Electronic Supplementary Information

Homogeneous coating of photonic macroporous oxides with inorganic nanocrystals

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Supporting Information

General:

Oleic acid ($C_{18}H_{34}O_2$, 90 % and 99 %), Sodium oleate ($C_{18}H_{33}O_2Na$, 82 %), Octyl Ether ($C_{16}H_{34}O$, 99 %), Styrene (C_8H_8, 99 %), Potassium persulfate ($K_2S_2O_8$, 99 %), Iron (III) chloride ($FeCl_3$, 97 %), Titanium tetraisopropoxide ($Ti(OC_3H_7)_4$, 97 %), Zirconium acetate solution in dilute acetic acid ($Zr[OCOCH_3]_4$, 16 % Zr), Tetraethyl-orthosilicate ($Si[OC_2H_5]_4$, 99 %), Cadmium oxide (CdO, 99.99 %), 1-Octadecene ($C_{18}H_{36}$, 90%) and Sulphur (reagent grade) were purchased from Sigma Aldrich and used as received.

PXRD patterns were recorded on a Bruker-AXS D8 Advance instrument with Lynx eye detector, using Cu Kα radiation, scanning in the range 5 – 90 (2θ), with a 0.02 ° step size, and each data point collected for 0.05 or 0.1 s. SEM images were obtained using an FEI Sirion scanning electron microscope operating at 5 - 10 kV. Prior to imaging, samples were supported on an aluminium stub with an adhesive carbon tab and sputter coated with a 10 nm layer of carbon using an Agar auto carbon coater. Energy Dispersive Analysis of X-rays (EDX) was performed using an attached EDAX Phoenix X-ray spectrometer. TEM images were obtained using a JEOL 2011 transmission electron microscope operated at 200 kV accelerating voltage. TEM samples were ground, sonicated in methanol and a drop of the dispersion evaporated onto a holey carbon, copper grid. Electron diffraction, dark field imaging and STEM/EDX mapping were performed at the University of Leeds on a Tecnai TF20 FEGTEM. Diffuse Reflectance UV spectra were recorded on an Ocean Optics HR2000+ High Resolution Spectrometer with DH-2000-BAL Deuterium/Helium light source (200 - 1100 nm) and data was converted to F(R) using the Kubelka-Monk equation.

1. Syntheses of templates and precursors

Synthesis of Polystyrene Sphere Template: Polystyrene spheres of diameter 400 and 500 nm were synthesised by emulsifier free emulsion polymerisation according to 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 a constant speed of 245 rpm. Water (1133 mL) was added to the flask and heated (at 80 ± 2 °C for 400 nm spheres or 70 ± 2 °C for 500 nm spheres,) 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. Cubic close packed polystyrene sphereswere isolated by centrifugation of the colloidal solution (4000 rpm, 3 h) and were dried at 66 °C overnight before use to give the template as a white brittle solid.

Macroporous materials: Impregnation of the polystyrene sphere template was achieved using a modified version of a literature method.[1] To prepare the template for impregnation the polystyrene template (1 g) was crushed using a pestle and mortar to a fine powder and layered on a glass sinter funnel. The template was soaked with ethanol for 15 mins and dried under reduced pressure immediately prior to impregnation.

***mac*-SiO_2:** Tetraethylorthosilicate (3 mL, 13.4 mmol), ethanol (2 mL), water (1.5 mL) and 1 M HCl (0.5 mL) were mixed in this order and stirred for 15 min. The solution was transferred via pipette onto the template and allowed to soak for 30 min, followed by removal of excess solution under reduced pressure. The impregnated template was dried at room temperature for 24 h prior to calcination at 550 °C (1 °C / min) for 10 h, to yield *mac*-SiO_2 (50-100 mg) as an opalescent green-white powder.

***mac*-ZrO_2:** Zirconium acetate in acetic acid (16 wt % Zr, 3 mL) and methanol (3 mL) were stirred for 15 min. The solution was transferred via pipette onto the template and allowed to soak for 1 h, followed by removal of excess solution under reduced pressure. The impregnated template was dried at room temperature for 24 h prior to calcination at 450 °C (1 °C / min) for 4 h, to yield *mac*-ZrO_2 (50-100 mg) as a blue powder.

TiO_2 nanocrystals (*nan*-TiO_2): Were prepared using a modified literature procedure.[2] Oleic acid (90 %, 35 g, 0.124 mol) was degassed under nitrogen in a 3-neck round bottom flask and heated to 100 °C. Titanium isopropoxide (2.84 g, 10 mmol) was added and the solution stirred for 5 min. Triethylamine (1.01 g, 10 mmol) in ethylene glycol (6.4 g, 0.103 mol) was subsequently added, and the mixture refluxed at 100 °C for 48h. After cooling the solution, nanoparticles were precipitated by addition of excess ethanol (100 mL). Centrifugation (4000 rpm, 30 min) was used to isolate the nanoparticles, which were then washed twice with ethanol (40 ml) to remove residual surfactant to give an orange solid (2.1 g). Elemental Analysis Found(%) C 62.6; H 9.72; N 0; Calc. $TiO_2.1.25C_{18}H_{34}O_2$. Nanoparticle size distributions were determined by averaging the diameter of at least 100 particles.

Fe_3O_4 nanocrystals (*nan*-Fe_3O_4): Were prepared using a modified literature procedure.[3] Initially Fe(oleate)$_3$ was synthesised from reaction between $FeCl_3$ (6.49 g, 40 mmol) dissolved in a water:ethanol (60:80 mL) solution and sodium oleate (36.5 g, 120 mmol) dissolved in hexane (140 mL). In a 2-necked round bottom flask, the biphasic solution was refluxed at 65 °C for 4 h, with stirring. After cooling the organic phase was separated and washed three times with water (30 mL), and dried over $MgSO_4$. The volatiles were then removed under reduced pressure to yield a red/brown viscous liquid. Yield = 24.2 g, 67 %.

Fe(oleate)$_3$ (1 g, 1.1 mmol), oleic acid (99%, 0.35 mL, 1.1 mmol) and octyl ether (20 mL) were added to a 2-necked round bottom flask at room temperature. With vigorous stirring, the mixture was heated to 290 °C (5 °C / min), and refluxed at this temperature for 1 hour. After cooling to room temperature, the nanoparticles were precipitated by addition of ethanol (50 mL). The nanoparticles were separated by centrifugation (4400 rpm, 30 min), and washed twice with ethanol (40 mL) to give Fe_3O_4 nanoparticles as a black powder (0.5 g). Elemental Analysis Found (%) C 54.83; H 8.12; N 0; Calc. $Fe_3O_4.2.01C_{18}H_{34}O_2$.

CdS nanocrystals (*n*-CdS): CdS quantum dots were synthesised by a literature method.[4] CdO (12.8 mg, 0.10 mmol), oleic acid (0.8474 g, 3 mmol) and 1-octadecene (3.1398 g) were added to a 3 neck round bottom flask and heated to 300 °C under Ar. A solution of sulphur (1.6 mg, 0.05 mmol) in 1-octadecene (1.9984 g) was rapidly injected into the reaction mixture, and the temperature held at 270 °C for nanocrystal growth. After 180 s the reaction was quenched in an ice bath. The nanocrystals were precipitated by addition of excess ethanol followed by centrifugation (4400 rpm, 30 mins). The supernatant was discarded and the nanocrystals twice redispersed in toluene, precipitated with ethanol and centrifuged (4400 rpm, 30 mins). Finally, nanocrystals were dispersed in toluene for further processing. Elemental Analysis Found(%) C 51.21; H 8.19; N 0; Calc. CdS. $1.04C_{18}H_{34}O_2$.

Estimating Loadings

BET surface area *mac*-SiO_2 = 90 m^2g^{-1}

Area and volume of spherical *nan*-TiO_2 particle (diameter 10 nm);

Area = 78 nm^2 (7.8×10^{-17} m^2); Volume = 523 nm^3 (5.23×10^{-25} m^3)

Number of *nan*-TiO_2 to cover 1g of *mac*-SiO_2 assuming hexagonal packing (91 % covering density) = $0.91 \times 90/7.8 \times 10^{-17} = 1.15 \times 10^{18}$

Mass of 1.15×10^{18} *nan*-TiO_2 particles = $1.15 \times 10^{18} \times 5.23 \times 10^{-25} \times 4230$ (density of TiO_2) = 2.55×10^{-3} kg (2.55g)

Therefore 5 - 80 wt% loading of *nan*-TiO_2 covers approximately 2 – 30 % of the available surface area of *mac*-SiO_2.

Deposition of nanoparticles: Macroporous materials were initially coated with oleic acid by dispersing 40 mg in a hexane solution of oleic acid (0.05 M, 40 mL). After 30 min, the solid was collected by vacuum filtration and dried at 60 °C for 1 hr. Nanocrystals corresponding to a loading of 5 - 60 wt% metal oxide or sulphide were dispersed in oleic acid in chloroform (0.1 M, 1 mL) by sonication and the dispersion was added to the macroporous material followed by evaporation of the chloroform at 40 °C over 2 hr. Oxide nanocrystal composites of *mac*-SiO_2 were calcined at 500 °C for 5 hr (heating rate 5 °C min^{-1}). Oxide nanocrystals of *mac*-ZrO_2 composites were calcined at 450 °C for 4 hr (1 °C min^{-1}). For *nan*--CdS composites calcination was performed at 450 °C for 4 hr (1 °C min^{-1}) under an Ar flow (60 mL min^{-1}).

