Pt/t-ZrO_2/g-C_3N_4 [13]	300 W Xenon Lamp (λ > 420 nm)	10 vol% triethanolamine Mass of catalysts = 50 mg	722 μmol h^{-1} g^{-1}	0.215 %
3	1 wt% Pt/DR-ZnS [14]	300 W Xenon Lamp (λ > 420 nm)	Na_2S = 0.1 M Na_2SO_3 = 0.1 M Mass of catalysts = 20 mg	70 μmol h^{-1}	2.4 %
4	0.37 wt.% Pt- 2C–KNb_3O_8 [15]	300 W Xe-lamp	20% Methanol Mass of catalysts = 50 mg	1148 μmol h^{-1} g^{-1}	Not reported
5	3wt% WS_2/$ZnIn_2S_4$ [16]	300 W Xe lamp (λ ≤ 420 nm)	lactic acid Mass of catalysts = 30 mg	2.55 mmol h^{-1} g^{-1}	3.2 %
6	$ZnIn_2S_4$/$LaNiO_3$ [17]	300 W Xe lamp (λ ≤ 420 nm)	TEOA Mass of catalysts = 20 mg	1600 μmol $h^{-1}g^{-1}$	Not reported
7	Core-shell TiO_2-CdS [Our previous work] [4]	150 W Xenon solar simulator	Na_2S = 0.125 M Na_2SO_3 = 0.175 M Mass of catalysts = 40 mg	954 μmol h^{-1} g^{-1}	3.53%
8	CdS@G@TiO_2 [current work]	150 W Xenon solar simulator	Na_2S = 0.125 M Na_2SO_3 = 0.175 M Mass of catalysts = 40 mg	1510 μmol h^{-1} g^{-1}	5.78%

Table. S4. Estimated values of valence band potential (E_{VB}), conduction band potential (E_{CB}) bandgap (E_g) and difference in the valance band potential (ΔE_{VB}) for pure CdS and pure TiO_2 nanoparticles. The valence band maximum (E_{VBM}) measured by valance band XPS.

Sample	**E_{VB} (eV)**	**E_{CB} (eV)**	**E_g (eV)**	**ΔE_{VB} (eV)**	**E_{VBM} (eV)**	**ΔE_{VBM} (eV)**
Pure CdS	2.00	-0.31	2.31		1.6	
				0.95		0.9
Pure TiO_2	2.95	-0.05	3.0		2.5	

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