

Supplementary Information for

Contribution of organic carotenoid and carbonaceous biomass of *Tagetes erecta* flowers for enhanced solar hydrogen generation

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Experimental Section

1. Materials used

The chemicals and reagents used during the experiments are of analytical grade and no further purification was required. Cadmium acetate dihydrate [$\text{Cd}(\text{CH}_3\text{CO}_2)_2 \cdot 2\text{H}_2\text{O}$, 98%], Sodium Hydroxide (NaOH) and thiourea ($\text{CH}_4\text{N}_2\text{S}$, 99.0%) were obtained from Sigma-Aldrich. Ethanol ($\text{C}_2\text{H}_5\text{OH}$, 99.9%) was acquired from Loba Chemie. During the experiments, the deionised water of type-II grade with a conductivity of $<1 \mu\text{S}/\text{cm}$ was used.

2. Synthesis section

2.1 Preparation of *Tagetes erecta* powder

The waste *Tagetes erecta* flowers were collected from various sources including florist shops, events and ceremonies, religious institutions and household waste within 24 hours and frozen for storage ($\leq 4^\circ\text{C}$). The waste flower *Tagetes erecta* was washed thoroughly three times with deionized water and dried in an electric oven in a dark condition (8 hours, 70°C) for the removal of the contamination. The moisture content of the *Tagetes erecta* flowers ranged from ~84-90%, are sensitive to microorganisms, and should be processed within 3 days [1]. Hence, the removal of moisture content is necessary to increase the shelf life of the flowers. The *Tagetes erecta* flowers were immersed in

liquid nitrogen, freeze-dried for 24 hours and grounded in a mortar pestle to convert it into a yellow powder. The flower powder was screened through a 100-mesh filter in the final step to remove large particles. The extracted flower *Tagetes erecta* fine powder was stored in a sealed container in a dark condition. The freeze-drying prevents the isomerisation of the carotenoid present in the *Tagetes erecta* flowers [1].

2.2 Synthesis of CdS

The synthetic route for the synthesis of CdS has been reported referring to the previous study [2]. For the synthesis, aqueous cadmium acetate dihydrate was taken and stirred under magnetic stirring (800rpm) for 1 hour (70° C). Another aqueous solution of Thiourea was stirred under magnetic stirring (800rpm) for 1 hour (70° C). Both aqueous Cadmium acetate dihydrate and the aqueous Thiourea solution were mixed and stirred continuously for 10 hours at a speed of 800 rpm. After 12 hours of continuous stirring and heating (80° C), the mixture's colour changed from tangerine to yellow indicating the synthesis of CdS. The solution was further calcined at 300°C in an electric oven for 2 hours under a restricted supply of ambient oxygen. After filtering, the mixture was repeatedly cleaned with deionized water and allowed to dry in an electric oven at 70°C for three hours. The obtained CdS was stored in a vacuum-sealed container.

2.3 Synthesis of Carotenoid –CdS

The extracted *Tagetes erecta* powder was dissolved in acetone and stirred for 4 hours at room temperature in a dark environment. The mixture was further carried in a vortex (spinix) for next the 0.25 hours and then continued in a centrifuge for next the 0.5 hours (7000rpm) to separate the carotenoid extract from the residue. The extraction was repeated until the residue became pale and the accumulated supernatants were dried. The dried carotenoid was kept at -10°C in the dark. The extracted carotenoid was dissolved in 0.2(M) sodium hydroxide solution with vigorous stirring in a dark condition for 2 hours of activation. Similarly, CdS is dispersed homogeneously in sodium hydroxide solution by the ultra-sonication method (50 Hz, UP50H Hielscher ultrasonic processor) for 4 hours. The mixture solution was charged in a 50-ml Teflon autoclave at 100°C for 12 hours at a rate of 40°C. The carotenoid-CdS solution was filtered, dried, and kept in a vacuum chamber after many 3 times washes with deionized water. The final product is separated by using centrifugation at 5000 rpm for 5 minutes and subsequently dries at 70°C for 8 hours in an electric air oven in dark conditions.

2.4 Synthesis of Tagetes erecta-CdS

The extracted *Tagetes erecta* powder was dissolved in 0.2(M) sodium hydroxide solution with vigorous stirring and heating (600 rpm, 70^o C) in a dark condition for 2 hours' activation. The resulting Vermilion-coloured solution will be rich in Anthocyanin, carotenoids, and flavonoid pigments [1]. Similarly, CdS is dispersed homogeneously in sodium hydroxide solution by the ultra-sonication method (50 Hz, UP50H Hielscher ultrasonic processor) for 4 hours. Finally, the CdS solution is added to the *Tagetes erecta* solution and continuously stirred for 4 hours (800 rpm, 70^o C). The mixture solution was charged in a 50-ml Teflon autoclave at 180^oC for 18 hours at a rate of 40^oC. Natural cooling brought the resultant solution down to room temperature. The *Tagetes erecta* -CdS solution that resulted was filtered, dried, and kept in a vacuum chamber after many 3 times washes with deionized water and ethanol. The final product is separated by using centrifugation at 5000 rpm for 5 minutes and subsequently dries at 70^oC for 8 hours in an electric air oven in dark conditions. The ratios between *Tagetes erecta* and the CdS photocatalyst used in the work were 1, 3, 5, 7, and 10 wt.%. For comparison, CdS without the addition of *Tagetes erecta* was synthesized similarly to check the performance as a photocatalyst.