2. SEM

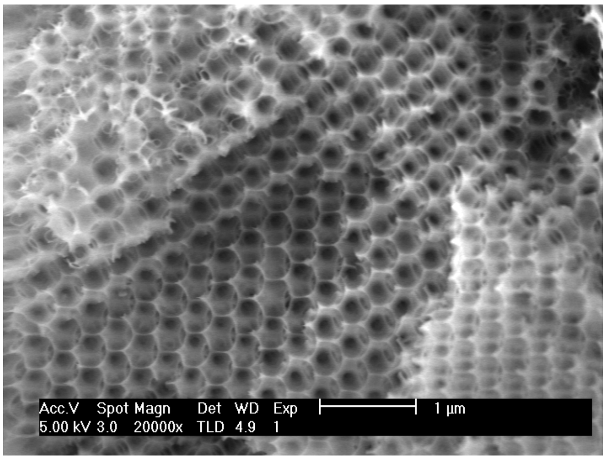


Figure S2a. SEM 65 wt% *nan*-Fe_3O_4@*mac*-SiO_2.

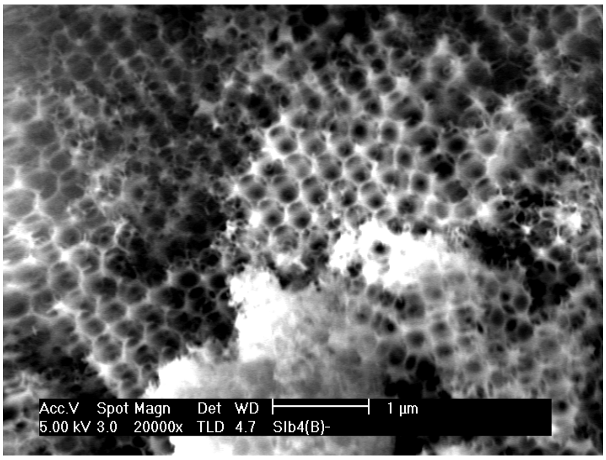


Figure S2b. SEM 13 wt% *nan*-CdS@*mac*-SiO_2

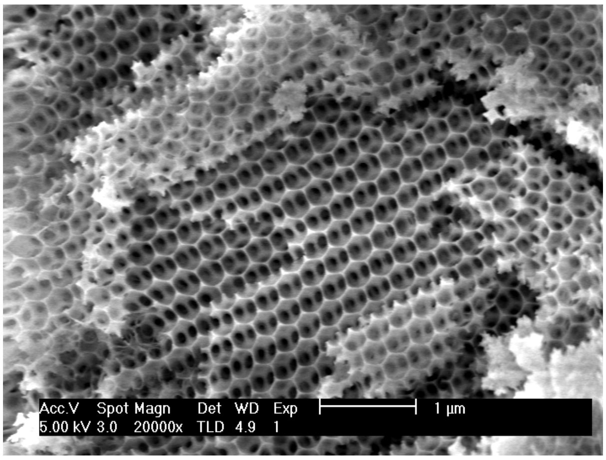


Figure S2c. SEM *mac*-ZrO_2.

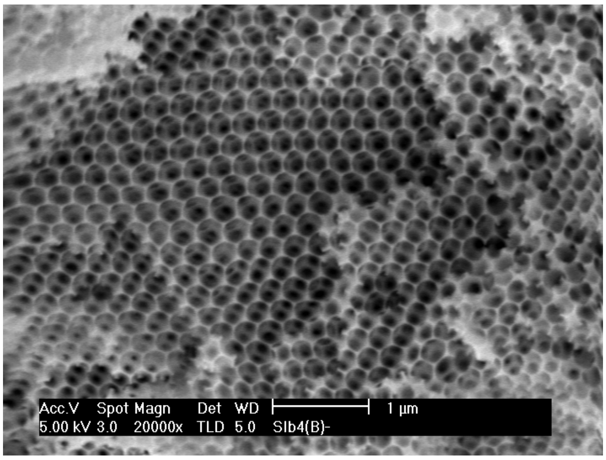


Figure S2d. SEM 7 wt% *nan*-TiO_2@*mac*-ZrO_2.

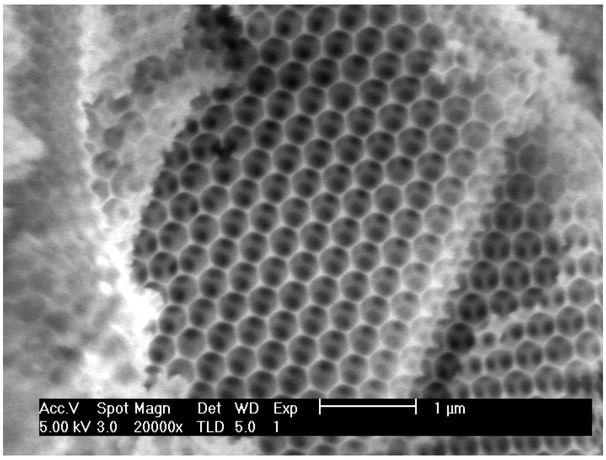


Figure S2e. 8 wt% *nan*-Fe_3O_4@*mac*-ZrO_2.

3. TEM

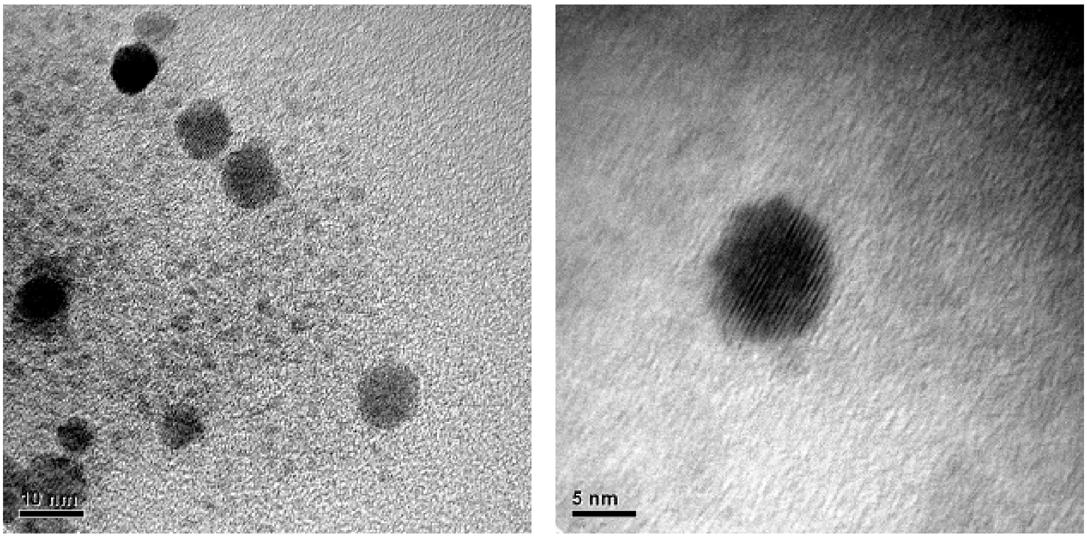


Figure S3a. *nan*-Fe_3O_4

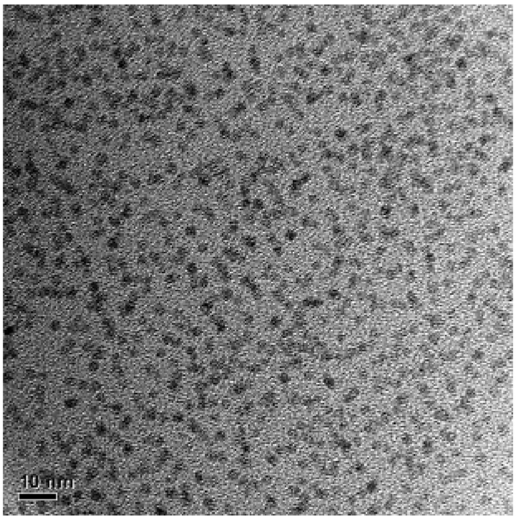


Figure S3b. *nan*-CdS

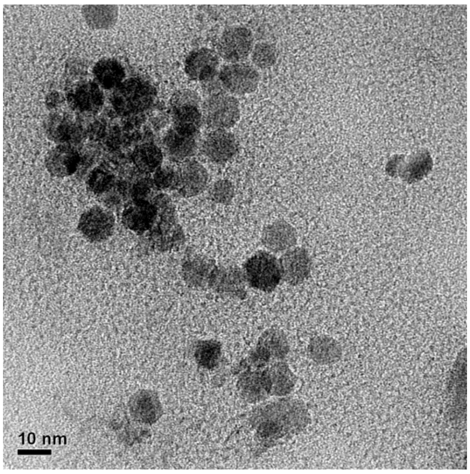


Figure S3c. TEM of *nan*-TiO_2

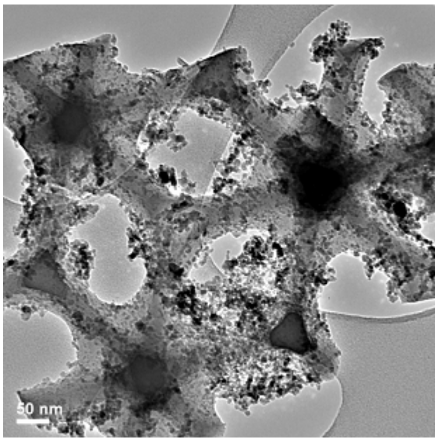


Figure S3d. 36 wt% *nan*-TiO_2@*mac*-SiO_2 showing agglomeration of TiO_2 nanoparticles on deposition from an oleic acid/hexane (0.1 M, 5 mL) nanoparticle dispersion. This result is typical of dispersions where the nanoparticle-macropore interaction is weaker than the nanoparticle-nanoparticle interaction.

