Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A

jiSi quantum dots-assisted synthesis of mesoporous black TiO_2 nanocrystals with high photocatalytic activity

Supporting Information

1. Experimental Section

All reagents were purchased from Sigma–Aldrich and used without further purification.

Synthesis of MPBT nanocrystals:

The MPBT nanocrystals were obtained based on a two-step chemical process. Before electrolytic deposition, the Ti foil (1×5 cm^2, 2 mm thickness) was washed with ethanol for three times. The SiQDs were synthesized according to our group's method.[16] The average size of SiQDs was determined to be 5.0 nm from the particle size distribution on the basis of 200 dots in TEM image, as shown in Figure S1. In the first step, the SiQDs were electrolytic deposited on the surface of Ti foil. In second step, the obtained Ti foil with SiQDs and HF acid (5 mL, 30%) were simultaneously transferred to sealed plastic vessel. After 3 days, the MPBT nanocrystals were obtained.

Synthesis of BT

The black TiO_2 nanocrystals were prepared according to the reported method by Chen et al. with minor modifications.[12] The TiO_2 precursor solution consists of titanium tetraisopropoxide (TTIP), hydrochloric acid (HCl), Pluronic F127, ethanol, and deionized water, with molar ratios of TTIP/HCl/F127/H_2O/ethanol at 1:0.5:0.005:15:40 was heated at 40°C for 24 h and then evaporated and dried at 110°C for 24 h. The dried powders were calcinated at 500°C for 6 h to remove the organic

template and enhance the crystallization of TiO_2. The resulting white-colored powders were maintained in a vacuum for 1 h. And then, the sample was placed in the sample chamber of H_2/Ar mixture gas with volume fraction of 3:7 and hydrogenated at about 200°C for 10 days.

Synthesis of TiO_2 nanoparticles

In a typical procedure, 0.5 ml of tetrabutyl titanate was added into 10 ml of ethanol. The solution was magnetically stirred for 8 h at room temperature. After that, the solution was poured into a mixture of 2.0 ml of water and 150 ml of acetone and was vigorous stirred for one hour. The TiO_2 precursor was obtained by centrifugation, followed by washing with ethanol. To obtain the TiO_2 nanoparticles, the calcination was carried out at 500 ◦C for 2 h.

Photocatalytic degradation of MO and MB

The visible light degradation of methyl blue (MB) and MO was conducted by irradiating the sample solution with a cutoff filters (150 W, Xenon lamp, $\lambda > 420$ nm). Typical photocatalytic degradation of MO (or MB) was carried out in a 100 mL (MO, 4000 ppm or MB, 50 ppm) solution and 50 mg different catalysts (MPBT, BT, and WT). Before the irradiation, the solution was stirred for 1h without light to ensure the establishment of an adsorption–desorption equilibrium.

Photocurrent measurement

The photocurrent measurement was carried out in 0.1 M Na_2SO_4 solution under simulated sunlight irradiation (I_0 = 33 $mW{\cdot}cm^{-2}$). The MPBT nanocrystals, BT

nanocrystals, WT nanoparticles, and P25 were respectively placed in a two-electrode cell system with Pt as the counter electrode.

2. Characterization

SEM images were taken on a FEI-quanta 200F scanning electron microscope with acceleration voltage of 20 kV. The SEM sample was prepared by dropping the sample solution onto a copper foil. The TEM image and HRTEM images were obtained with a FEI/Philips Tecnai 12 BioTWIN transmission electron microscope operated at 200 kV with EDX analyses. The TEM samples were prepared by dropping the sample solution onto a copper grid covered with carbon and dried in air. The XRD patterns were obtained on a Rigaku D/max 2500V PC diffractometer using Cu-Ka radiation. Raman spectra of samples were measured using a LabRAM HR800 microspectrometer using an excitation wavelength of 514 nm. The EPR spectra were recorded on a Bruker EMX EPR spectrometer at an X-band frequency of 9.363 GHz, sweep width of 500.00 Gauss, and center field of 3390.00 Gauss. The XPS was carried out on a Kratos Axis UltraDLD equipped with a monochromatized Al Kα source in an ultra-high vacuum with a base pressure of 5 × 10-10 Torr, with samples placed on a copper foil. DRS absorption and reflectance spectra were obtained with a PerkinElmer Lamda 750 UV-Vis Spectrophotometer.