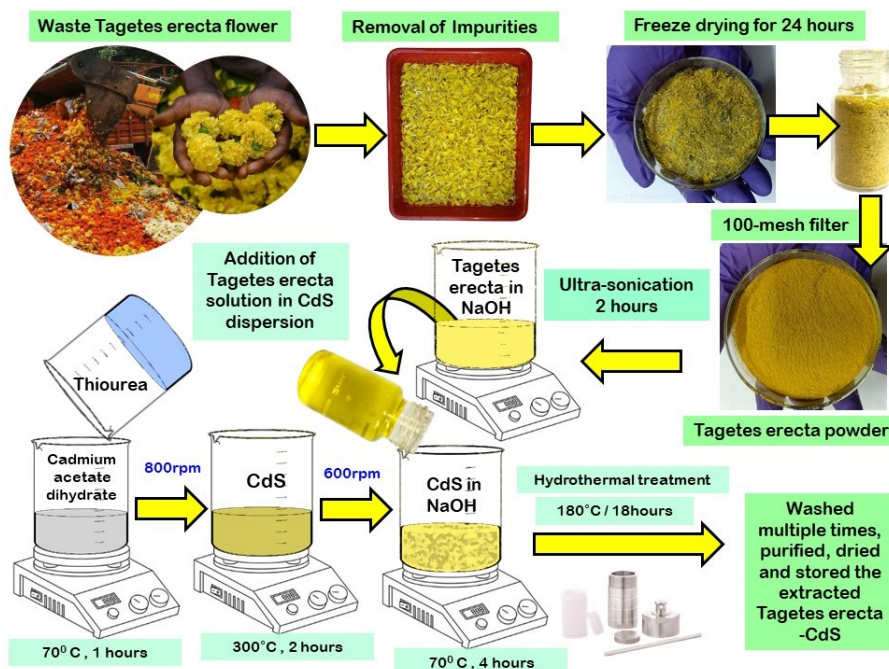


Figure S1: Scheme of the collection of waste *Tagetes erecta* flower, transformed into fine powder and synthesis of *Tagetes erecta* -CdS

3. Physicochemical Characterization

Multiple characterization approaches were used to characterise the physicochemical parameters of the powder photocatalyst. X-ray diffraction was used to analyse the materials morphology and crystallinity using XRD: X'Pert3 powder and Empyrean, PANalytical (scanning range: 10-80°). Field emission scanning electron microscopy with energy dispersive X-ray spectroscopy (FESEM-EDS: Hitachi S-3400, 15.0 KV, WD: 5.5 mm) and high-resolution transmission electron microscopy (HR-TEM: JEOL F-200 multipurpose electron microscope, 200 kV) Fourier transform infrared spectroscopy (FTIR: PerkinElmer Spectrum-2 Imaging System, 400–4000 cm⁻¹) was used to examine the materials' chemical stability. Horiba FluoroMax Plus (1700nm, 25ps) was used to analyse photoluminescence spectra, and UV-Vis (Perkin Elmer Lambda 365 UV/Vis Spectrophotometer) was used to analyse the optical characteristics and band-gap of the materials. Model AXIS Supra X-ray Photoelectron Spectroscopy (XPS) under Al K α irradiation was used to investigate the surface elemental interactions. In a disposable foldable capillary cell, the materials zeta potential and particle size were determined using a (Malvern Zetasizer Nano Z zeta potential analyser). Using a surface area and porosity analyser (Quantachrome TouchWin) at 77.3 K, the nitrogen adsorption and desorption isotherms, specific surface area, and porosity parameters of the samples were determined. Brunauer-Emmett-Teller (BET) was used to calculate the specific surface area. Using a PerkinElmer TGA 4000, the thermogravimetric analysis was carried out at a temperature of 850°C and a scan rate of 15°C. On an Auto Lab (PGSTAT 204) electrochemical workstation equipped with an impedance analyser in a three-electrode configuration [Ag/AgCl; 3(M) KCl and Pt counter electrode], electrochemical impedance spectroscopy (EIS) and transient photocurrent studies were carried out. After pre-mixing DMF and Nafion, Tagetes erecta-CdS photocatalyst was added. After one hour of ultra-sonication, a coated film was fabricated by doctor blade technique on ITO glass using the slurry and functions as working electrodes. The coating on ITO glass was dried in an electric oven at 80°C for 12 hours under atmospheric oxygen.

4. Photocatalytic Hydrogen Generation:

The solar water splitting for hydrogen generation is shown in our previous report [3]. The capability/performance of the photocatalyst has been investigated with its recyclability properties. For the batch hydrogen generation, the pH, electrical conductivity and the dissolved solids of 25 ml of deionised water were measured using a portable pH/EC/TDS checker (Hanna Instruments, USA; HI991300P). A solar simulator (manual shutter, Newport Oriel LCS-100) was used to imitate the sun with an intensity of 113 mW cm⁻². The LCS-100 solar simulator (Class ABB), when fitted with the AM

