Electronic Supplementary Information

One-Pot Synthesis of Highly Crystalline Mesoporous TiO_2 Nanoparticle Assemblies with Enhanced Photo-catalytic Activity

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Materials

Brij 58 surfactant ($HO(CH_2CH_2O)_{20}C_{16}H_{33}$, M_n ~ 1124), titanium(IV) chloride (99.9%), anatase TiO_2 (99.8%) absolute ethanol (99.8%) and Aldrich anatase (product no. 232033) were purchased from Sigma-Aldrich. Titanium(IV) propoxide (≥98%) were purchased from Merck. Cadmium nitrate ($Cd(NO_3)_2{\cdot}4H_2O$, 98.5%) and sodium sulfide ($Na_2S{\cdot}9H_2O$, 98%) were purchased from Alfa-Aesar. TiO_2 nanoparticles (P25) was purchased from Degussa AG (Germany). TiO_2 Hombikat UV-100 (100% anatase) was supplied by Sachtleben Chemie GmbH.

Synthesis of MTA

The synthesis of mesoporous TiO_2 nanoparticle assemblies (MTA) was accomplished by a surfactant-directed evaporation induced self-assembly method. In a typical experiment, 1 g of Brij 58 ($HO(CH_2CH_2O)_{20}C_{16}H_{33}$) surfactant was dissolved in anhydrous ethanol at room temperature. Consequently, $TiCl_4$ and titanium(IV) propoxide (TPP) precursors were slowly added to the surfactant solution under vigorous stirring and were kept at room temperature for 2 h. The molar composition of the sol was 0.9 Brij 58 : 171 ethanol : 1.6 $TiCl_4$: 5.6 TPP. The transparent yellow colored solution was then transferred in an oven at 40 ^oC and left undisturbed during aging for 7 days. The TiO_2/Brij 58 composite structure is very delicate on the removal of the surfactant and easily collapse if this is not done properly. To efficiently remove the template and induce crystallization and intraparticle connection, the resulting monolithic gel was dried at 100 ^oC for 12 h under vacuum and gently calcined in air for 6 h at 260 ^oC and, then for 4 h to 350 ^oC (heating rate of 0.5 ^oC min^{-1}). For the preparation of MTA-1 and MTA-2 samples, a similar to MTA procedure was used, except that the sol solution was aged for 5 and 14 days, respectively.

Synthesis of CdS-MTA

The mesoporous CdS-TiO_2 nanocomposite (CdS-MTA) was prepared in a similar procedure to MTA, but with addition of 72 mg cadmium nitrate ($Cd(NO_3)_2{\cdot}4H_2O$) in the starting mixture. Typical, 100 mg of template-removal CdO/TiO_2 nanocomposite was sulfurized by immersing for 1h in a 0.015 M ethanolic solution (20 ml) of $NaS_2{\cdot}9H_2O$. The pale yellow solid was collected by filtration, washed with water and ethanol, and dried at 80 ^{o}C.

Physical Characterization

Thermogravimetric analysis (TGA) was performed using a Pelkin-Elmer Diamond system. Thermal analysis was conducted from 40 to 600 ^{o}C in a nitrogen flow of 100 ml min^{-1} with a heating rate of 5 ^{o}C min^{-1}.

Small-angle X-ray scattering (SAXS) measurements were performed on a Rigaku S-MAX 300 high-brilliance system using Cu Kα radiation (80 kV and 40 mA). The sample-to-detector distance and center of the beam were precisely measured using a Ag-behenate standard (d_{001} = 58.38 Å). The two-dimensional diffraction images were integrated into a one-dimensional diffraction pattern, as a function of q, with the Fit2D program. Scattering data were corrected for dark current and empty tube scattering.

X-ray diffraction (XRD) patterns were collected on a PANanalytical X´pert Pro MPD X-ray diffractometer using Cu Kα radiation (45 kV and 40 mA) in in Bragg–Brentano geometry.

Transmission electron microscopy (TEM) images were taken with a JEOL JEM-2100 electron microscope (LaB_6 filament) operating at an accelerated voltage of 200 kV. Samples were prepared by dispersing fine powders in ethanol using sonication, followed by depositing a drop of solution onto the carbon-coated Cu grid and evaporating the solvent in air. Alternatively, samples were prepared by casting finely ground powders on a holey carbon-coated Cu grid. The particle size distributions were estimated by measuring the size of 70-90 (MTA, MTA-2) or 200 (MTA-1) individual nanoparticles in several TEM images.

Nitrogen adsorption and desorption isotherms were measured at 77 K with a Micromeritics Tristar II 3020 volumetric analyzer. Before analysis, the samples were degassed at 150 ^{o}C under vacuum ($<10^{-4}$ mbar) for 12 h. The surface areas were calculated using the Brunauer-Emmett-Teller (BET) model on the adsorption data for 0.05 – 0.25 relative pressure (p/p_o) region, the total pore volumes were calculated from the adsorbed amount at the p/p_o of 0.99, and the distributions of pore sizes were derived from the adsorption branch of isotherms, using the density functional theory (DFT) method for slit pore geometry.

Elemental compositions were obtained using a JEOL JSM-6390LV scanning electron microscope (SEM) operated at 20 kV. Data acquisition was performed using an 100 s accumulation time.

Diffuse reflectance UV-vis/near-IR spectra were obtained on a Perkin Elmer Lambda 950 optical spectrophotometer in the wavelength range 200 – 2500 nm. $BaSO_4$ powder was used as a 100% reflectance standard and base material on which the powder sample was coated. Diffuse reflectance data were converted to absorption using the Kubelka-Munk function $\alpha/S = (1-R)^2/(2R)$, where R is the measured reflectance and α, S are the absorption and scattering coefficients, respectively. The band gaps of the samples were estimated from the onset of absorption data converted from reflectance[1].