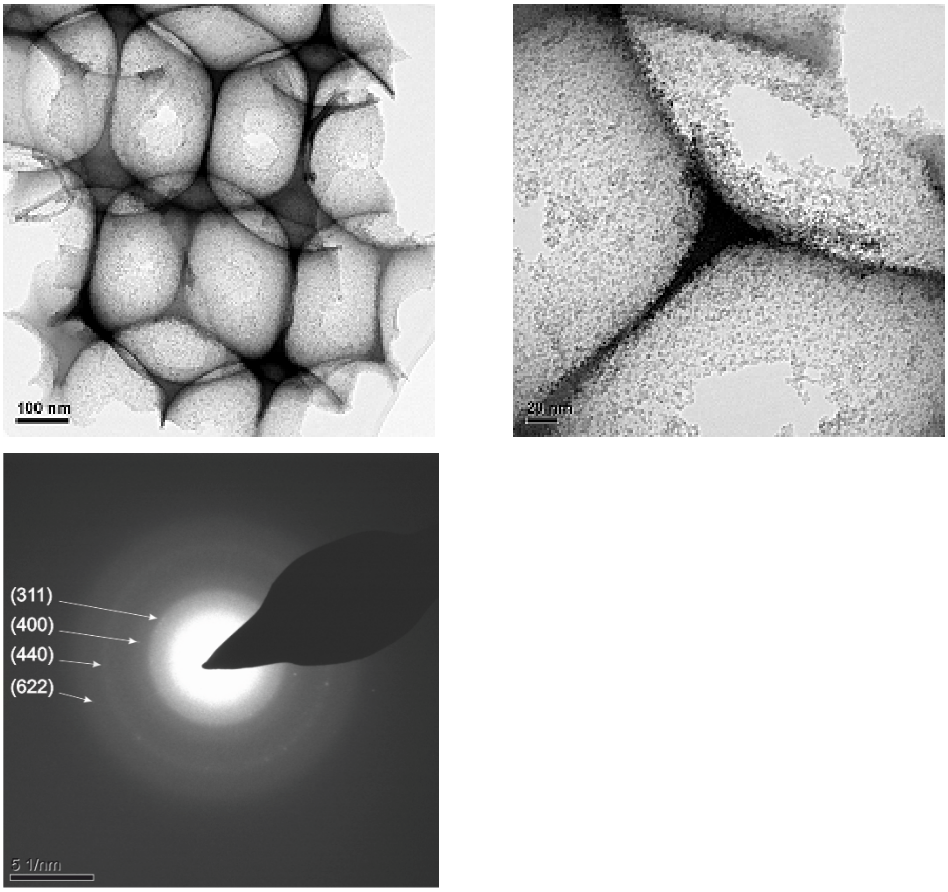


Figure S3e. 65 wt% *nan*-Fe_3O_4@*mac*-SiO_2 and SAED.