1.5G air mass filter, may achieve class-A spectral performance with an output of 1 sun irradiance, in accordance with IEC and ASTM specifications. The analysis of hydrogen production was conducted using the water column displacement method. Before the hydrogen generation experiment, 50mg of the photocatalyst were dispersed in 25ml of deionized water and Na₂S (sacrificial agent) was added. The mixture was treated ultra-sonication for 1 hours for the homogenous dispersion. A vacuum pump (Rivotek, 30 LPM) was used to remove O₂ (air) from the glass reactor before each photocatalytic reaction experiment. For ensuring anaerobic state. The photocatalyst is loaded in a special glass made photoreactor which is shown in our previous report with a real life video [3]. Until the rate of hydrogen generation diminishes to zero, the photocatalytic process is carried out for over six hours. The produced gas was passed through a C₆H₃K₃O₃ solution to absorb any produced oxygen and the displacement of water was used to calculate the total amount of hydrogen produced over the time. After each hydrogen generation experiment, the powder photocatalyst was separated using centrifuge, washed with deionised water and dried in an electric oven at 60 °C for 3 hours. The photocatalysts recyclability was investigated over the course of four successive cycles (0, 7,14 and 21 days). A particular photocatalysts performance is examined in terms of apparent quantum efficiency and photocatalytic activity. Based on the cumulative hydrogen production versus time data, the various photocatalysts' photocatalytic activity (mmol_{hydrogen} g⁻¹ hr⁻¹) is calculated. The solar simulator's whole-band spectrum and band-pass filters at 420 nm are used in the experiments. A 420 nm band-pass filter is used to calculate apparent quantum yields.

Table S1: More details of used water and solar simulator has been provided:

Ultra-pure type-II water (25°C)	pH	6.87
	Electrical conductivity	0.09 μS/cm
	Total Dissolved Solids	0.007ppm
Newport Oriel LCS-100 (Class ABB)	Lamp type	Xenon 100 W
	Output Beam Size	38 x 38 mm
	Beam Divergence, Half Angle	<6 °
	Typical Output Power	1.0 sun (100 mW/ cm ²)
	Output Intensity measurement	Newport 843-R
Photocatalytic Activity	CdS Full band (wavelength ≥ 420 nm)	5.05 mmole h ⁻¹ g ⁻¹
	CdS-Carotenoid Full band (wavelength ≥ 420 nm)	14.88 mmole h ⁻¹ g ⁻¹
	Tagetes erecta-CdS 420 nm band pass filter	29.7 mmole h ⁻¹ g ⁻¹
	Tagetes erecta-CdS Full band (wavelength ≥ 420 nm)	34.97 mmole h ⁻¹ g ⁻¹

5. Additional Results

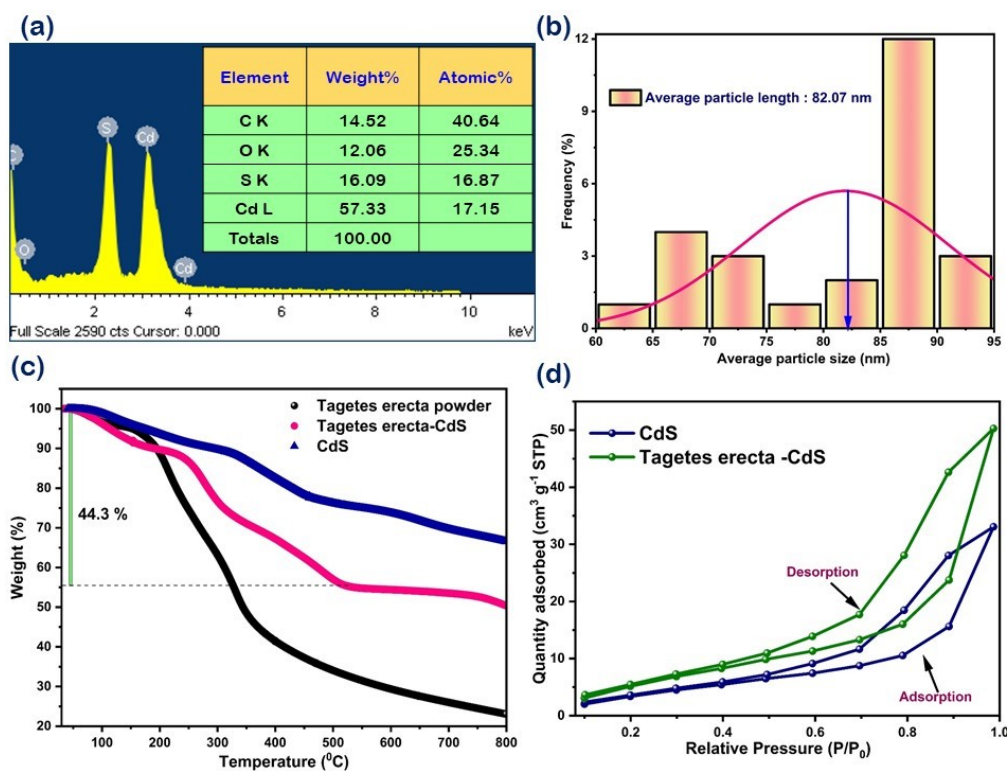


Figure S2: (a) EDX spectra of *Tagetes erecta*-CdS (b) Average particle size of *Tagetes erecta*-CdS (c) TGA spectra of CdS and *Tagetes erecta*-CdS (d) BET Analysis of CdS and *Tagetes erecta*-CdS