Catalytic photo-oxidation of 1-phenylethanol

The photo-oxidation of 1-phenylethanol were carried out as follows: A solution of 1-phenylethanol ($3.0x10^{-2}$ M) and appropriate amount of catalyst (45 mg) in oxygen-bubbled (ca. 25 ml min^{-1}) acetonitrile (HPLC-grade), was irradiated with a Variac Cermax 300 W Xenon lamp (λ>300 nm) as the light source. Before switching on the lamp, the catalytic grains were kept in suspension by vigorous magnetic stirring for 30 min. During irradiation, the reaction mixtures were cooled with ice water bath (ca. 5 ^{o}C) and monitored by gas chromatography (GC) and NMR spectroscopy. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AMX 300 MHz spectrometer, in $CDCl_3$. The products analysis was performed on a Shimadzu GC-17A chromatograph equipped with a 60-m HP-5 capillary column and a Shimadzu GC MSQP5050A apparatus equipped with a 50-m HP-5 capillary column and a 5971A MS detector.

For recycling experiments, the photocatalyst was recovered by centrifugation, pre-treated for 1 h in 1 M HCl (20 ml) to alleviate the side-on Ti-peroxide species[16a], dried under vacuum, and used for the next catalytic run.

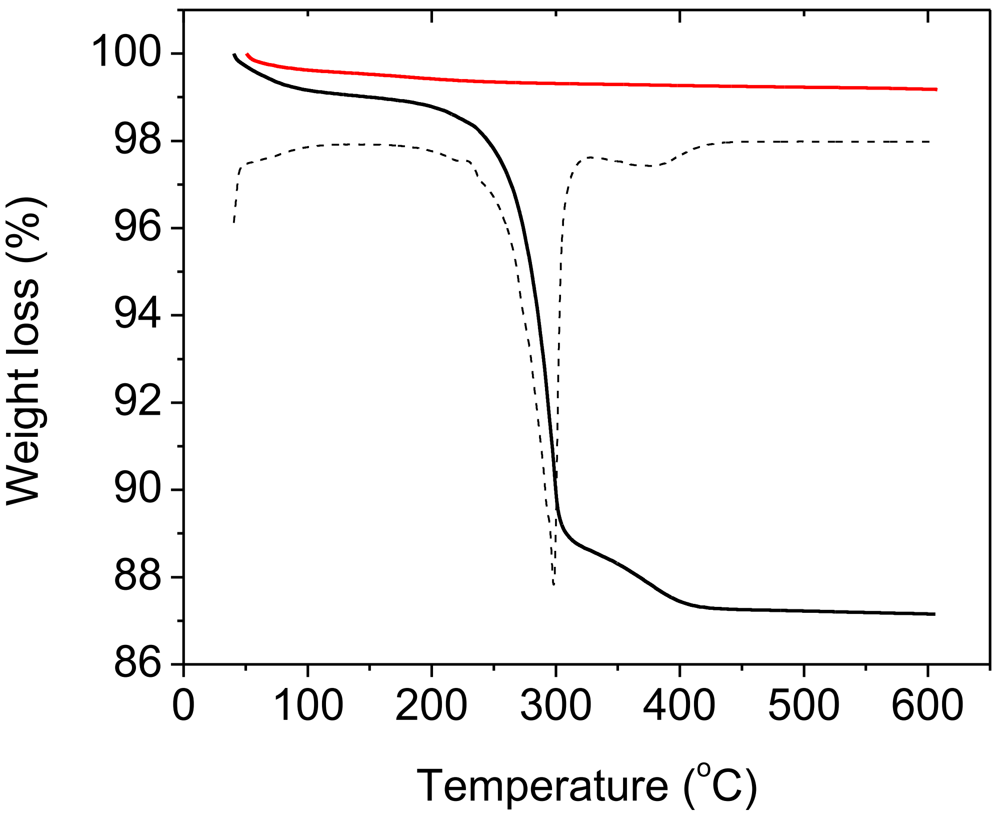

Fig. S1 TGA profiles (solid lines) of as-prepared (containing surfactant) MTA (black) and heat-treated (at 350 °C) material (red). The as-prepared material shows a weight loss of 11.7 % in the temperature range 200-425 °C, while the calcined sample indicates no appreciate weight loss (~0.16 %) in the 200-600 °C temperature range. The weight loss in as-prepared samples, indicated by the corresponding differential thermogravimetric (DTG) curve (dashed lines), is attributed to the decomposition of surfactant.

