

Electronic Supplementary Information (ESI)

Quantum Dots Self-Decorated TiO₂ Nanosheets

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Experimental Section

Materials:

Rhodamine B (RhB), tetrabutyl titanate (TBT), hydrofluoric acid (HF, 40 wt.%), sodium hydroxide (NaOH), ethanol and AgNO₃ were all reagent grade and purchased from Tianjin Guangfu Fine Chemical Research Institute. Deionized water was used in all experiments. All the reagents were used as received.

Sample preparation:

In a typical synthesis route, 3.5 mL of HF aqueous solution (40 wt%. Caution! Hydrofluoric acid is extremely corrosive and a contact poison, and it should be handled with extreme care) was mixed with 25 mL TBT under vigorous stirring. The suspensions were stirred for 20 min, and then transferred to a Teflon-lined autoclave and heated at 180 °C for *t* hours (*t* = 24, 72 and 168), respectively. After crystallization, the products were collected by centrifugation and washed with deionized water and ethanol for several times. The samples were then dried at 60 °C in air overnight. 0.5 g of as-prepared sample was dispersed in 20 mL of 10 M NaOH aqueous solution under vigorous shaking for 60 min in an ultrasonic cleaner. Then, the sample was centrifuged, and washed for 5 times with deionized water and ethanol, then dried at 60 °C in air overnight. The prepared samples are named as “A-*t*”.

Post-treatment. After hydrothermally treated in water at 100 °C for 24 h, the samples are named as “A-*t*H”. After the samples (A-*t*) were calcined in air at 500 °C for 2 h at a heating rate of 5 °C min⁻¹, they are named as “A-*t*C”.

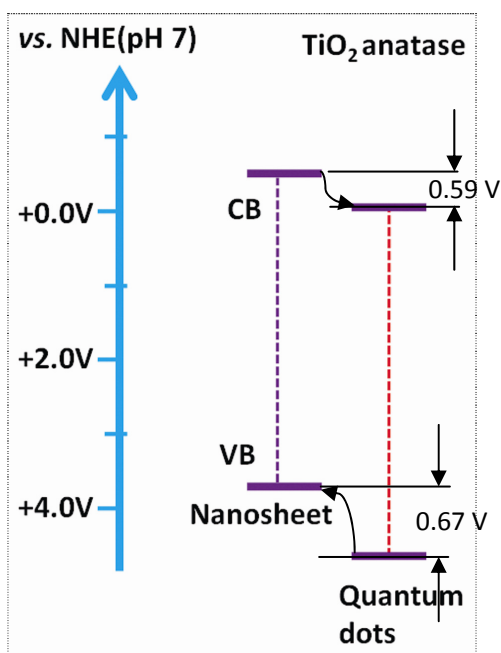
Photoreaction:

Photodegradation of dye was conducted in a closed quartz chamber (150 mL) vertically irradiated by a 300 W high-pressure xenon lamp (PLS-SXE300UV, Beijing Trusttech. Co. Ltd.) located on the upper position. UV light (<450 nm, 15.4±0.5 mW cm⁻² at 365 nm) was separated by UV-ref optical filters. The irradiation area was *ca.* 20 cm². Reaction conditions: temperature, 25± 0.2 °C; *C*₀(RhB)= 20 μmol L⁻¹, TiO₂: 0.2 g L⁻¹; no acid or alkaline reagents were added. Reaction was conducted by magnetic stirring under atmosphere, after stirring for 20 minutes in black to achieve adsorption equilibrium. Samples were withdrawn, centrifuged and analyzed using UV-vis spectrometer (U-3010, Hitachi Ltd.).

Photodeposition of Ag particles (0.8 wt%). The reaction conditions are the same with the photodegradation, but the reaction compositions are as follows: *m*(TiO₂)= 30 mg; *C*(AgNO₃)= 74.1 μmol L⁻¹; *V*(H₂O)= 30 mL; irradiation time, 30 min. Then, the sample was centrifuged, and washed for 5 times with deionized water and ethanol, then dried at 60 °C in air overnight.