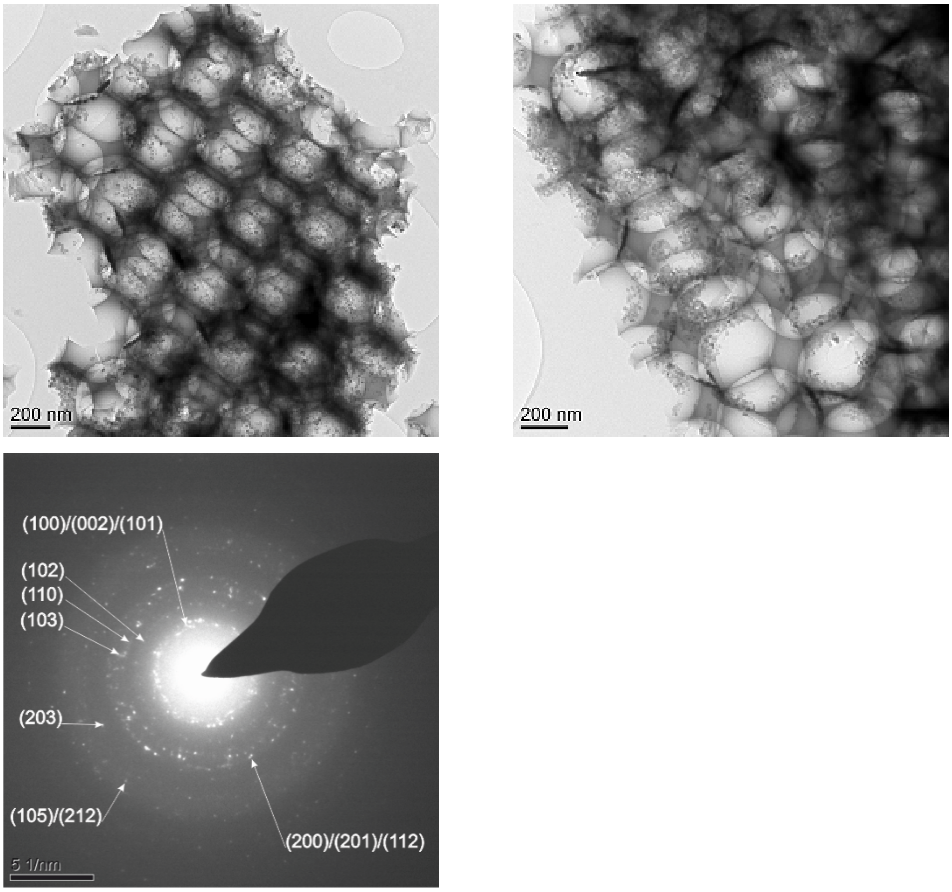


Figure S3f. 26 wt% *nan*-CdS@*mac*-SiO_2

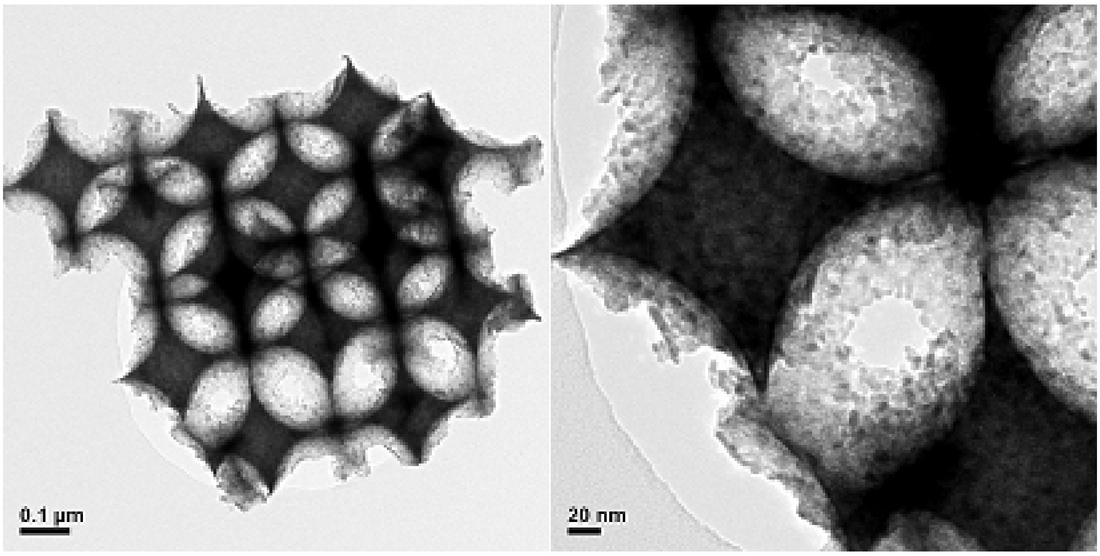


Figure S3g. 7 wt% *nan*-TiO_2@*mac*-ZrO_2

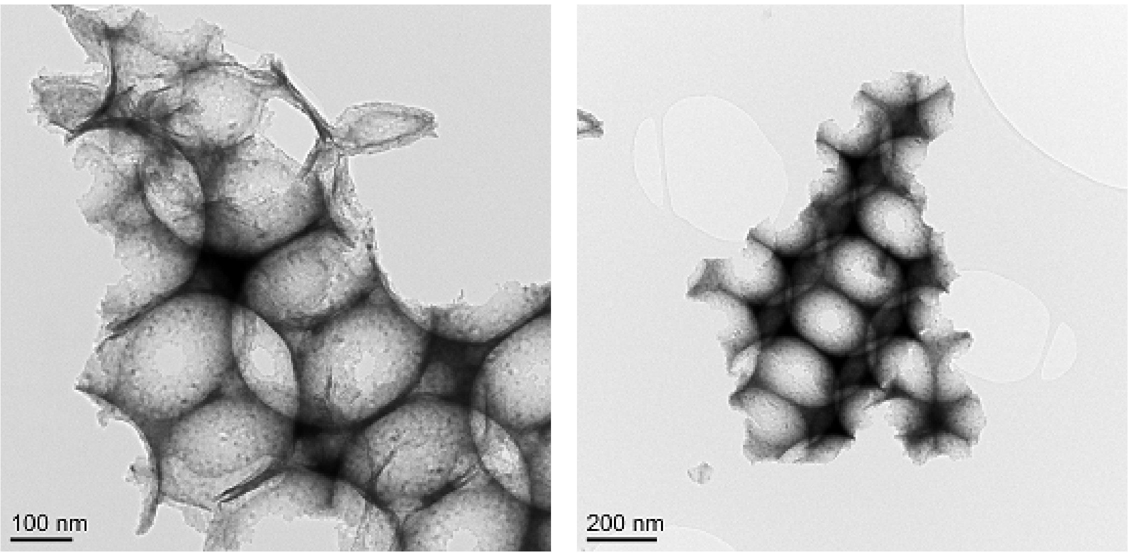


Figure S3h. 16 wt% *nan*-Fe_3O_4@*mac*-ZrO_2

4. EDX Maps

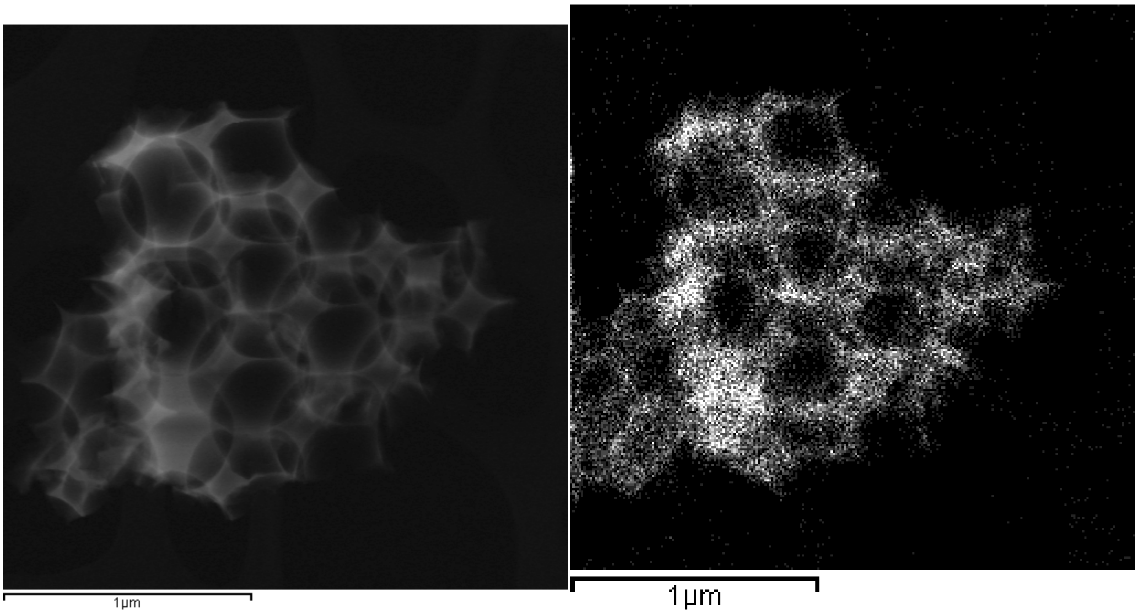
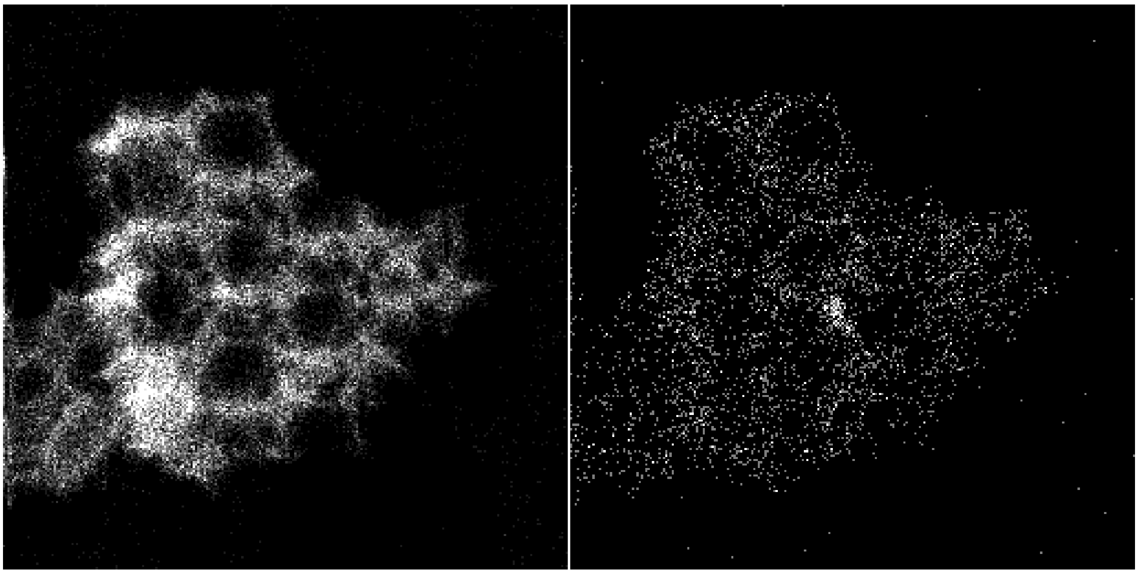


Image O map



Si map Ti map

Figure S4a. 7 wt% *nan*-TiO_2@*mac*-SiO_2

5. Powder X-ray Diffraction

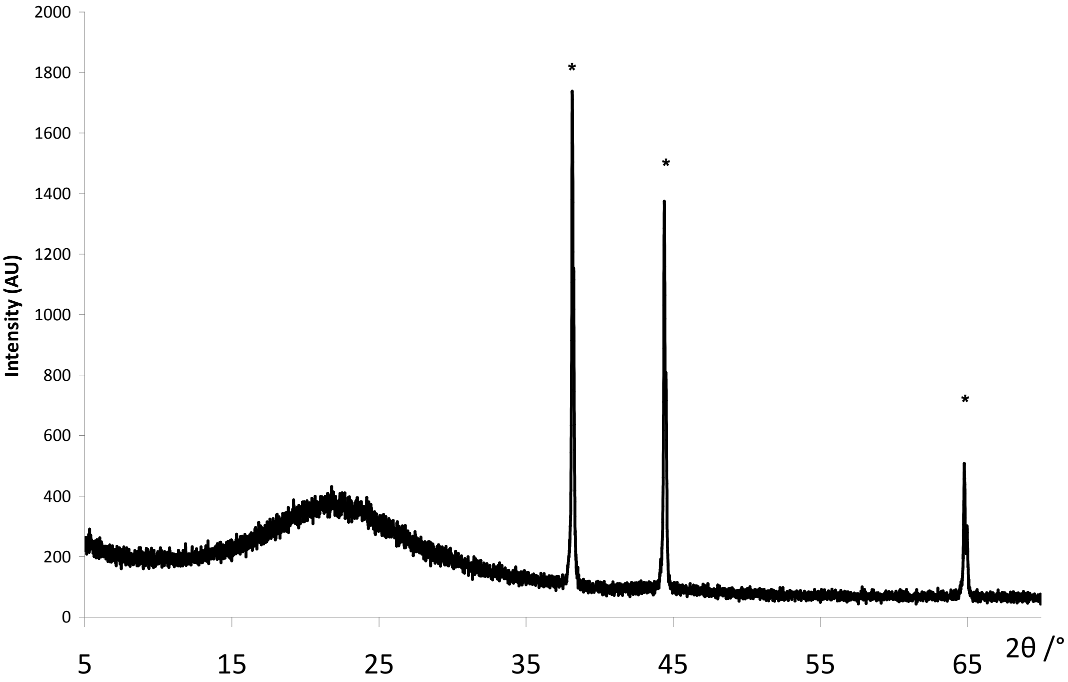


Figure S5a. *mac*-SiO_2 * = Al holder.