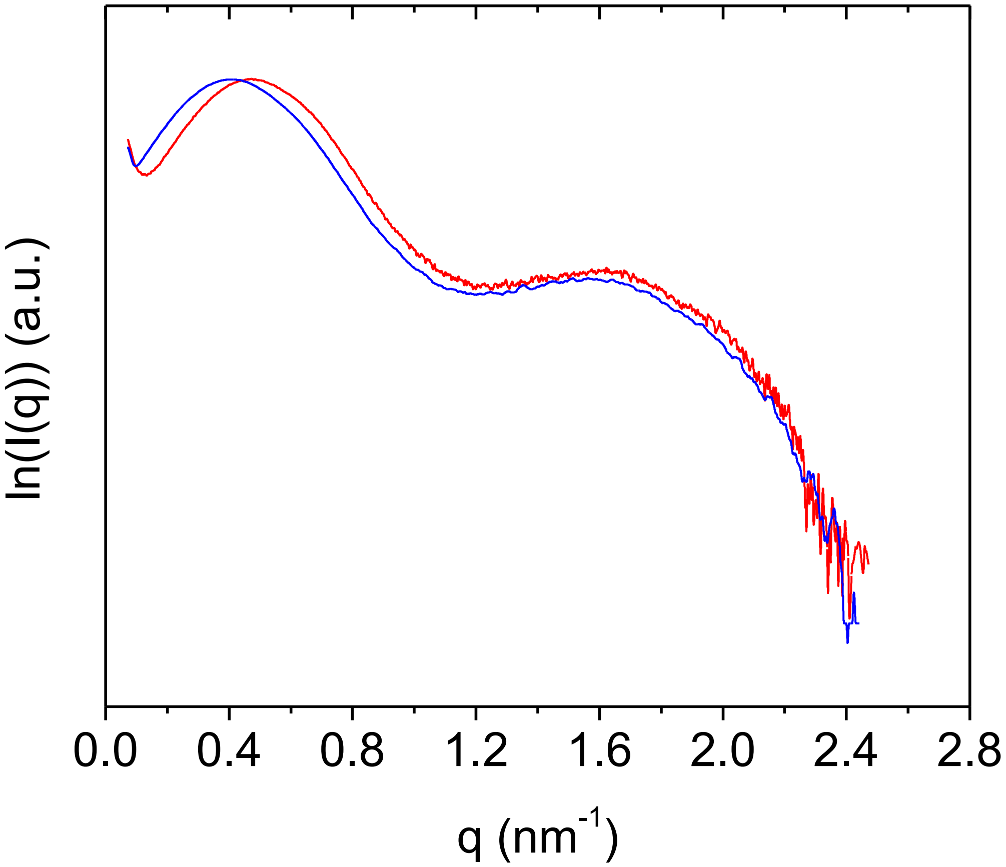

Fig. S2 Small-angle X-ray scattering (SAXS) patterns of MTA obtained after aging for a period of 5 (MTA-1, red line) and 15 (MTA-2, blue line) days. The angular position of the strong peak at scattering wave vector *q* region 0.47 and 0.41 nm^{-1} gives an intraparticles distance of 13.3 and 15.3 nm for MTA-1 and MTA-2, respectively.

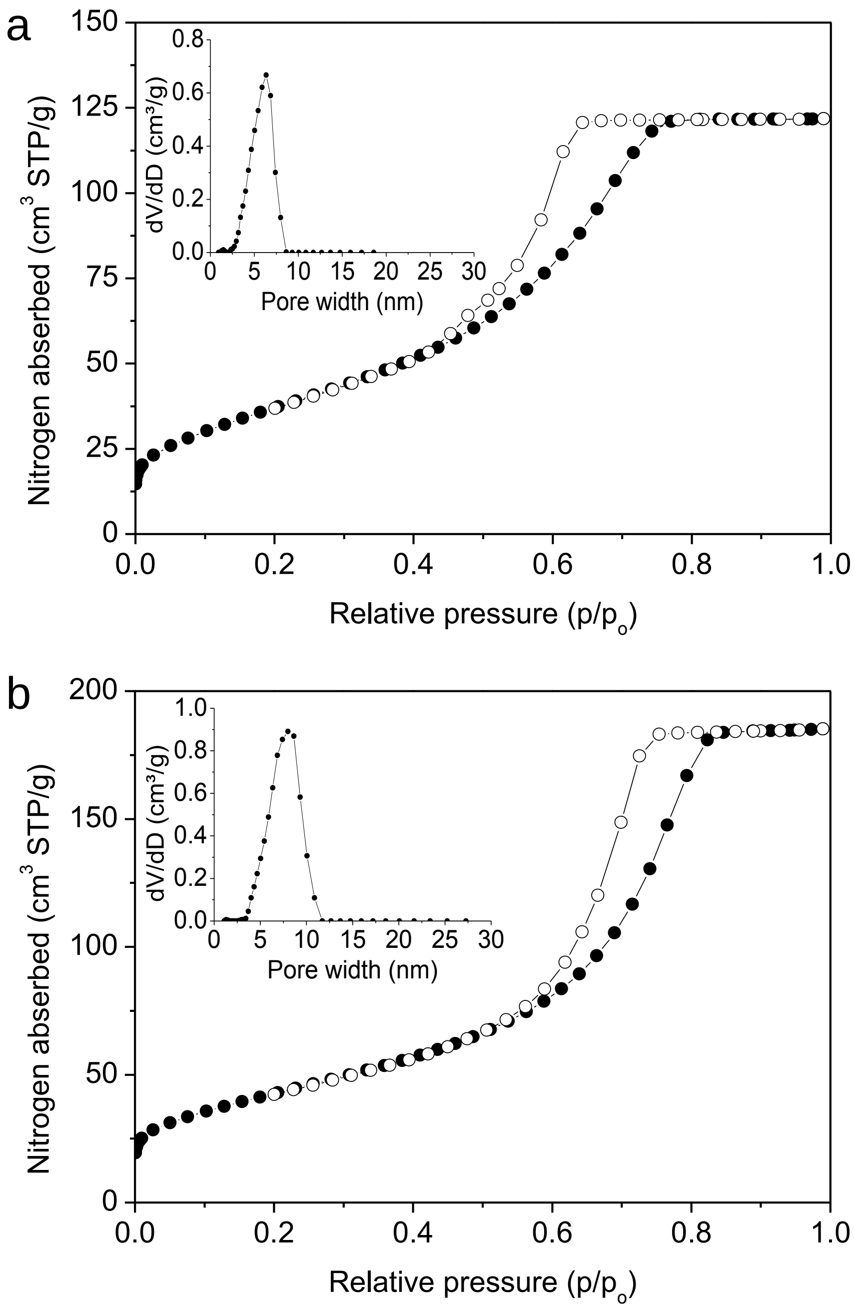

Fig. S3 Nitrogen adsorption-desorption isotherms at 77 K and corresponding DFT pore size distributions (insets), calculated from the adsorption branch of the isotherms, for (a) MTA-1 and (b) MTA-2 materials. The adsorption data indicate BET surface areas of 134 and 154 m^{2}g^{-1}, pore volumes of 0.20 and 0.29 cm^{3}g^{-1}, and pore diameter of 6.2 and 8.3 nm for MTA-1 and MTA-2, respectively.