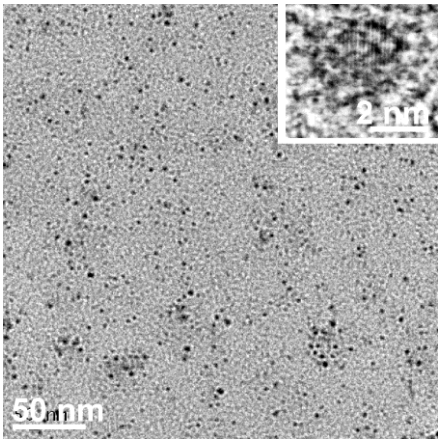

Figure S1. TEM image of SiQDs.

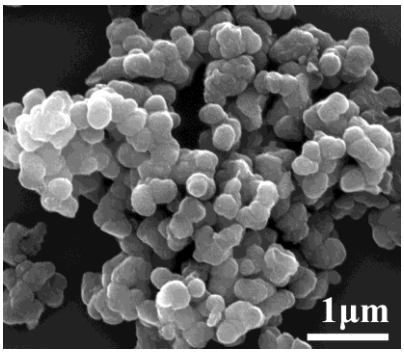

Figure S2. SEM image of white anatase phase TiO_2 (WT) nanoparticles.

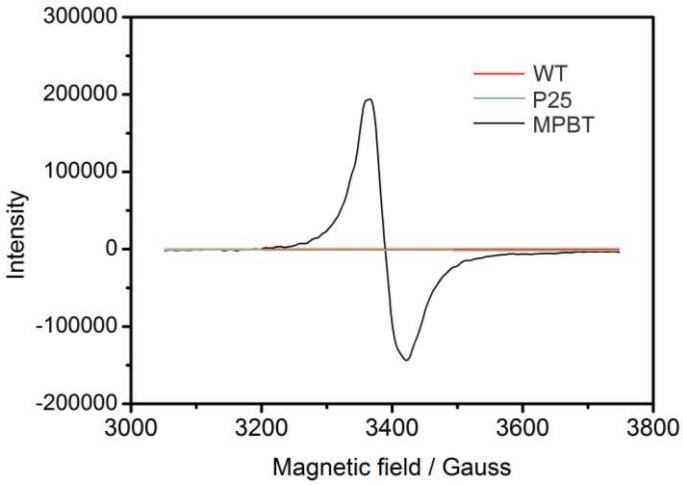

Figure S3. EPR spectra of WT nanoparticles, commercial P25, and MPBT nanocrystals recorded at 100 K.

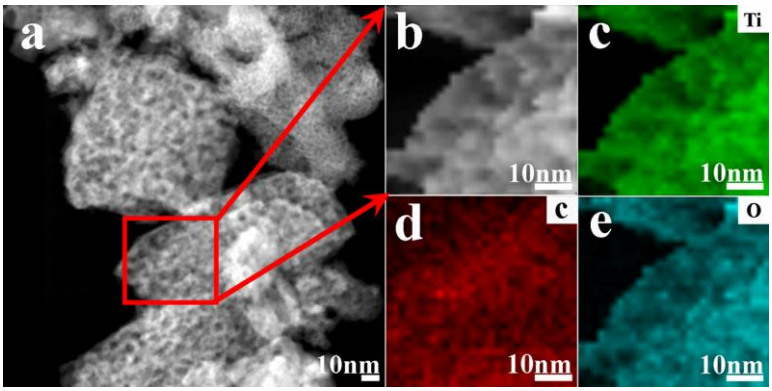

Figure S4. STEM images and EDX elemental maps of MPBT nanocrystals: (a) STEM image, b-e) corresponding partially STEM image and elemental maps. Elemental maps of Ti (green), C (red) and O (blue). The carbon element attributed to amorphous carbon films supported by standard Cu grids.