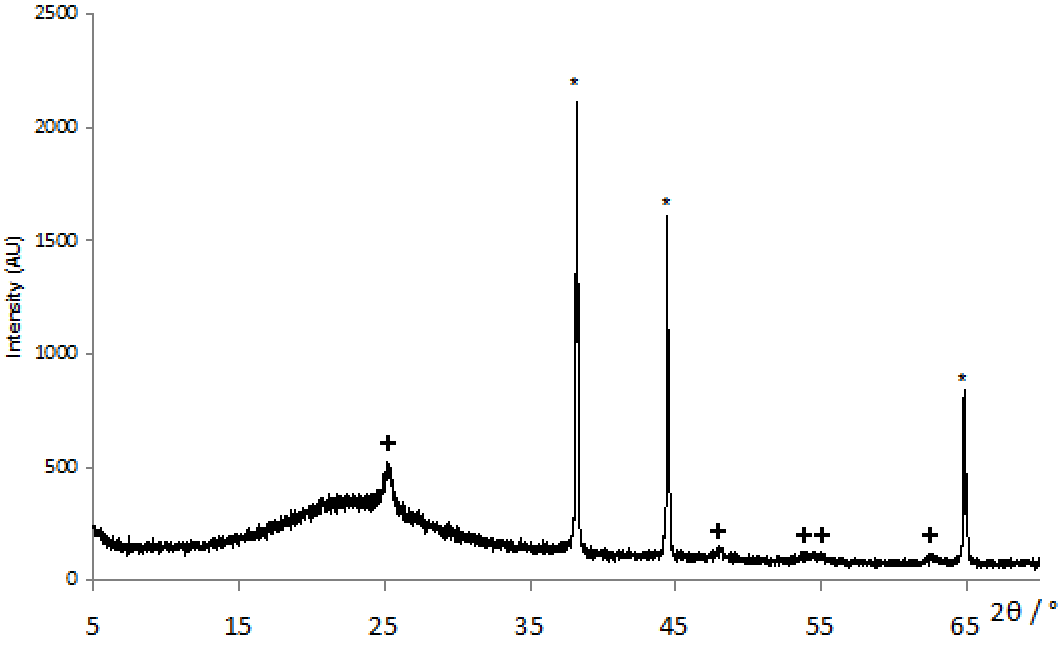


Figure S5b. 58 wt% *nan*-TiO_2@*mac*-SiO_2, * = Al holder, + = Anatase, syn TiO_2, JCPDS 01-078-2486.

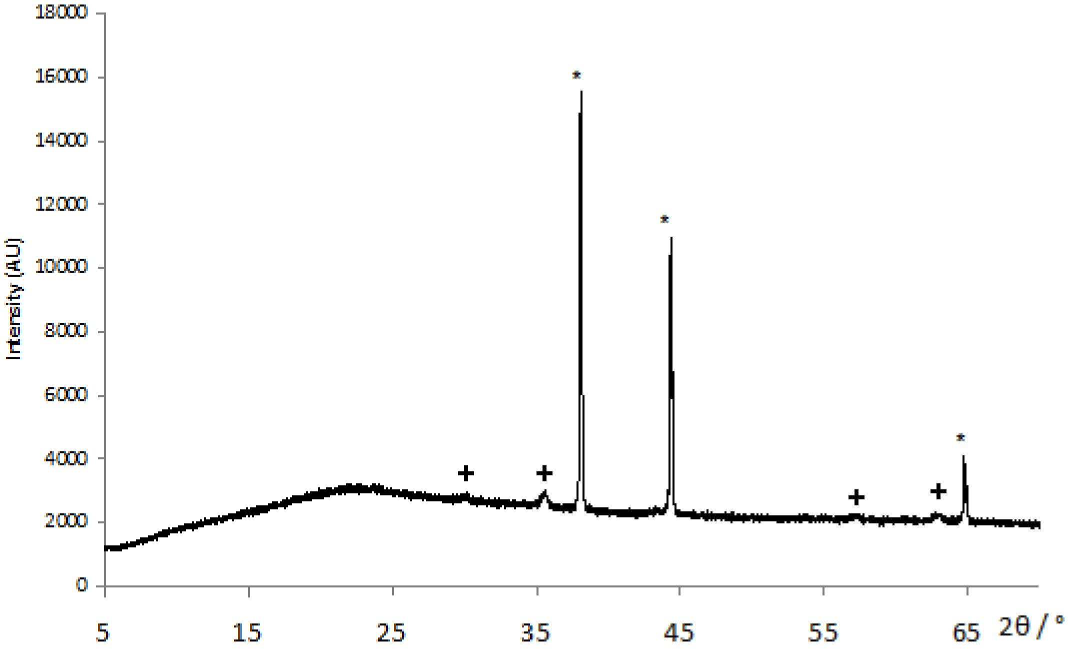


Figure S5c. 49 wt% *nan*-Fe_3O_4@*mac*-SiO_2, * = Al holder, + = Iron Oxide Fe_3O_4, JCPDS 01-079-0416.

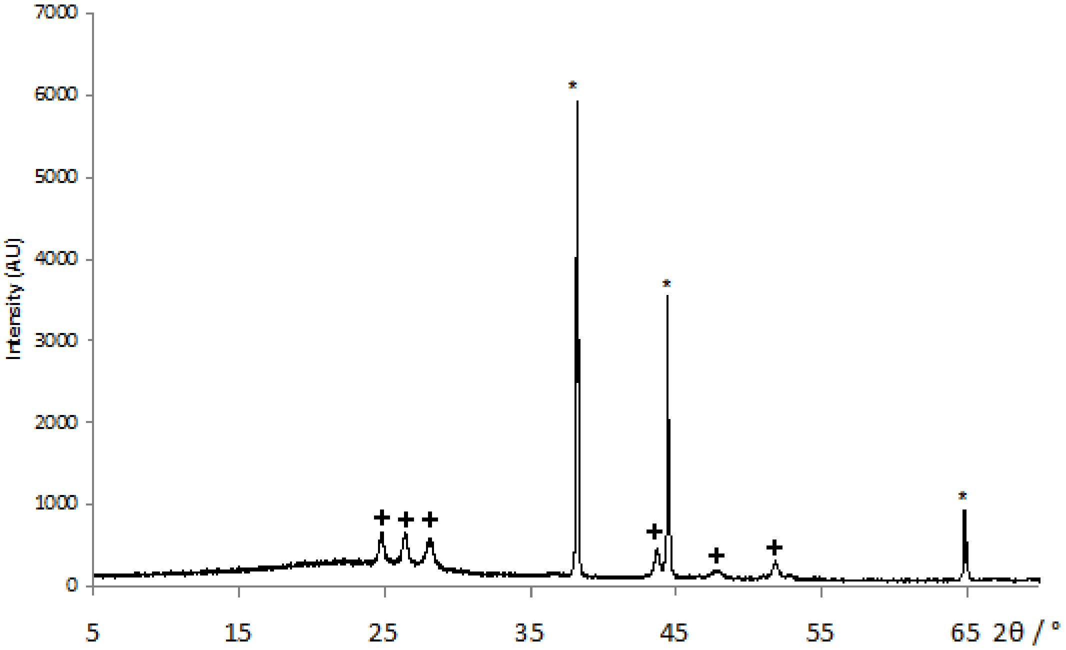


Figure S5d. 18 wt% *nan*-CdS@*mac*-SiO_2, * = Al holder, + = Cadmium Sulphide CdS, JCPDS 01-075-1545.

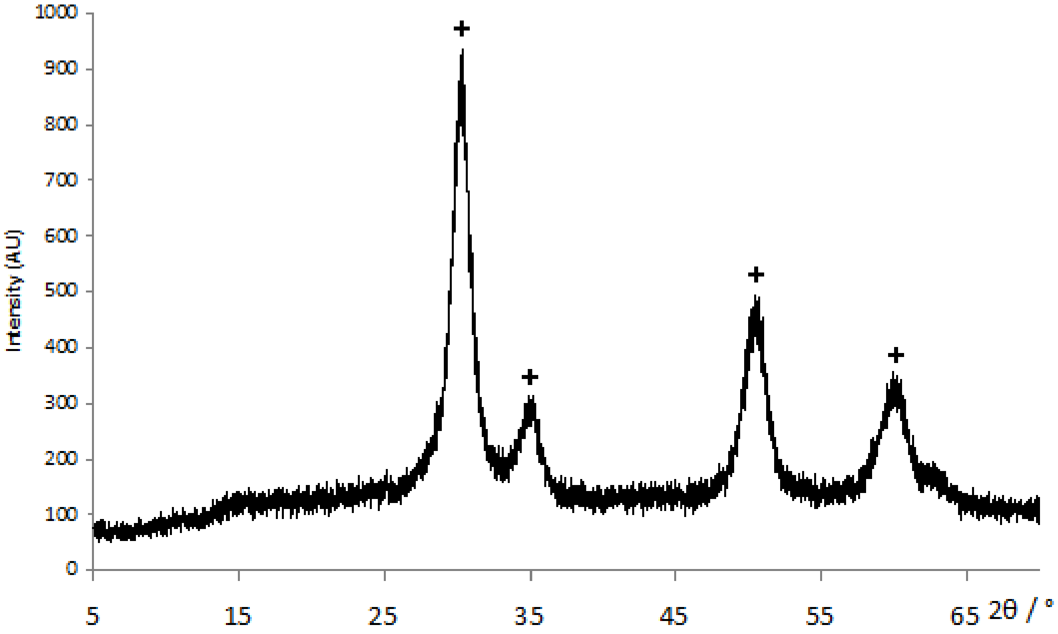


Figure S5e. *mac*-ZrO_2, + = Zirconium Oxide ZrO_2, JCPDS 00-049-1642.