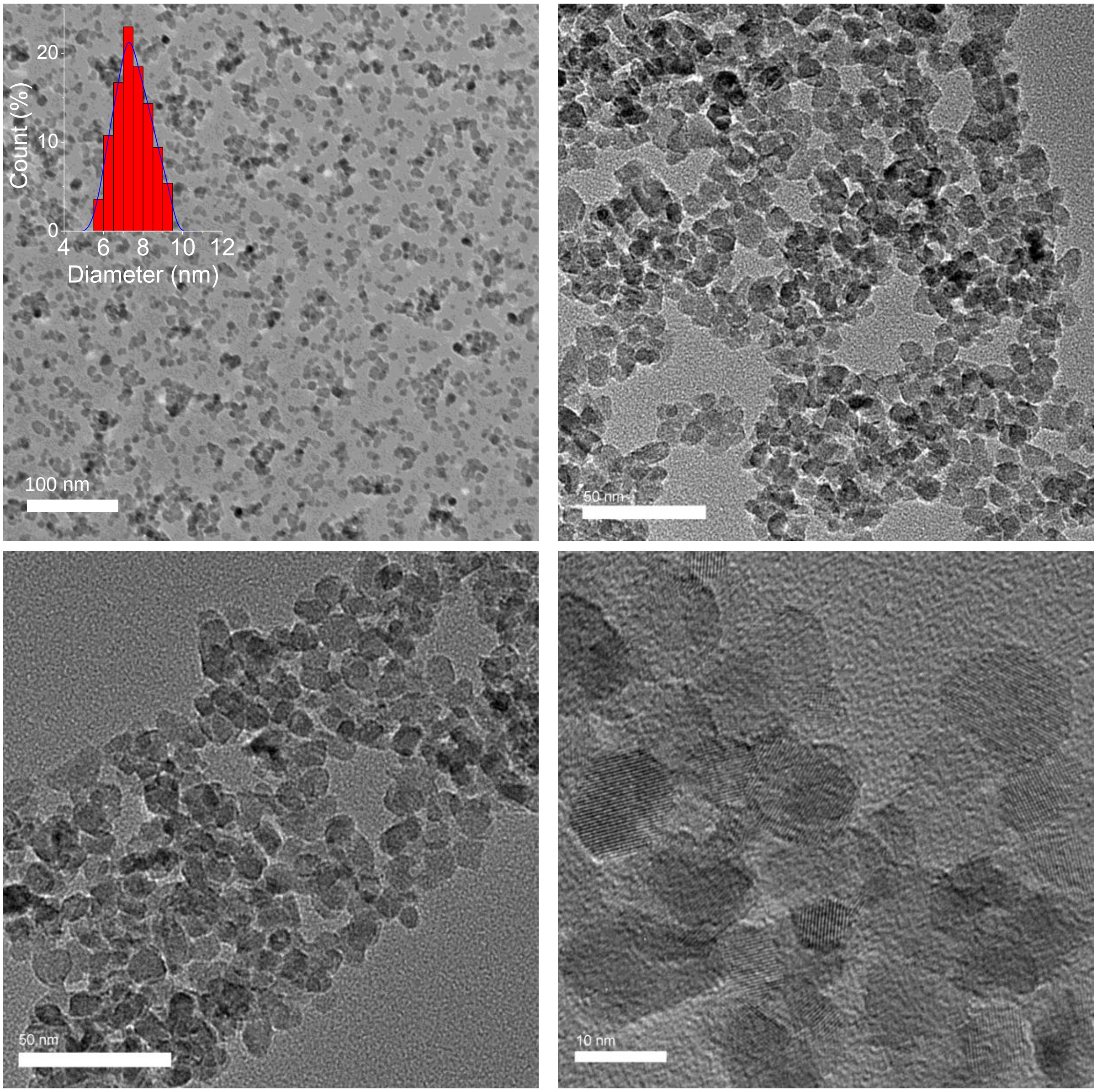

Fig. S4 Representative TEM images of MTA-1 at different magnifications. Inset: the corresponding particle size distribution.