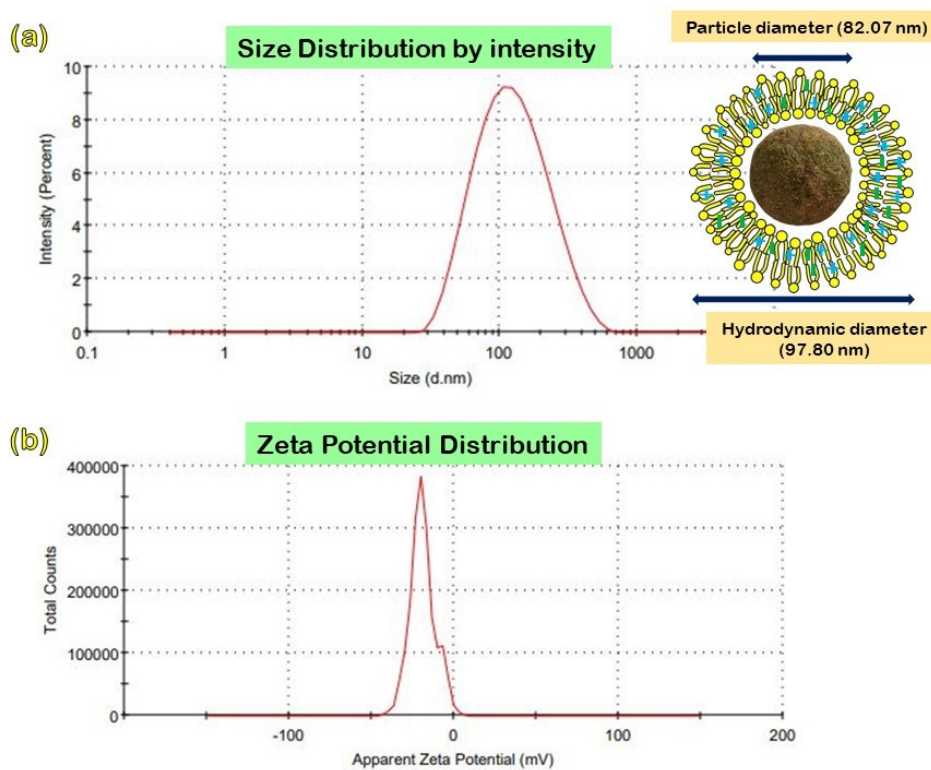


Figure S3: (a) Particle size of *Tagetes erecta*-CdS (b) Zeta potential of *Tagetes erecta*-CdS

