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Enhancement of Hydrogen Production Using Photoactive Nanoparticles on a Photochemically Inert Photonic Macroporous Support

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1. Syntheses and characterisation of templates and precursors

Synthesis of Polystyrene Sphere Templates: Polystyrene spheres of diameter 300 - 600 nm were synthesised by emulsifier free emulsion polymerisation modifying a literature method.¹ A 3-necked round bottom flask was fitted with a reflux condenser, overhead motorised stirrer, thermometer and dropping funnel for addition of reagents. Reactions were stirred at constant speed between 245-360 rpm. Water (1133 mL) was added to the flask and heated to 70 - 80 ± 2 °C under flowing nitrogen. Styrene (140 mL, 1.218 mol) was washed four times with NaOH (0.1 M, 140 mL) and four times with water (140 mL) in a separating funnel to remove inhibitors. Inhibitor free styrene (133 mL, 1.157 mol) was added to the round bottom flask and the temperature stabilised. After nitrogen purging for 30 min, $K_2S_2O_8$ (0.442 g, 1.635 mmol) dissolved in water (66 mL) was added, and the reaction allowed to proceed for 28 hours. The solution was cooled to room temperature, and filtered through glass wool to remove polymer agglomerates.

polyvinylpyrrolidone as a stabiliser as described in a literature method.²

Sphere	Total	Styrene	$K_2S_2O_8$	PVP	Temp (°C)	Stir speed	Reaction
Size (nm)	volume	volume	initiator	stabiliser		(rpm)	Time (h)
	(mL)	fraction(%)	mass (g)	added(g)			
260±20	133	9.7	0.3	0.25	70±2	200	24
400±13	1333	9.7	0.442	0	80±2	245	28
430±9	1333	9.7	0.221	0	70±2	245	28
500±17	1333	9.7	0.442	0	70±2	245	28

Table S1 Summary of reaction conditions used for polystyrene sphere synthesis.

Polystyrene spheres were packed into colloidal crystal templates by centrifugation of the colloidal solution (4000 rpm, 3 h) and then dried at 66 °C overnight to give the template as a white brittle solid.

Table S2. Relationship between polystyrene sphere template diameter and the resultingmacroporous structure. Analysed by SEM

Material	Template	Periodicity ^a	Fill factor,
	Diameter/ nm	/ nm	φ (%) ^ь
1	260±20	165±7	16
2	400±13	255±17	17
3	430±9	270±12	17
4	500±17	320±20	16

^aPeriodicity was determined from approximately 100 independent measurements of 1-10 pores.

^bCalculated using Equation 1 in the main text.



Figure S1a. TGA (blue line) of oleic acid coated *mac*- ZrO_2 . The red line is the corresponding DSC. 11.6 mg of oleic acid coated *mac* ZrO_2 gave a 2.2 % (0.255 mg) mass loss.

Oleic acid has an estimated footprint of 48 $Å^{2.3}$ 0.255 mg of oleic acid = 0.26 m².

The surface area of *mac*- $ZrO_2 = 25 m^2g^{-1}$.

The area of the TGA sample = $(11.6-0.255 \text{mg}) \times 25 \text{ m}^2\text{g}^{-1} = 0.28 \text{ m}^2$. Therefore the oleic acid is a monolayer coverage.



Figure S1b. ZrO₂ and *mac*-ZrO₂ powders of varying periodicity. a) commercial ZrO₂; b) **1**; c) **2**; d) **3**; e) **4**.



Figure S1c. *nan*-CdS@ZrO₂ and *nan*-CdS@*mac*-ZrO₂ powders. a) **5-CdS**; b) **1-CdS**; c) **2-CdS**; d) **3-CdS**; e) **4-CdS**.



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Figure S2a. SEM of *mac*-ZrO₂ $\mathbf{1} - \mathbf{4}$ and commercial ZrO₂ $\mathbf{5}$.

3. TEM



Figure S3a. TEM of nan-CdS.







Figure S3b. TEM of mac-ZrO₂ and electron diffraction.





Figure S3c. TEM of **4-CdS** and electron diffraction.

4. Powder X-ray Diffraction



Figure S4a. *mac*-ZrO₂, + = Zirconium Oxide ZrO₂, JCPDS 01-079-1763.



Figure S4b. *nan*-CdS@*mac*-ZrO₂, * = AI holder, x = Zirconium Oxide ZrO₂, JCPDS01-079-1763, + = Cadmium Sulphide CdS, JCPDS 01-075-1545.

5. Diffuse Reflectance Uv-Vis Spectroscopy



Figure S5a. DRUVS data for **1** – **4** in water.



Figure S5b. DRUVS data for 1-CdS - 5-CdS in air before photocatalysis.



Figure S5c. DRUVS data for 1-CdS - 5-CdS in air after photocatalysis.

Note: The lack of a CdS absorption edge at 520 nm in Figure 5b is due to calcination at 400 °C, which is required to completely remove the surface ligands of *nan*-CdS. Under these conditions partial oxidation of *nan*-CdS will occur. ⁴ However, it has been shown that oxide-sulphide ion-exchange occurs at room temperature in the presence of Na₂S and under the photocatalytic conditions, O-S exchange occurs.⁵ Analysis using PXRD, SEM, and TEM showed no significant evidence of structural or compositional change after several photocatalytic reactions and EDX after photocatalysis shows a Cd:S ratio of 1:1 within experimental error. The stop band positions of **1-CdS** – **4-CdS** before and after photocatalysis are identical, which is expected based on the very similar refractive index of CdS and CdO.



Figure S5d. DRUVS data for 1-TiO₂ - 5-TiO₂ in air.



Figure S5e. DRUVS data for $\textbf{1-TiO}_2$ - $\textbf{5-TiO}_2$ in water.

6. Photocatalysis



Figure S6a. Schematic of the apparatus used for photocatalytic reactions.



Figure S6b. Photocatalysis data for **1-TiO₂ - 5-TiO₂**.

7. Surface area measurements



Figure S7 a) Adsorption and desorption isotherms and BET plot for commercial ZrO_2 (5).



Figure S7 b) Adsorption and desorption isotherms and BET plot for **3**.

8. References

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