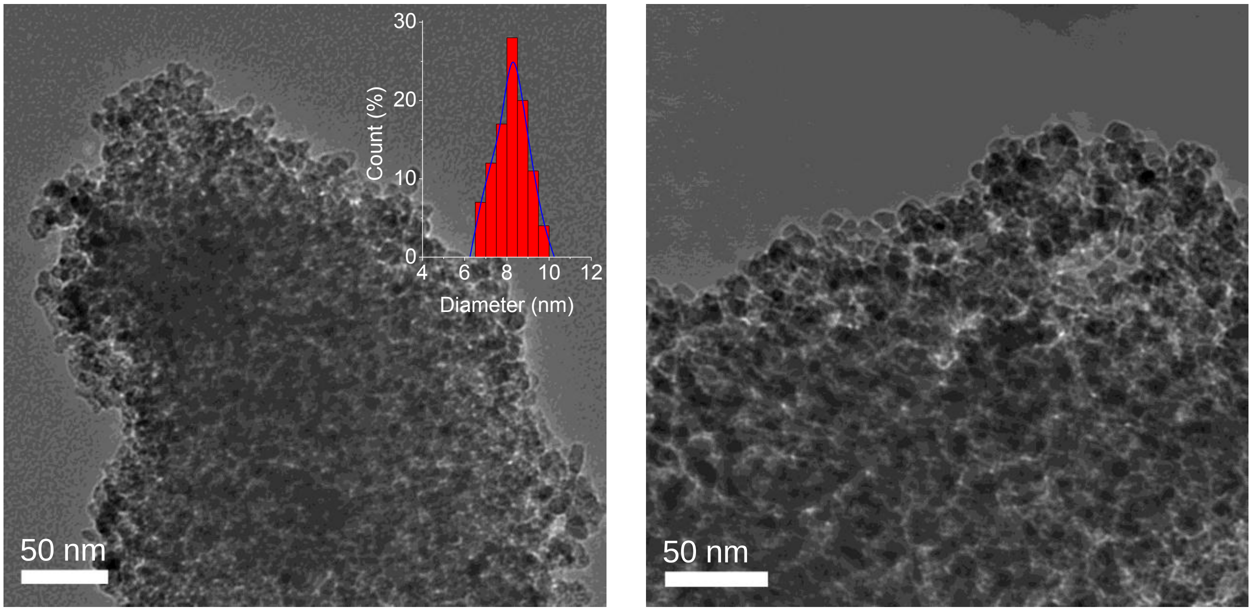

Fig. S5 Representative TEM images of MTA-2 at different magnifications. Inset: the corresponding particle size distribution.

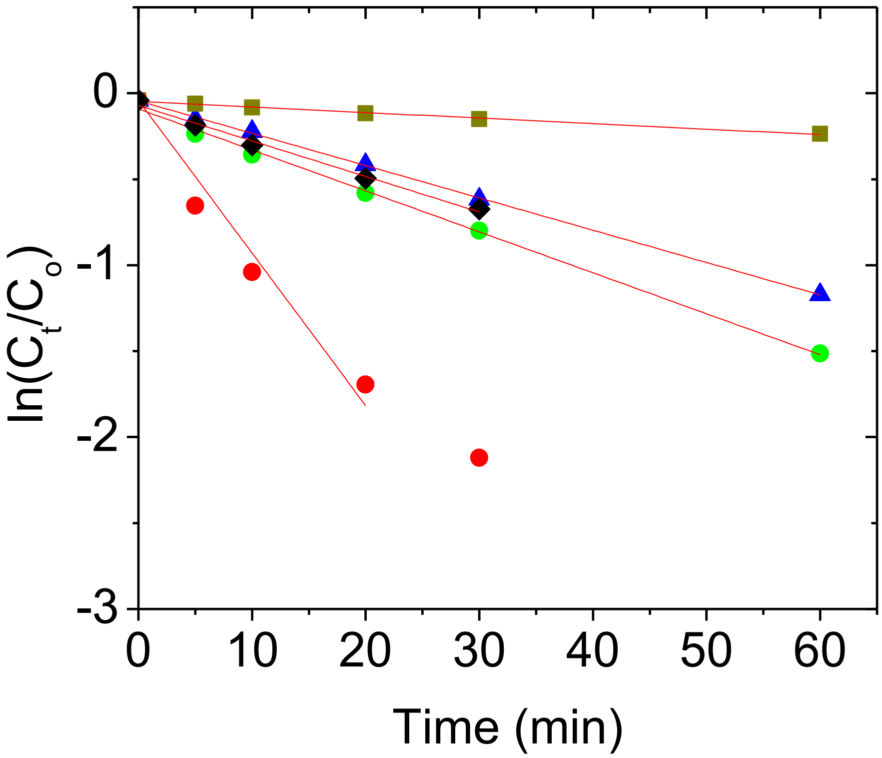

Fig. S6 The pseudo first-order rate plots (C_o, C_t are the initial and final (at time t) concentrations of 1-phenylethanol, respectively) for the photo-oxidation of 1-phenylethanol catalyzed by MTA (green), CdS-MTA (red) Aldrich anatase (yellow), Degussa P25 (blue) and Hombikat UV-100 (black). The corresponding red lines are fit to the data.

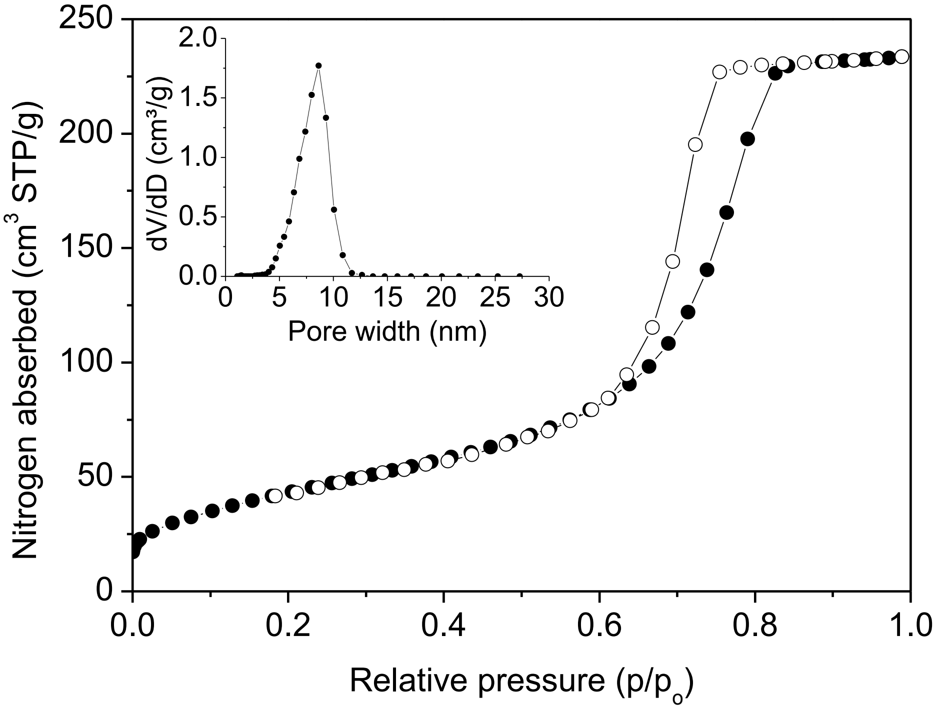

Fig. S7 Nitrogen adsorption–desorption isotherms at 77 K of CdS-MTA nanocomposite, showing BET surface area of 162 m^2g^{-1} and total pore volume of 0.36 cm^3g^{-1}. Inset: the corresponding pore size distribution calculated from the adsorption branch according to the DFT method, indicating pore size of ~ 8.3 nm.