Characterization:

XRD characterizations were conducted using D/MAX-2500 X-ray diffractometer equipped with Cu Kα radiation at 40 kV and 140 mA. Specific surface area (*S*_{BET}) was calculated based on N₂ adsorption/desorption isotherms using Micromeritics TriStar 3000 at -196 °C, all samples were outgassed under vacuum at 200 °C for 4 h. SEM images were observed using a field-emission scanning electron microscope (Hitachi S-4800). HR-TEM observations were carried out by a Tecnai G² F-20 transmission electron microscope with a field-emission gun operating at 200 kV. Energy dispersive spectrum (EDS) characterization was performed with an EDX system attached to TEM. Surface composition and chemical states were analyzed with a PHI-1600 X-ray photoelectron spectroscope (XPS) equipped with Al Kα radiation, and the binding energy was calibrated by the C1s peak (284.6 eV) of the contamination carbon. UV-vis diffuse reflectance spectra (UV-vis DRS) were recorded with a Hitachi U-3010 spectrometer equipped with a 60 mm diameter integrating sphere using BaSO₄ as the reflectance sample. Raman measurements were carried out at room temperature, and the signals were recorded by a Raman Microscope (DXR Microscope, ThermoFisher, USA). The 100-mW output of the 532-nm line of an Nd:YAG laser was used as the excitation source. The obtained Raman spectra were recorded with a resolution approximately 1 cm⁻¹. Electron Paramagnetic Resonance (EPR) studies were performed with a Bruker EMX-6/1 spectrometer under the temperature of 110 K.



Scheme S1. Band structures of anatase nanosheets and quantum dots.

Scheme S1 shows the band structure of clean nanosheets (A-24) and dots-decorated nanosheets (A-168). The quantum-size effect of nanodots is observed from the absorption-edge blueshift in UV-vis DRS and the corresponding K-M plots, as shown in Fig. 2a. The band gap of dots-decorated nanosheets (A-168) is increased by 0.08 eV, compared with the clean nanosheets (A-24). From the VB DOS (Fig. 2b), the high-energy shift of VB edge (0.67 eV) is observed for A-168. The VB-edge shift of dots-decorated nanosheets is larger than the band-gap enlargement, so the conduction band edges of A-168 must be lower than that of A-24. Considering the similar physiochemical properties of pristine nanosheets for all the samples, the quantum-size effect must be resulted from the quantum dots in the size of 1.5-3 nm, and the calculated change of CBM is $0.67-0.08=0.59$ V.

Table S1. Structural properties of TiO₂ nanosheets.

Sample	Side length/nm	Thickness/nm	Percentage of {001} facets/%	S _{BET} / (m ² g ⁻¹)
A-24	55.2	5.4	83.7	69.4
A-24H	55.1	5.6	83.1	68.5
A-72	80.5	9.2	81.3	43.8
A-72H	79.8	9.1	81.4	44.1
A-168	88.3	10.3	81.1	38.8
A-168H	89.0	10.1	81.6	36.8
A-168C	88.8	10.3	81.2	17.4

The percentage of {001} facet was approximately estimated by the following equation:

$$\%S_{\{001\}}_{\text{exp}} = S_{\{001\}} / (S_{\{101\}} + S_{\{001\}}) = 2a^2 / [4ab + 2a^2] \times 100 \quad (1)$$

where *a* and *b* correspond to the average side length and thickness of nanosheets by measuring more than 300 particles in TEM images.

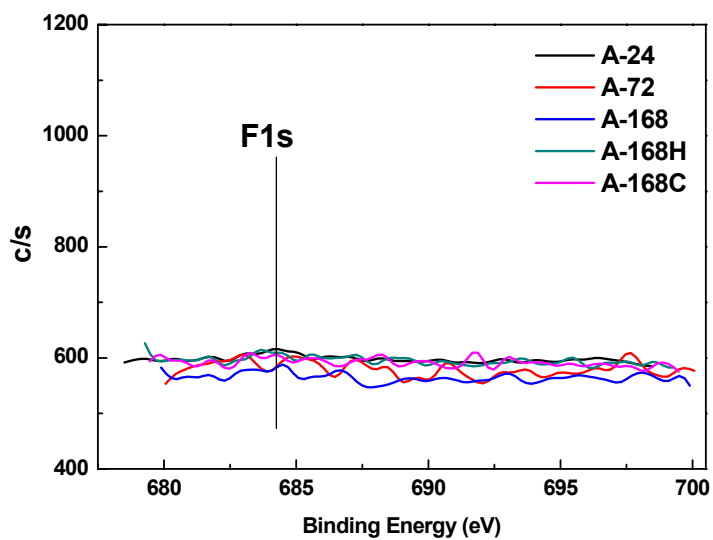


Fig. S1 F1s XPS of as-prepared samples.