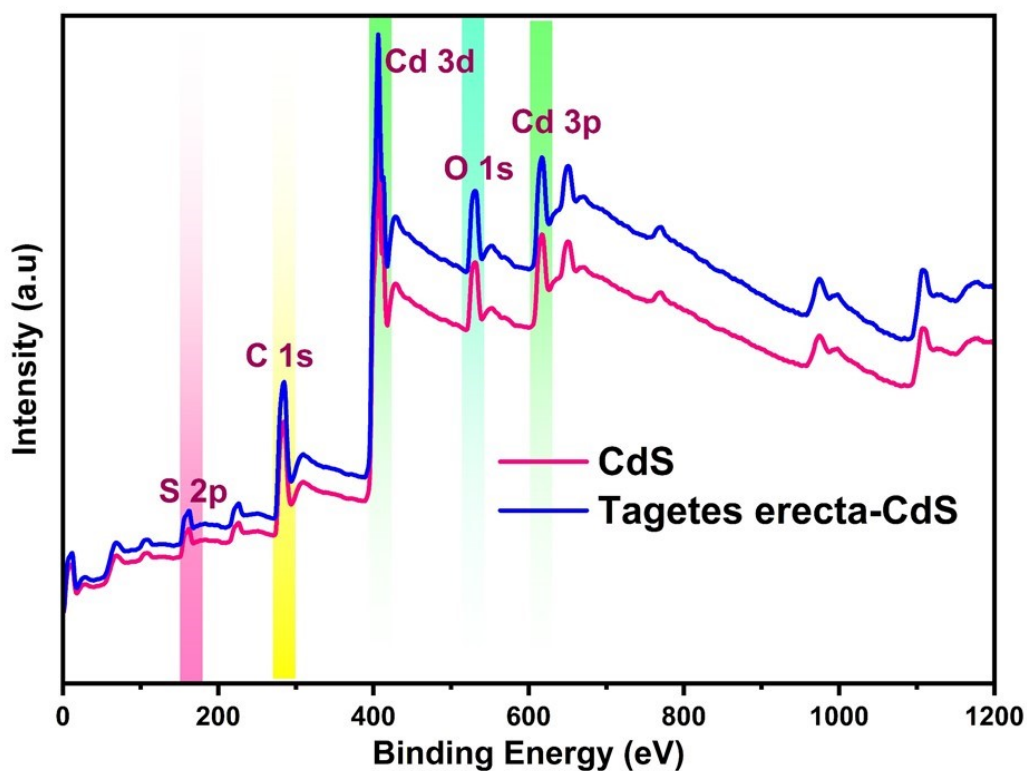


Figure S4: XPS survey scan of *Tagetes erecta*-CdS

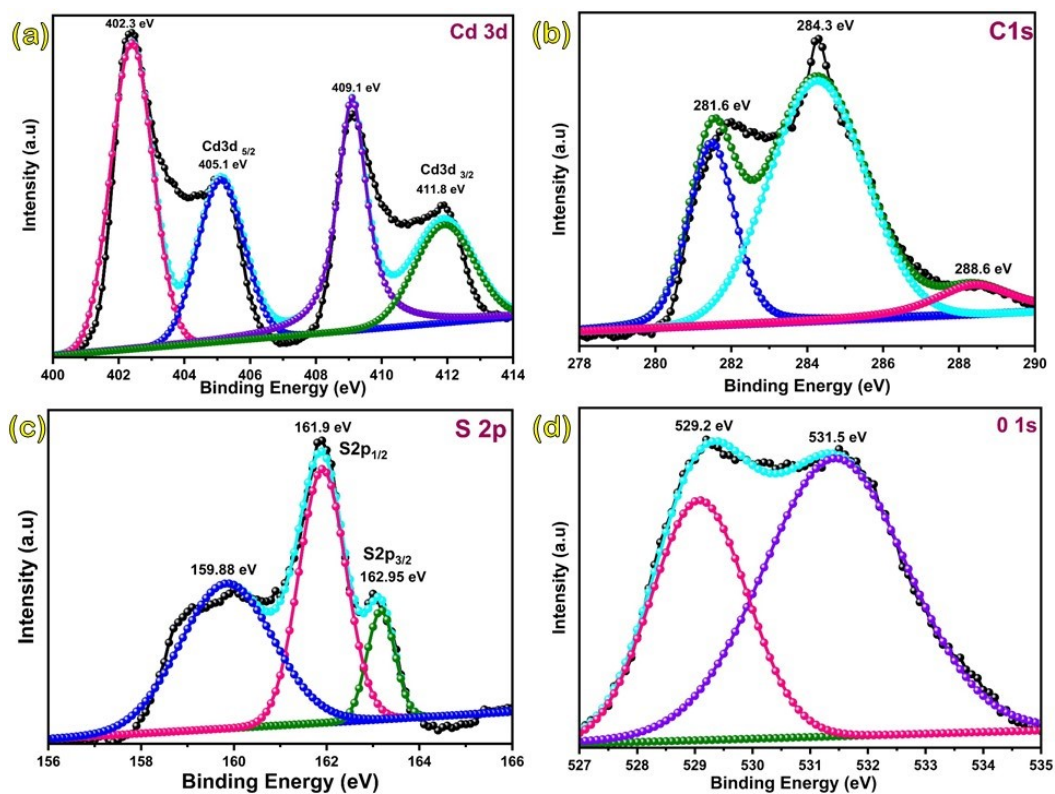


Figure S5: XPS spectra of the (a) Cd 3d (b) C 1s (c) S 2p (d) O 1s

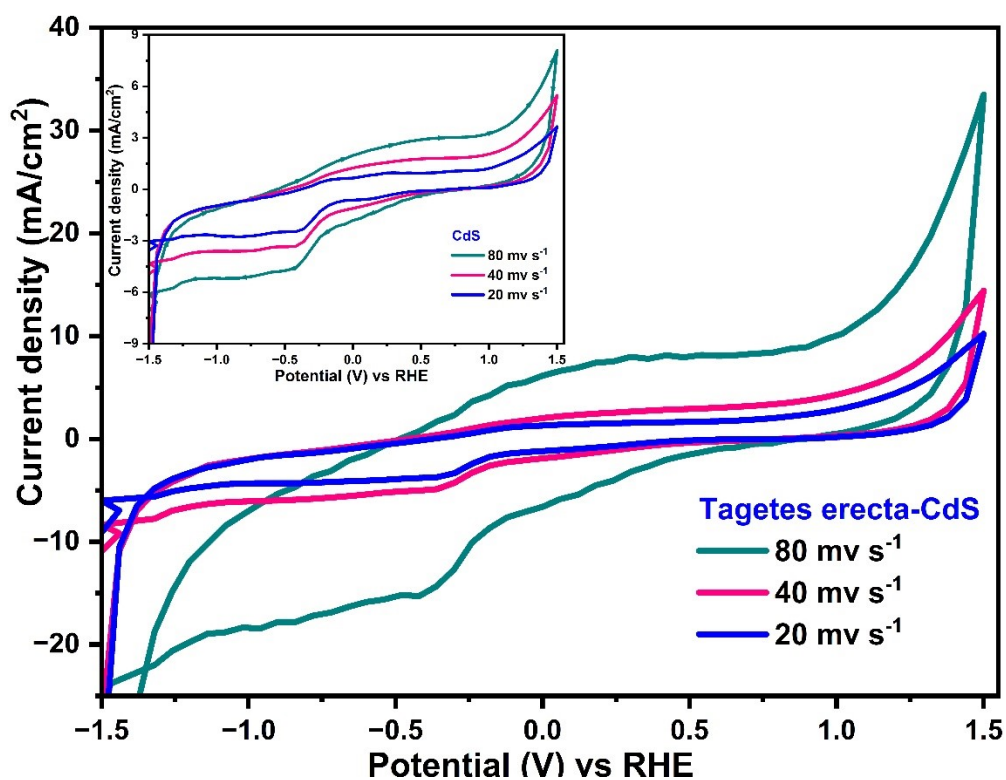


Figure S6: CV response at different scan rates (20, 40 and 80 mv S⁻¹) for TE-CdS and CdS (Inset) in 0.5(M) Na₂S