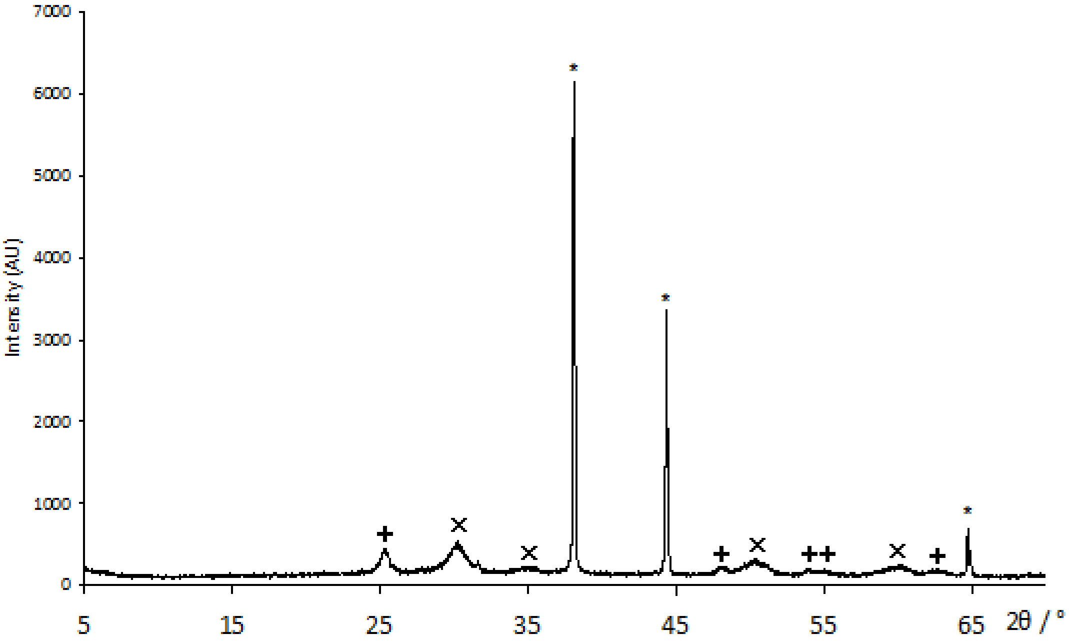


Figure S5f. 22 wt% *nan*-TiO_2@*mac*-ZrO_2, * = Al holder, x = Zirconium Oxide ZrO_2, JCPDS 00-049-1642, + = Anatase, syn TiO_2, JCPDS 01-078-2486.

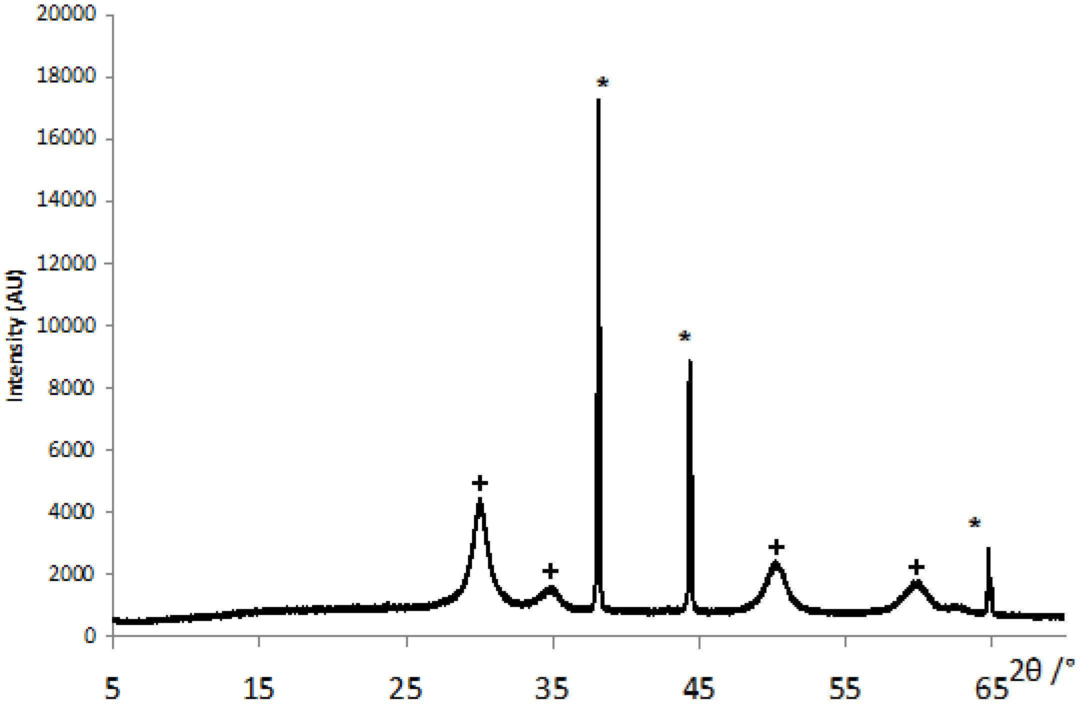


Figure S5g. 40 wt% *nan*-Fe_3O_4@mac-ZrO_2 * = Al holder, + = Zirconium Oxide ZrO_2, JCPDS 00-049-1642. Peaks for ZrO_2 and Fe_3O_4 are coincident at this resolution.

6. Diffuse Reflectance Uv-Vis Spectroscopy

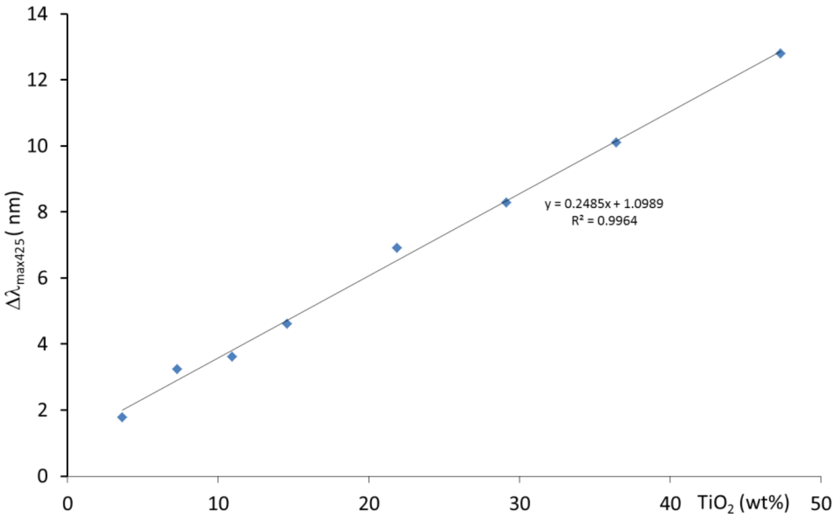
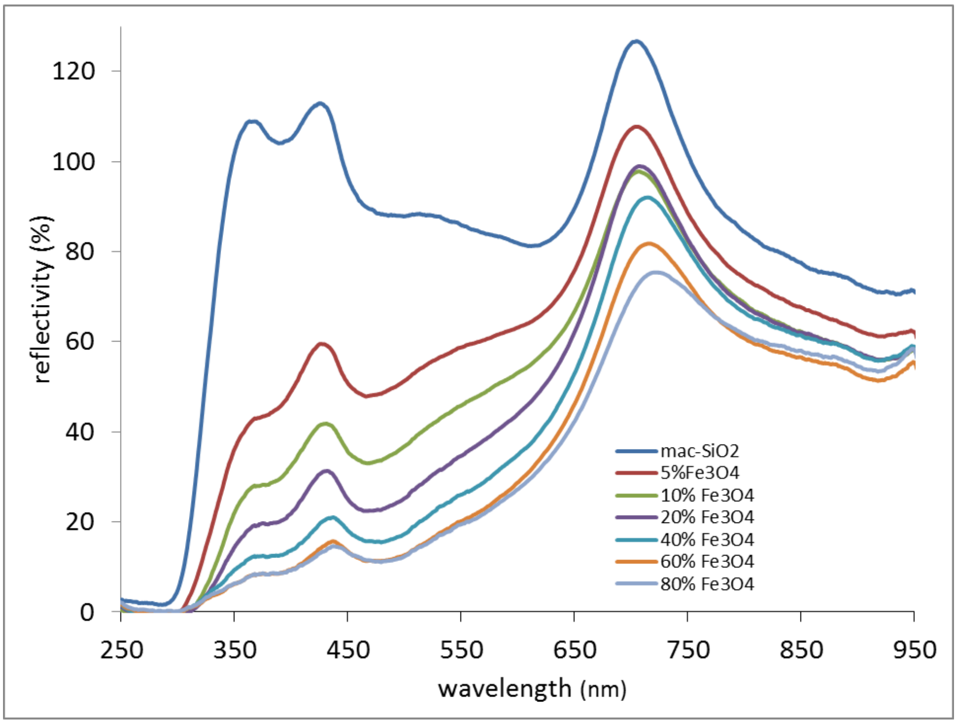
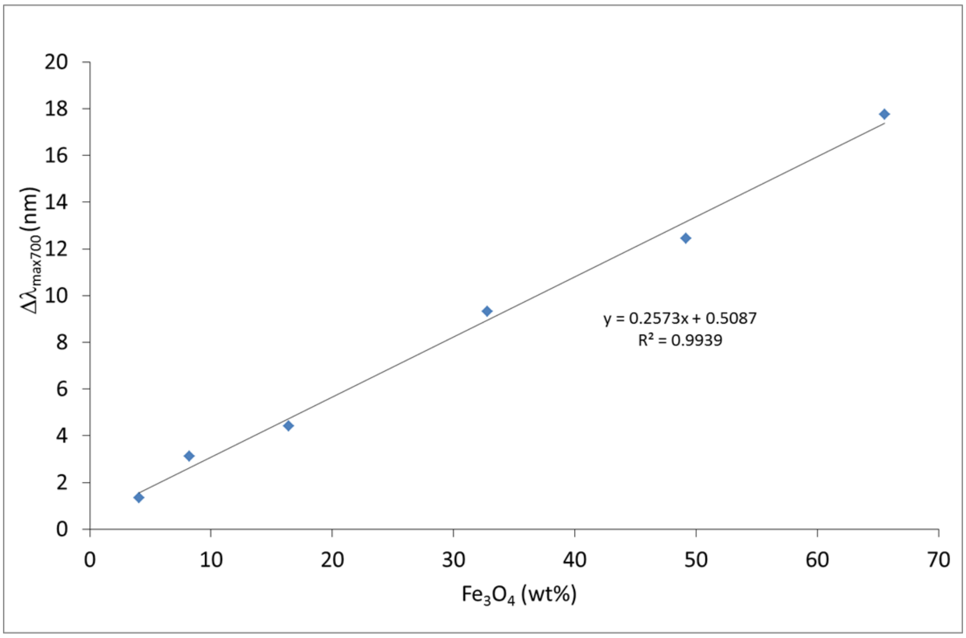


Figure 6a. Shift in λ_{max} of the stop band centred at 425 nm (Figure 2a) as a function of *nan*-TiO_2 loading.