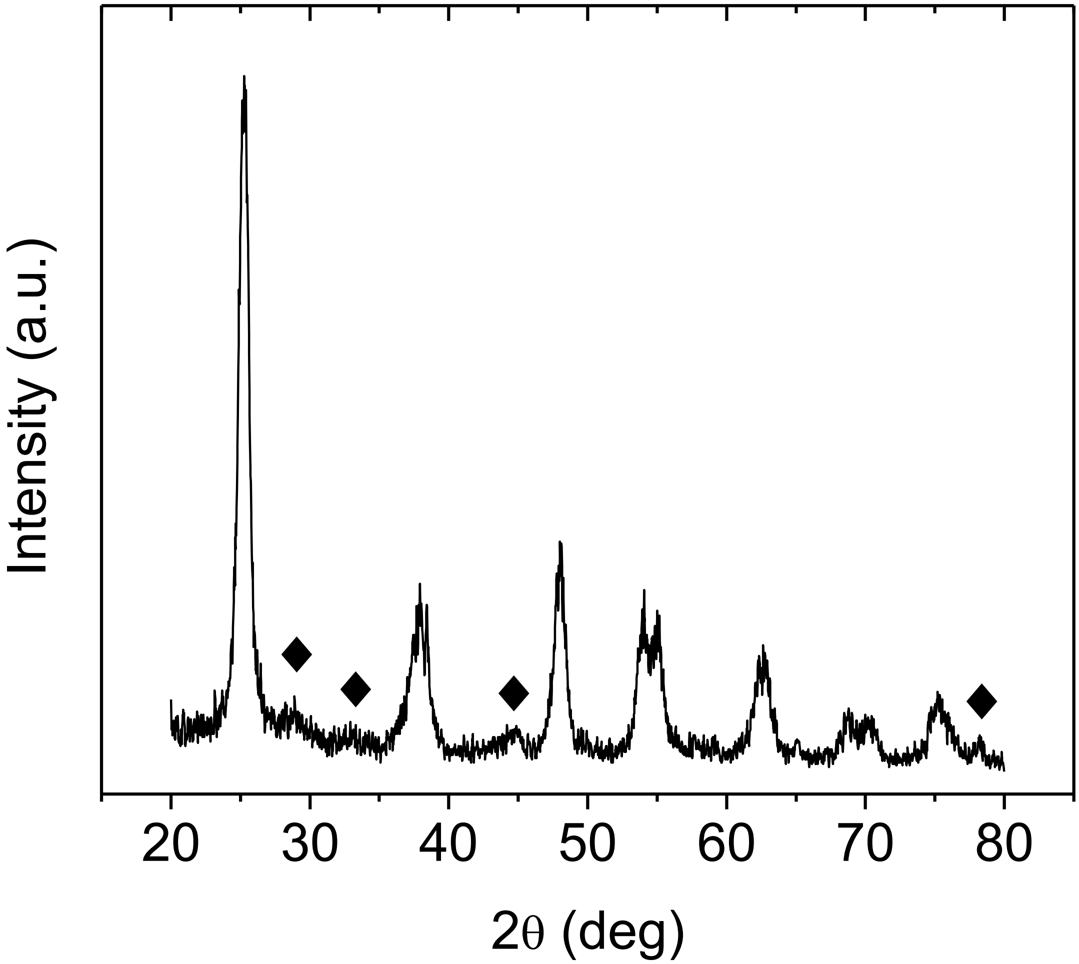

Fig. S8 X-ray diffraction pattern of CdS-MTA nanocomposite. The strong diffraction peaks are assigned to the anatase TiO_2 (JCPDS Card No. 21-1272). Additional peaks indicated by symbols are attributed to the hexagonal structure of CdS (JCPDS Card No. 65-3414).