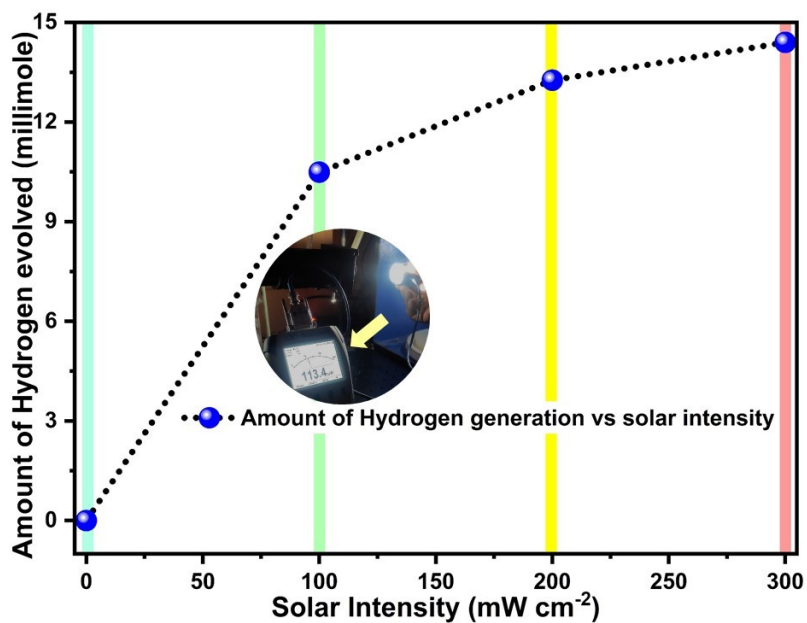


Figure S7: Variation of hydrogen evolution over six hours (mmol) with respect to change in solar intensity

Table S2: Recyclability analysis of CdS, Car-CdS and TE-CdS photocatalyst after 4-cycles usage

Photocatalyst	Millimole/g _{catalyst}				Performance decay (%)
	1 st cycle	2 nd cycle	3 rd cycle	4 th cycle	
CdS	30.2	24.6	23	21.8	27.33
Car-CdS	89.2	82.4	76.4	72	19.28
TE-CdS	209.8	191.8	173.8	172	18.02

Table S3 : Apparent quantum yields of *Tagetes erecta*-CdS photocatalyst and the parameters of the incident monochromatic lights.

Wavelength (nm)	Irradiation area (cm ²)	Power density* (mW cm ⁻²)	Amount of hydrogen production (mmol) in 1 hour	Apparent quantum efficiency (%)
420 ± 5.5	14.44	113	1.7	17.25

The AQE (%) were calculated based on the amounts of Hydrogen evolved under monochromatic light irradiation in one hour. The detailed calculation of apparent quantum efficiency (AQY) is shown in our previous report and by Yu.et.al [4]. The power density of the irradiated light was measured using a power meter (Newport 843-R) *. To evaluate the quantum efficiency of the photocatalyst, a 420nm band pass filter was used and the irradiation intensity was measured with a power meter (Newport 843-R). The quantum efficiency was calculated according to the following equation:

$$QE = \frac{\text{The number of evolved hydrogen atoms}(N_H)}{\text{The number of incident photons}(N_p)} \times 100\%$$

Cell Viability assay

In order to assess the environmental impact, we have performed the cell viability studies of TE-CdS, Carotenoid-CdS, and Pristine-CdS, and the results are shown in figure S8-b. The cell viability assay shows that after 72 h, the cell viability percentage of Car-CdS was 48.3%, followed by TE-CdS (47.1%), and pristine CdS (9.8%). Carotenoids moiety helps to prevent oxidative damage to the cellular structure by scavenging free radicles and thereby reduces the risk of UV-induced cell damage. Tissues, which are exposed to UV radiation, are associated with the photo-oxidative process leading to photo-damage. The cells were cultured into the 96 –well culture/reaction plates (Cole-Parmer) in 3-(4,5-Dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide (MTT-used to assess cell viability as a function

of redox potential), supplemented with 10 % Fetal Bovine Serum (supplement for in-vitro cell culture) ,1% antibiotic-antimytotic solution, and 1% NEAA (7 kinds of non-essential amino acids). The MTT reagent was added to each cell samples and incubated for 4 hours at a temperature of 310.15K in 5% CO₂ atmospheric condition. The same experiments are repeated three time over the span of 24, 48 and 96 hours. Formazan was created during the incubation process by the reduction of the metabolically active cells in the culture media as a result of a reaction between the dehydrogenase enzymes and the living cells' mitochondria. After the cell culture, the absorbance of the sample was recorded at a wavelength of 590 nm in a 96-well plate reader (Agilent BioTek microplate reader). Since, the absorbance obtained is directly proportional to the number of active cells, it can be used to determine the number of living cells.