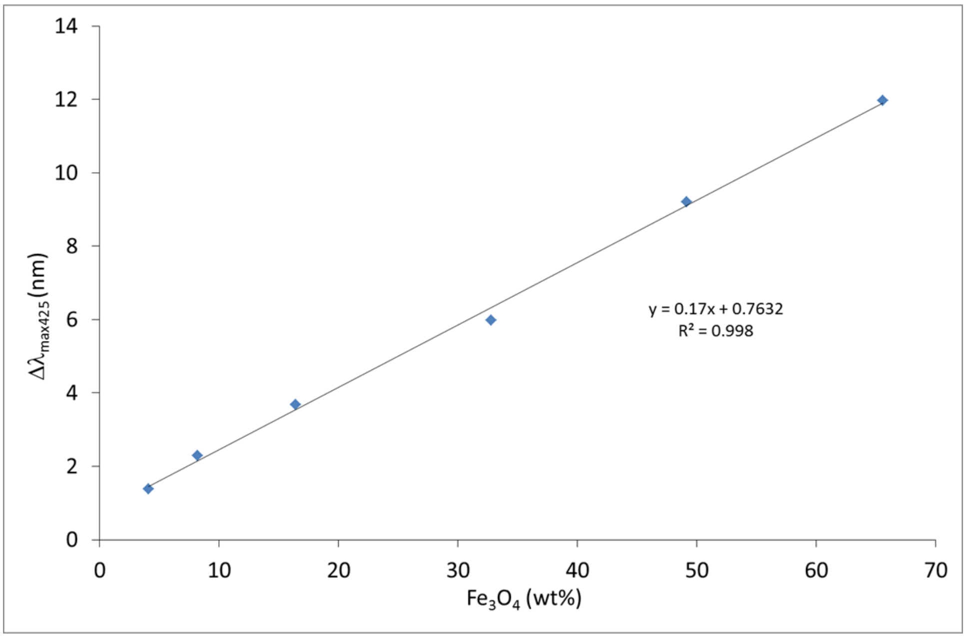
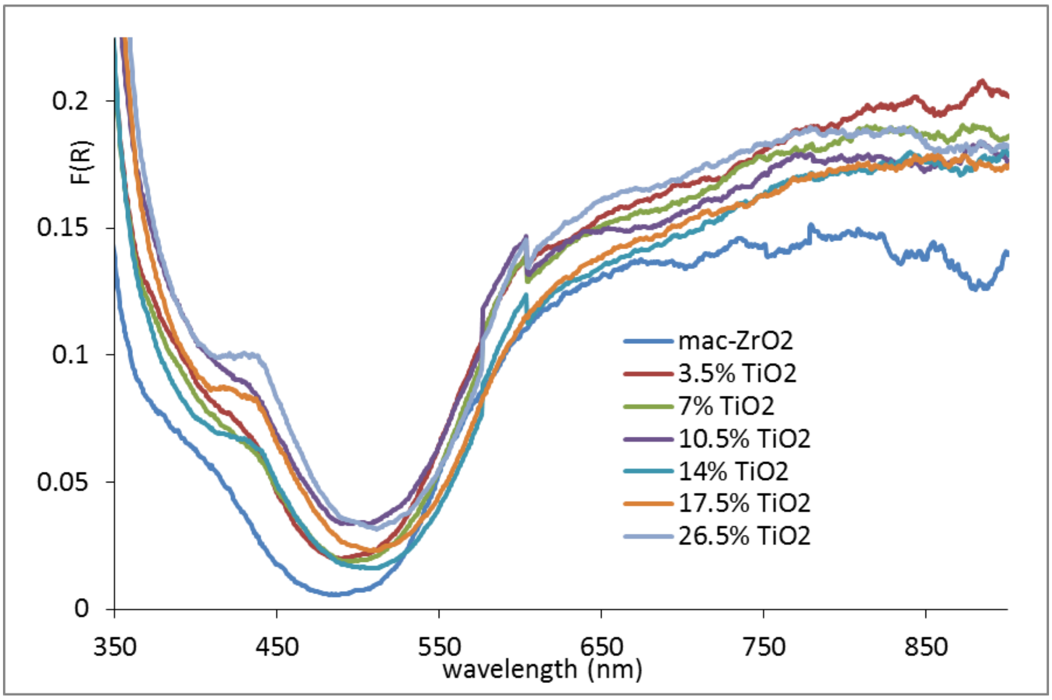


Figure 6b. DRUVS data for *nan*-Fe_3O_4@*mac*-SiO_2 at various loadings and plots of the shift in λ_{max} for the two stop bands centred at 425 and 700 nm. The Kubelka-Munk transformation was not applied because of the significant absorption from Fe_3O_4.



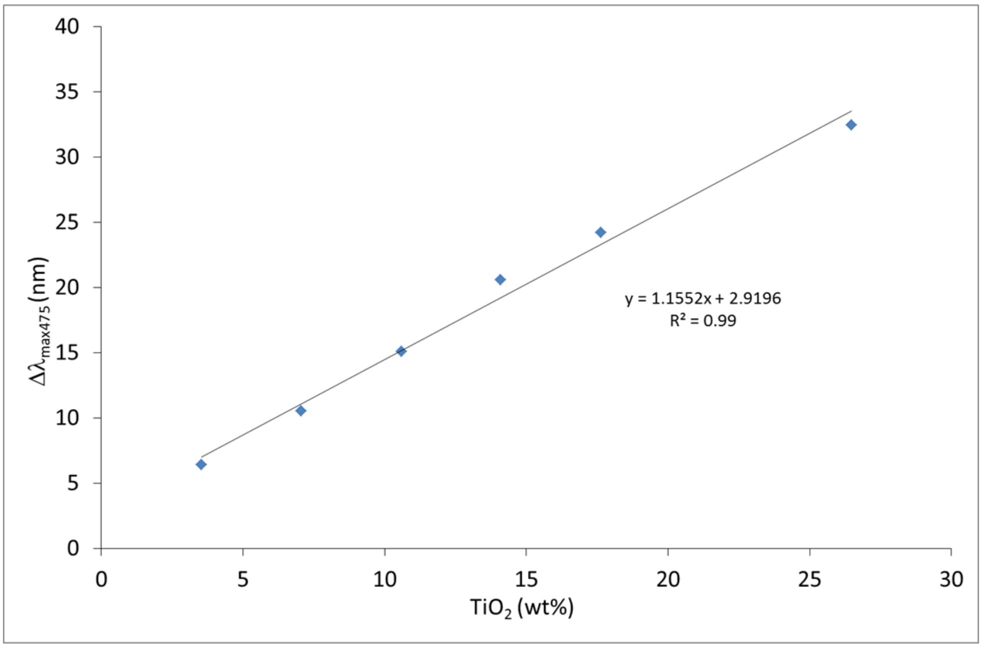


Figure 6c. DRUVS data for *nan*-TiO_2@*mac*-ZrO_2 at various loadings and plot of the shift in λ_{max} for the absorption centred at 475 nm.