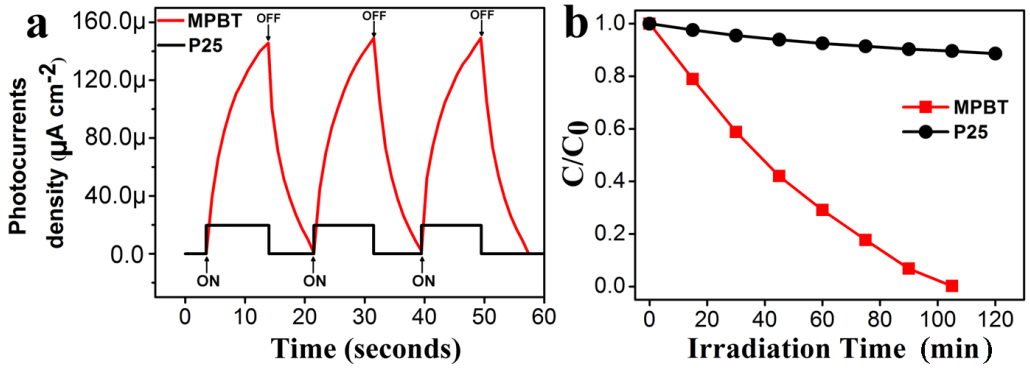

Figure S5. a) Photocurrent density versus time curves of MPBT nanocrystals and P25 nanoparticles measured in 0.1 M Na_2SO_4 solution under simulated sunlight irradiation (I_0 = 33 mW·cm^{-2}). b) Photocatalytic degradation of MO in the presence of MPBT nanocrystals and P25 nanoparticles under visible light irradiation (λ > 400 nm).

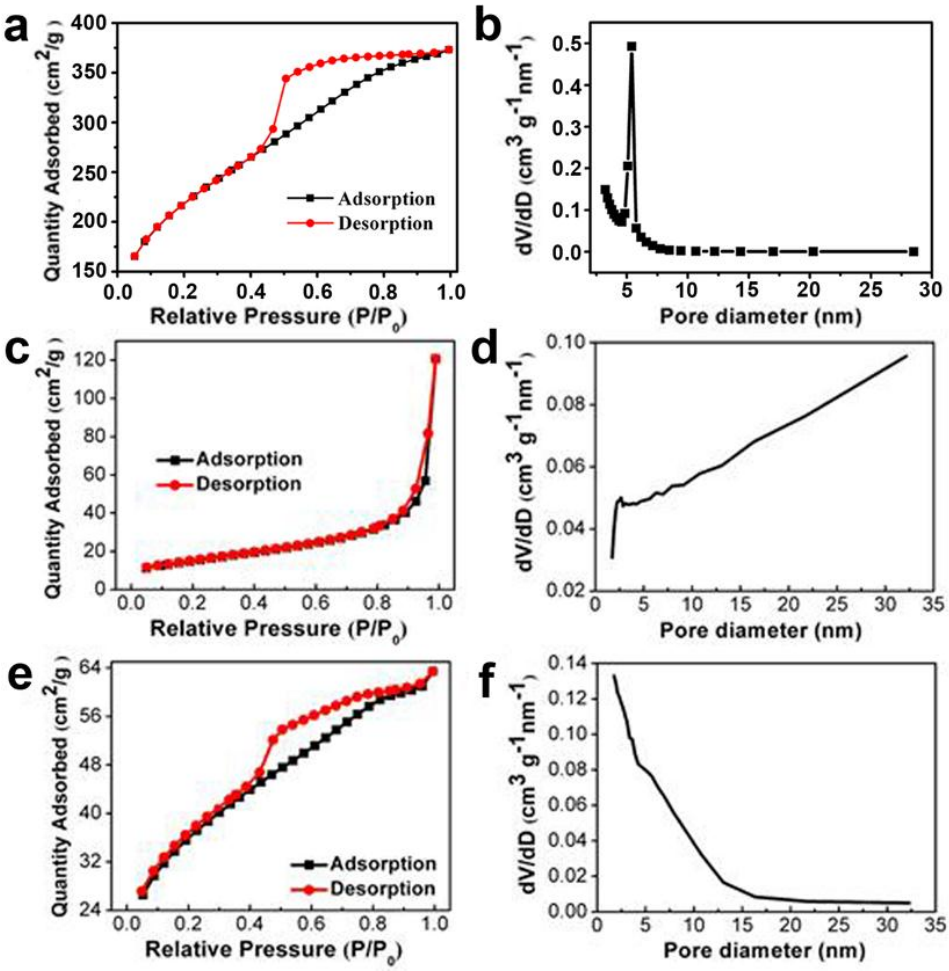

Figure S6. a) Nitrogen adsorption-desorption isotherm and b) pore size distribution curve of MPBT nanocrystals. c) Nitrogen adsorption-desorption isotherm and d) pore size distribution curve of BT nanoparticles. e) Nitrogen adsorption-desorption isotherm and f) pore size distribution curve of WT nanocrystals.