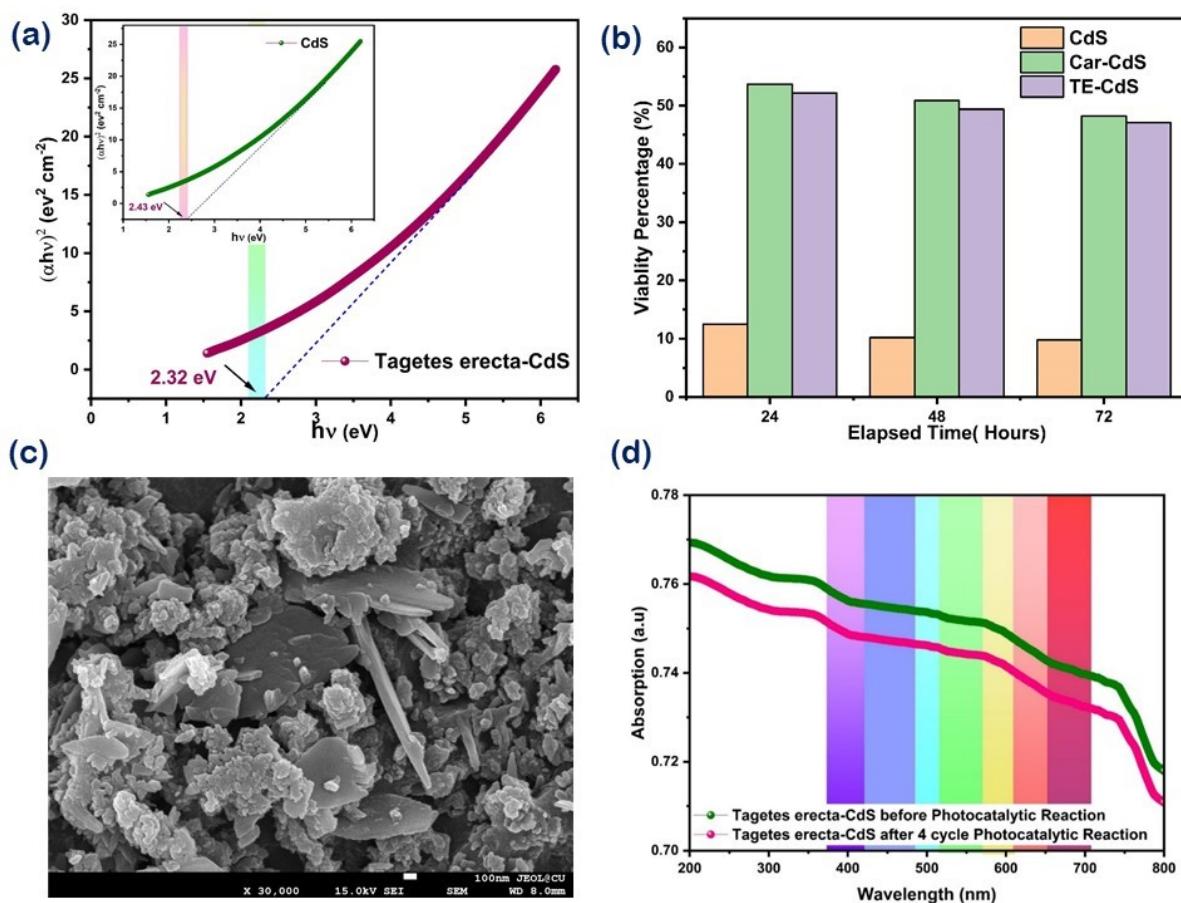


Figure S8: (a) Tauc plot of CdS (inset) and Tagetes erecta-CdS (b) Cell viability study of CdS, Car-CdS and TE-CdS. (c) FE-SEM of TE-CdS after 4 cycles of visible-light-driven H₂ evolution (d) Change in the absorption of Tagetes erecta- CdS after 4 cycle of photocatalytic hydrogen generation.

Table S4: Summary of dye-sensitized semiconductor systems for photocatalytic hydrogen generation

Materials/ photocatalyst	Light Source	Activity	units	Reference
EY-Pt/TiO ₂	Solar simulator	0.1	mmoles h ⁻¹	[5]
Eosin Y-fixed Pt/TiO ₂	Solar simulator	0.3	mmoles g ⁻¹ h ⁻¹	[6]
EY-Pt/rGO	Solar simulator	0.4		[7]
Pt loaded KTa(Zr)O ₃ / Rhodamin	Solar simulator	0.8		[8]
EY-Pt/MWCNT, TEA	Solar simulator	3.4		[9]
Ch-Car -dyad on TiO ₂	Solar simulator	9.1		[10]
Carotenoid-CdS	Solar Simulator	14.8		

Table S5: Summary of photocatalytic hydrogen generation system with different photo catalyst-substrate combination

Materials/ photocatalyst/Substrate	Light Source	Activity	units	Reference
Co/CdS/CdO _x - Grass	Solar simulator	1	mmoles g ⁻¹ h ⁻¹ 1	[11]
Co/CdS/CdO _x - Sawdust	Solar Simulator	0.75		
Co/CdS/CdO _x -Bagasse	Solar Simulator	0.37		
P3HT-g-C ₃ N ₄ , Na ₂ S-Na ₂ SO ₃	Solar simulator	3		[12]
C/CdS/ raisin tree leaves with lactic acid	Solar simulator	5.7		[13]
CdS-MoS ₂ -CoO _x	300 W Xenon arc lamp	7.4		[14]
CdS-Pd	300 W Xe lamp	8.4		[15]
Co/CdS	300 W Xe lamp, λ > 420 nm	8.6		[16]
CdS/WC	300 W Xe lamp, λ ≥ 420 nm	9.1		[17]
CoS _x /CdS	Xe lamp, λ > 420 nm	9.4		[18]
WO ₃ (H ₂ O)0.333/CdS(Ws)	Solar simulator	10.3		[19]
CdS/Co ₉ S ₈	300 W Xe lamp, λ > 420 nm	11.6		[20]
Pt/CdS	300 W Xe lamp, λ > 400 nm	13		[21]
Co ₃ O ₄ @CdS	300 W Xe lamp, λ > 420 nm	16.3		[22]
Ru(WC)/CdS	300 W Xe lamp, λ ≥ 420 nm	16.8	[23]	
CdS/WS ₂	300 W Xe lamp	19.8	[24]	