7. Surface area measurements

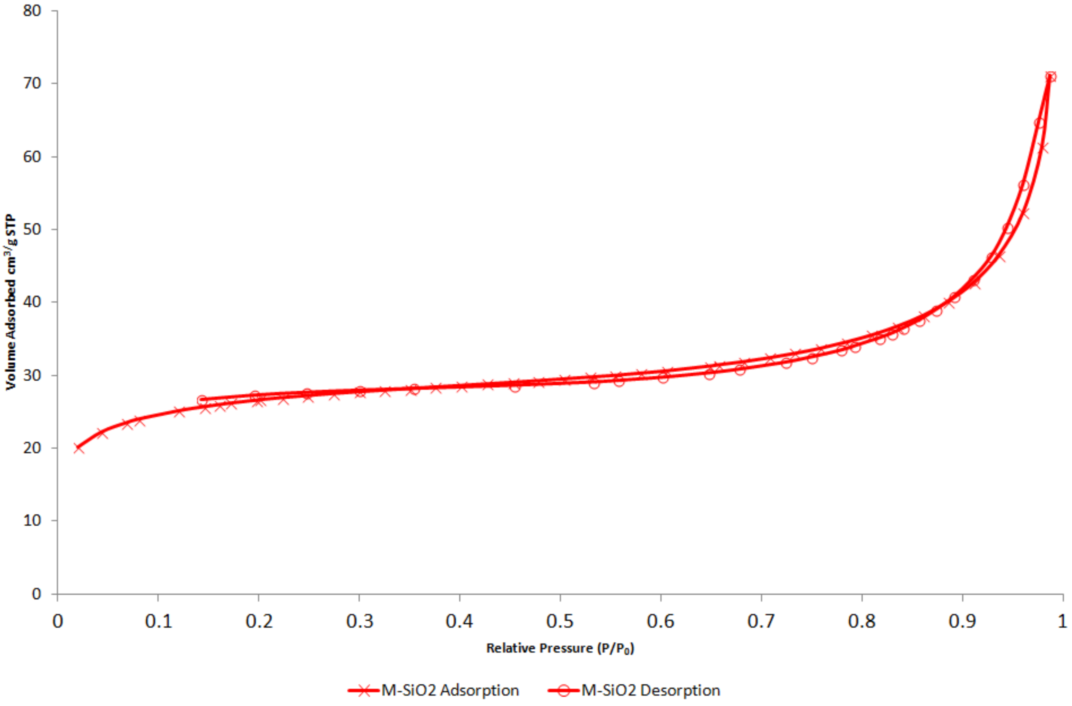


Figure 7a. Adsorption isotherm for *mac*-SiO_2

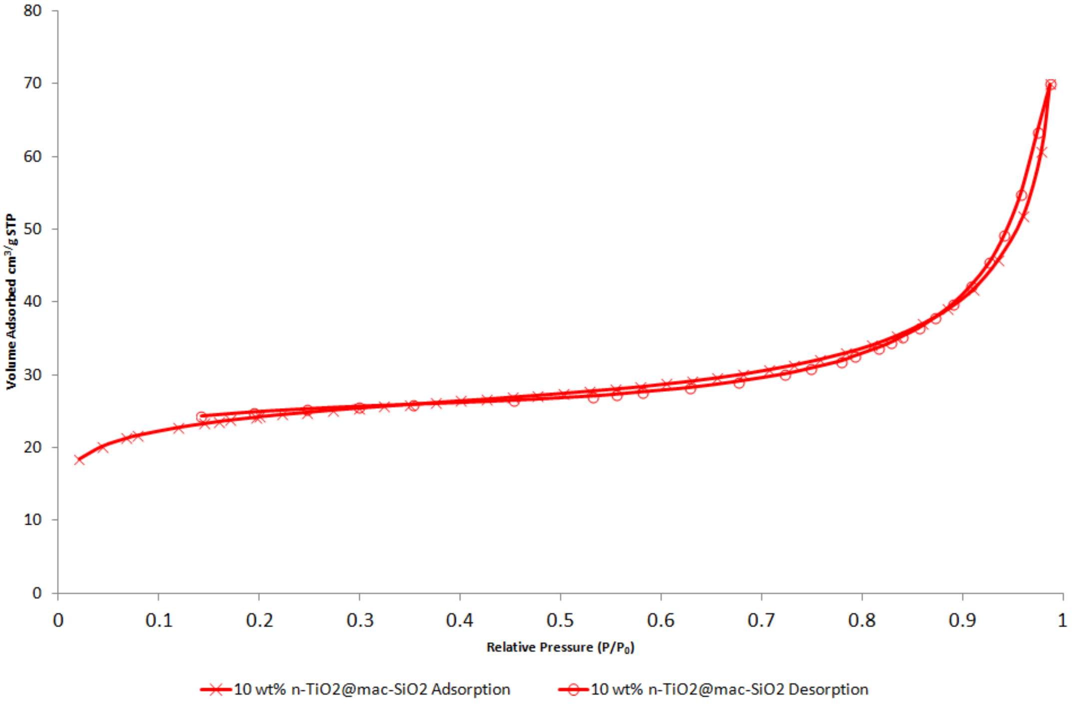


Figure 7b. Adsorption isotherm for 7 wt% *nan*-TiO_2@*mac*-SiO_2

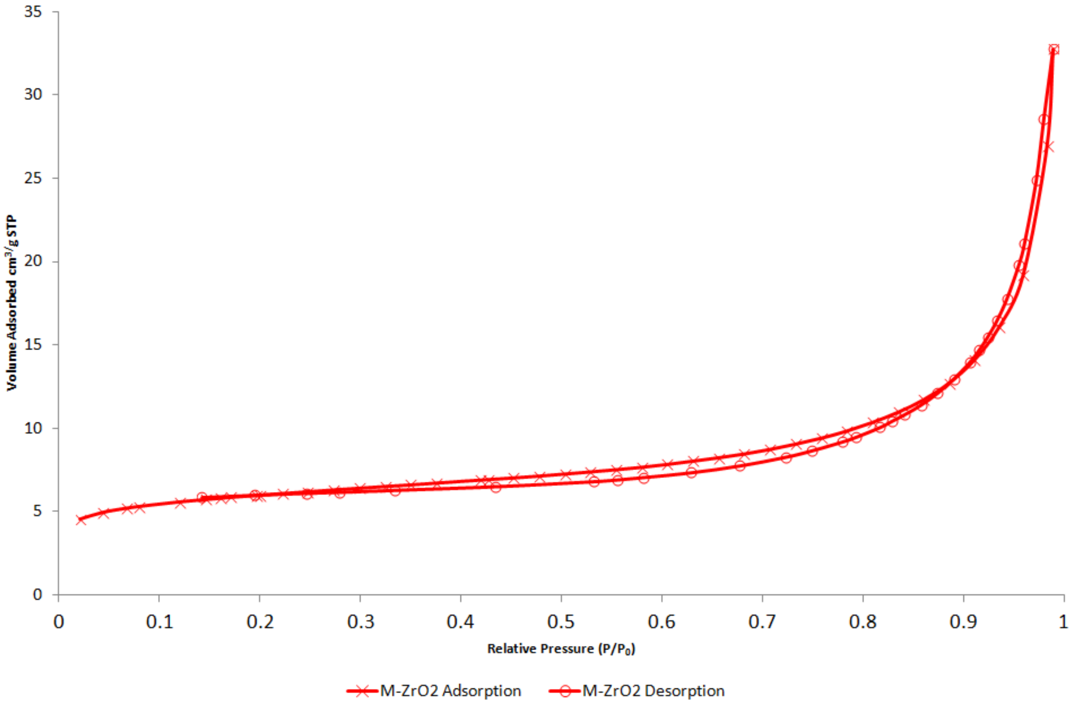


Figure 7c. Adsorption isotherm for *mac*-ZrO_2

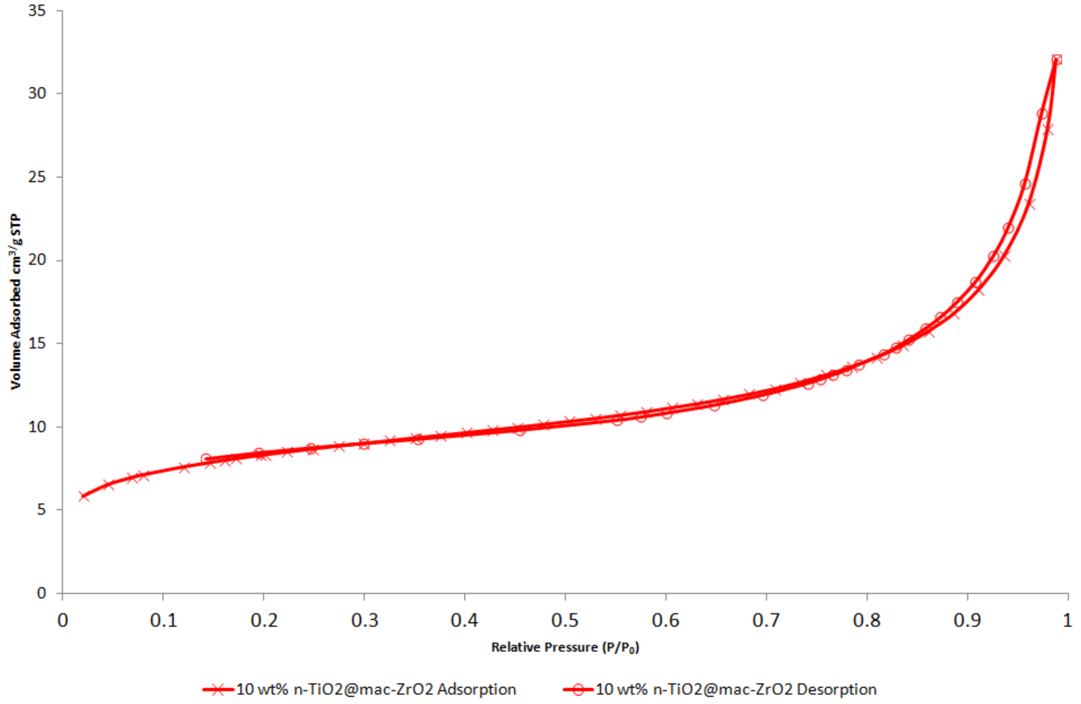


Figure 7d. Adsorption isotherm for 10 wt% *nan*-TiO_2@*mac*-ZrO_2

8. References

1. R. C. Schroden, M. Al-Daous, C. F. Blanford and A. Stein, *Chem. Mat.*, 2002, **14**, 3305.
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