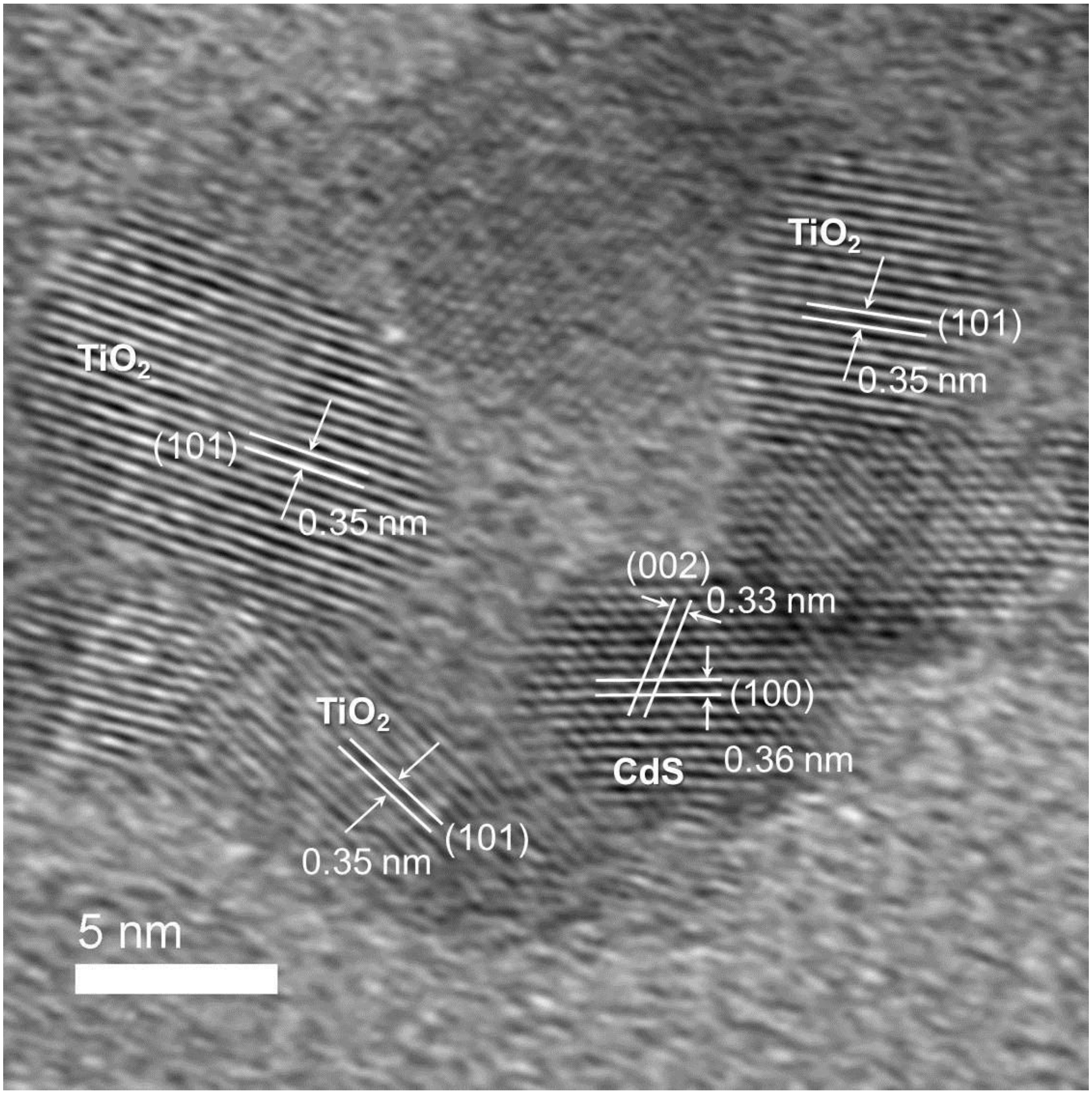

Fig. S9 High resolution TEM (HRTEM) image of CdS-MTA showing TiO_2 nanoparticles (~8 nm) in close connection with hexagonally shaped CdS QDs (~5-6 nm). The TiO_2 nanocrystals feature lattice fringes with d-spacing of about 0.35 nm, corresponding to anatase structure. The lattice fringes with 0.36 nm and 0.33 nm interplanar spacing can be assigned respectively to the (100) and (002) crystallographic planes of hexagonal CdS phase.

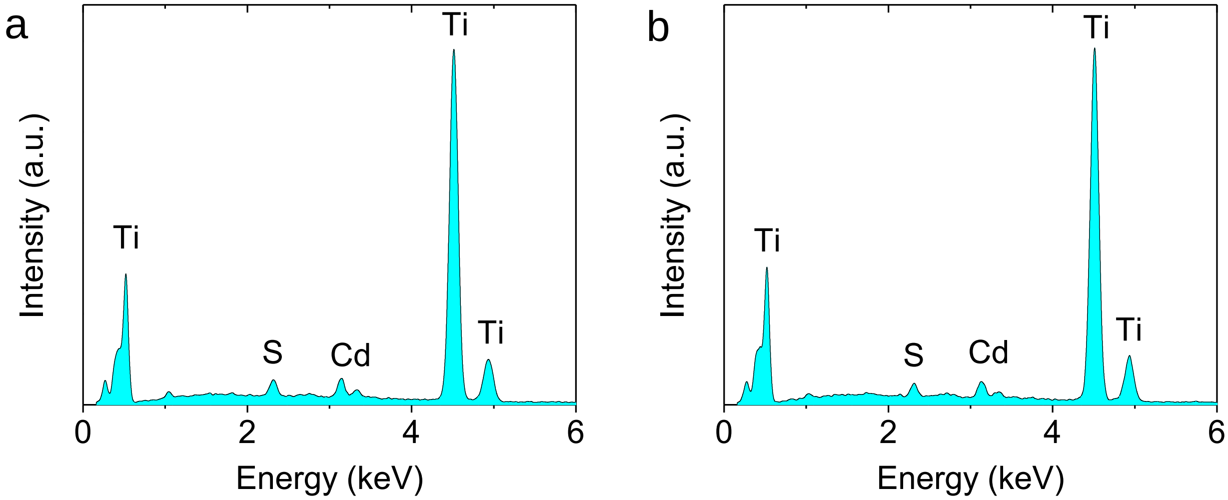

Fig. S10 Typical energy-dispersive X-ray spectroscopy (EDS) spectra of CdS-MTA (a) before and (b) after catalysis. The EDS data indicate average Cd/S/Ti atomic rations of ~2.9:2.9:94.2 and ~2.8:94.4:2.9, corresponding to a ~5.3 wt % and ~5.1 wt % of CdS content for fresh and four-time reused CdS-MTA photocatalyst.