Ni(OH) ₂ /CdS	300 W Xe lamp, $\lambda \geq 420$ nm	20.1		[25]	
(Pd/WC-F)/CdS	300 W Xe lamp, $\lambda > 420$ nm	24.5		[26]	
ZnO–4ABBN, MeOH	Visible; solar simulator	25.5	mmol h ⁻¹	[27]	
rGO /WO ₃ -TpPa-1-COF	300 W Xe lamp, $\lambda > 420$ nm	26.7	mmoles g ⁻¹ h ⁻¹	[28]	
Carotenoid -CdS	Solar simulator ; full band	14.8		¹	This work
Tagetes erecta-CdS	Solar simulator ; full band	34.9			This work

Cost Analysis of TE-CdS and CdS

The assessment for the overall cost-effectiveness (detailed comparative cost analysis) for hydrogen generation using TE-CdS and pristine CdS (base case) is performed and shown below

Basis: 1 gm photocatalyst, 1 day/24 hours operation (4 cycles of each 6 hrs operations considering recyclability of the catalysts). The cost is normalized with the production rate (mmol / g_{cat} day) in order to assess the cost effectiveness and benefits.

Table S6: Solar Hydrogen generation by pristine CdS photocatalyst (Base Case) :

	Chemicals	Approx. quantity	Cost (Dollar)
Synthesis of CdS			
Chemical used	Cadmium sulphide	1 g	0.42
	Deionized water	50 ml	00.00
Electricity Involved	Stirring	12 hours (6.6 KWh)	0.78
	Hydrothermal/ Calcination	10 hours (15 KWh)	1.76
	Centrifuge	0.15 hours (0.08 KWh)	0.0095
	Drying	6 hours (12 KWh)	1.69
Hydrogen generation performance in presence of solar simulator			
Chemical used	Sodium Sulfide	0.2g	0.00045
Electricity Involved	Ultra- sonication	0.5 hours (0.011 KWh)	0.0013
	Solar simulator	24 hours (2.4 KWh) (For 4 cycle)	0.288
Total			4.949
Amount of Hydrogen evolution in 4 cycle (Refer Recyclability table)			99.6 millimole (1day)
Normalized cost per photocatalytic activity		$= \frac{\text{Total Cost}}{\text{mmole } g_{\text{cat}} \text{ day}}$	0.049 \$/ mmole g_{cat}⁻¹ day⁻¹

Table S7: Solar Hydrogen generation by TE-CdS photocatalyst:

The detailed estimation of the Tagetes erecta-CdS photocatalyst cost to Hydrogen generation are categorised in several parts as follows:

	Chemicals	Approx. quantity	Cost (Dollar)
Collection of Tagetes erecta flowers			
Waste flowers were collected from residential, commercialization and religious places on a daily basis within the day. On daily basis, a lot of floral waste after being used, get waste and becomes garbage's.			
Pre-Processing of Tagetes erecta flowers			
Floral waste	Waste Flowers (Tagetes erecta)	1 kg (Approx.)	Waste
Electricity Used	Freeze drying (Vacuum pump, refrigeration and all accessories)	24 hours (20.1 KWh)	2.42
	Drying	8 hours (9.6 KWh)	1.13
Synthesis of Tagetes erecta-CdS			
Chemical used	Fine Tagetes erecta powder	0.05 g	00.00
	Deionized water	200 ml	-
	Cadmium sulfide	1 g	0.42
	Ethanol	100 ml	0.60
	Sodium hydroxide	8 g	0.11
Electricity Involved	Stirring	22 hours (12.1 KWh)	1.42
	Hydrothermal/ Calcination	20 hour (30 KWh)	3.53
	Centrifuge	0.25 hours (0.03 KWh)	0.035
	Drying	15 hour (30 KWh)	2.12
Hydrogen generation performance in presence of solar simulator			
Chemical used	Sodium Sulfide	0.2 g	0.00045
Electricity Involved	Ultra- sonication	0.5 hours (0.05 KWh)	0.0059
	Solar simulator	24 hours (2.4 KWh) (For 4 cycle)	0.28
Total			12.071
Amount of Hydrogen evolution in 4 cycle (Refer Recyclability table)			747.4 millimoles (1day)
Normalized cost per photocatalytic activity		$= \frac{\text{Total Cost}}{\text{mmole } g_{cat} \text{ day}}$	0.016 \$/ mmole $g_{cat}^{-1} \text{ day}^{-1}$

The normalized cost of TE-CdS based on the production rate and activity shows 0.016 \$/ mmole $g_{cat}^{-1} \text{ day}^{-1}$ which is lower than pristine CdS and the benefits of choosing TE will outweigh the costs.

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