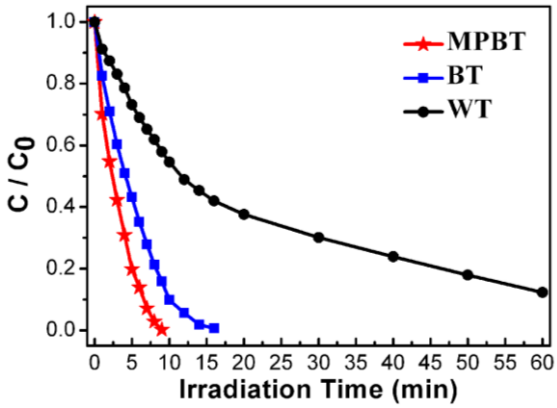

Figure S7. Photocatalytic degradation of MB in the presence of white anatase phase TiO_2 (black line), BT (blue line) and MPBT (red line) nanocrystals under visible light irradiation ($\lambda > 400$ nm).

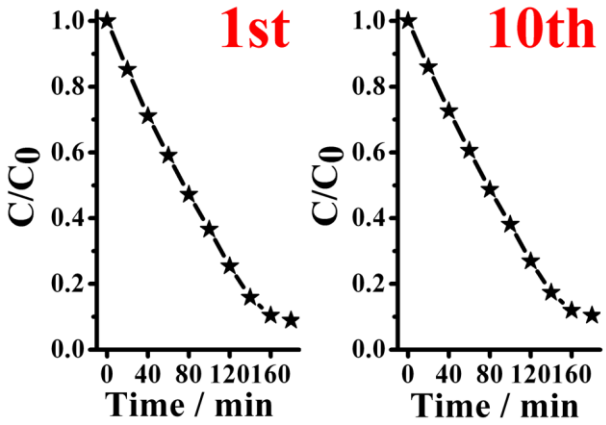

Figure S8. The repeatability experiments of MPBT nanocrystals in decomposing MO in ten times.

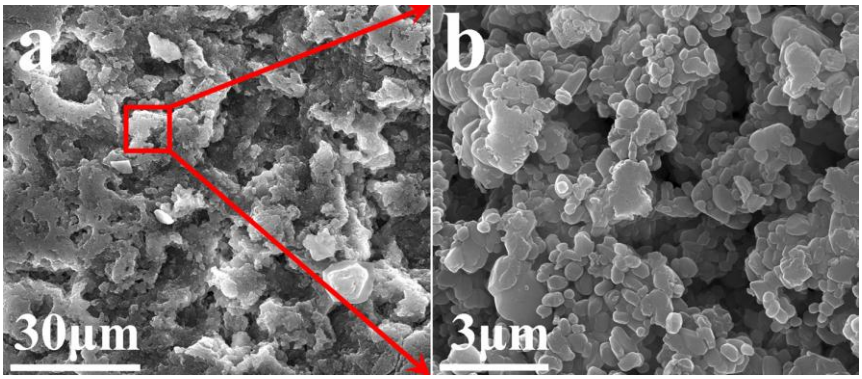

Figure S9. (a and b) SEM images of Ti foil after etching without SiQDs with different magnifications.

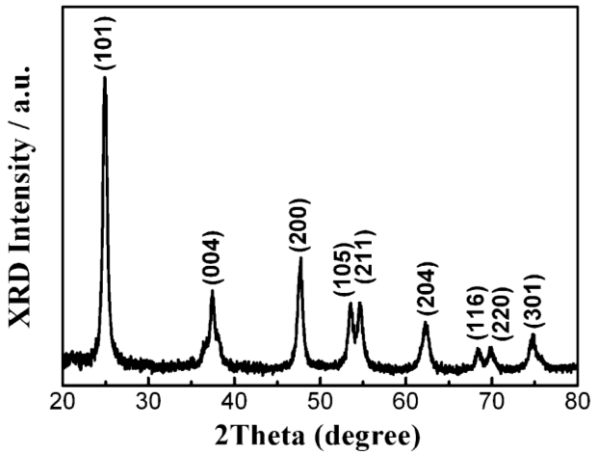

Figure S10. The XRD pattern of the obtained TiO_2 nanoaprticles by etching Ti foil without SiQDs.