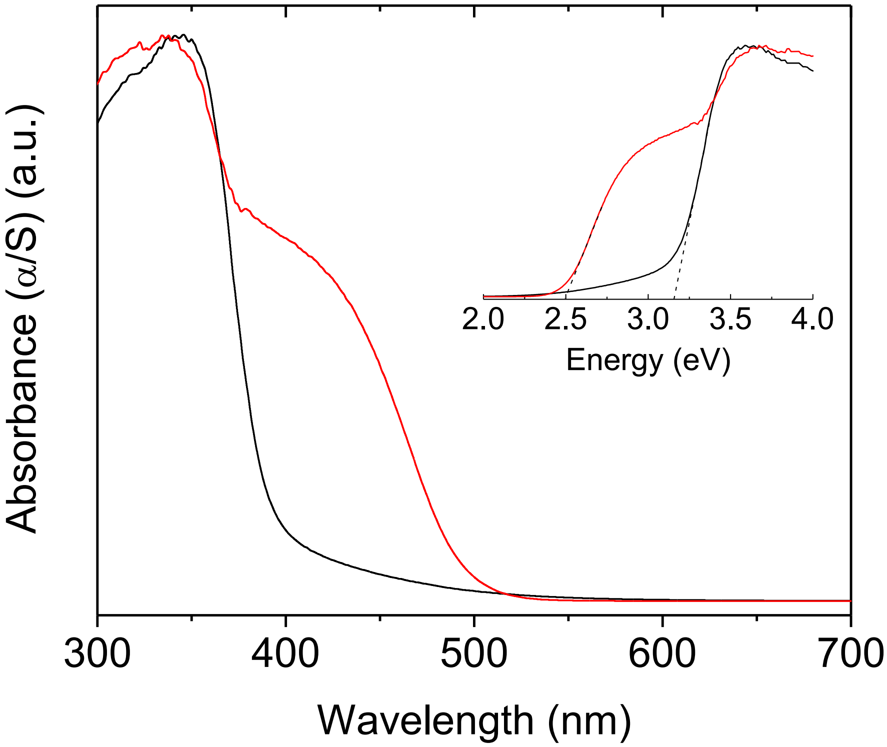

Fig. S11 Optical absorption spectra of MTA (black) and CdS-MTA (red line) photocatalysts showing a significant red shift of optical absorption onset from 3.2 to 2.5 eV after sensitization of TiO_2 nanocrystals with CdS QDs.

The average size of CdS nanocrystals can be estimated as a function of the energy band gap according to the mass approximation model[2]:

$$E_g = \frac{h^2}{8R^2}\left(\frac{1}{m_e^*} + \frac{1}{m_h^*}\right) - \frac{1.8e^2}{4\pi\varepsilon_o\varepsilon R} + E_{g,bulk} \qquad (1)$$

where E_g and $E_{g,bulk}$ are the energy band gaps of the nanocrystalline and bulk solid (2.25 eV) respectively, h is the Plank's constant, R is the radius of the particle, m_e

(=0.19 m_e) and m_h (=0.80 m_e) are the effective masses of the electron and hole in CdS respectively, ε_o is the vacuum permittivity, and ε is the relative permittivity of CdS (5.7)[3].

We also used the eq. (1) to estimate the coherent crystal size of spherical CdS nanoparticles, obtaining a particle size of about 5 nm. This value is in good agreement with the size of CdS nanocrystals obtained from TEM (see Fig. S9).

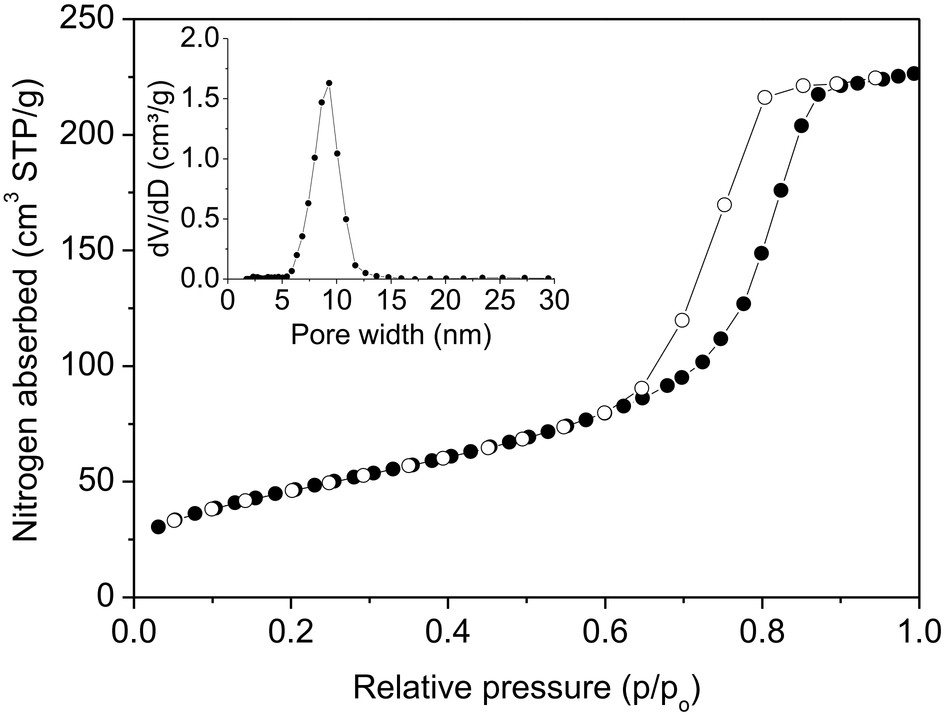

Fig. S12 Nitrogen adsorption–desorption isotherms at 77 K of four-times reused CdS-MTA catalyst. BET analysis on adsorption data indicates a surface area of 168 m^2g^{-1} and total pore volume of 0.35 cm^3g^{-1}. Inset: the corresponding pore size distribution calculated from the adsorption branch according to the DFT method, indicating pore size of ~ 9 nm.

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[1] W. W. Wendlandt, H. G. Helcht, in *Chemical Analysis: Reflectance Spectroscopy*, Interscience, Vol. 21, New York, 1966.

[2] L. E. Brus, *J. Chem. Phys.* 1984, **80**, 4403.

[3] P. E. Lippens, M. Lannoo, *Phys. Rev. B* 1989, **39**, 10935.