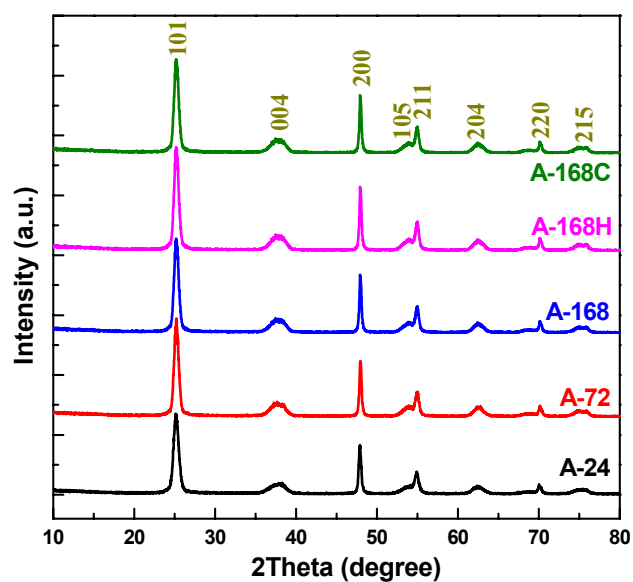


Fig. S2 XRD patterns of the prepared samples.

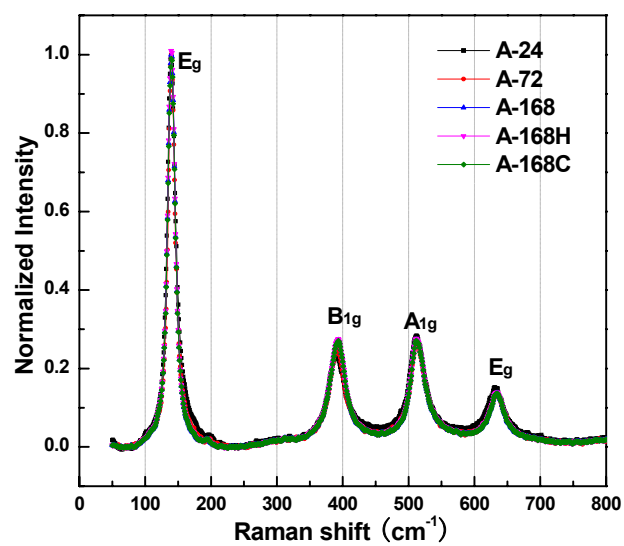


Fig. S3 Raman spectra of the prepared samples.

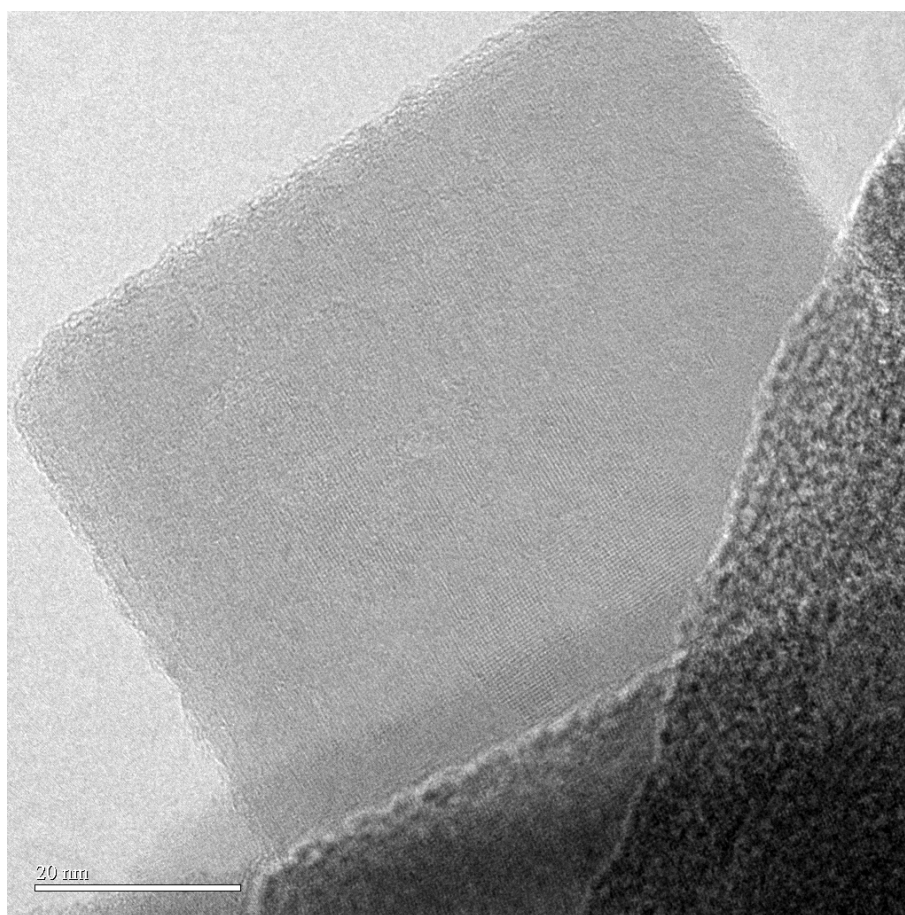


Fig. S4 TEM images of A-24.

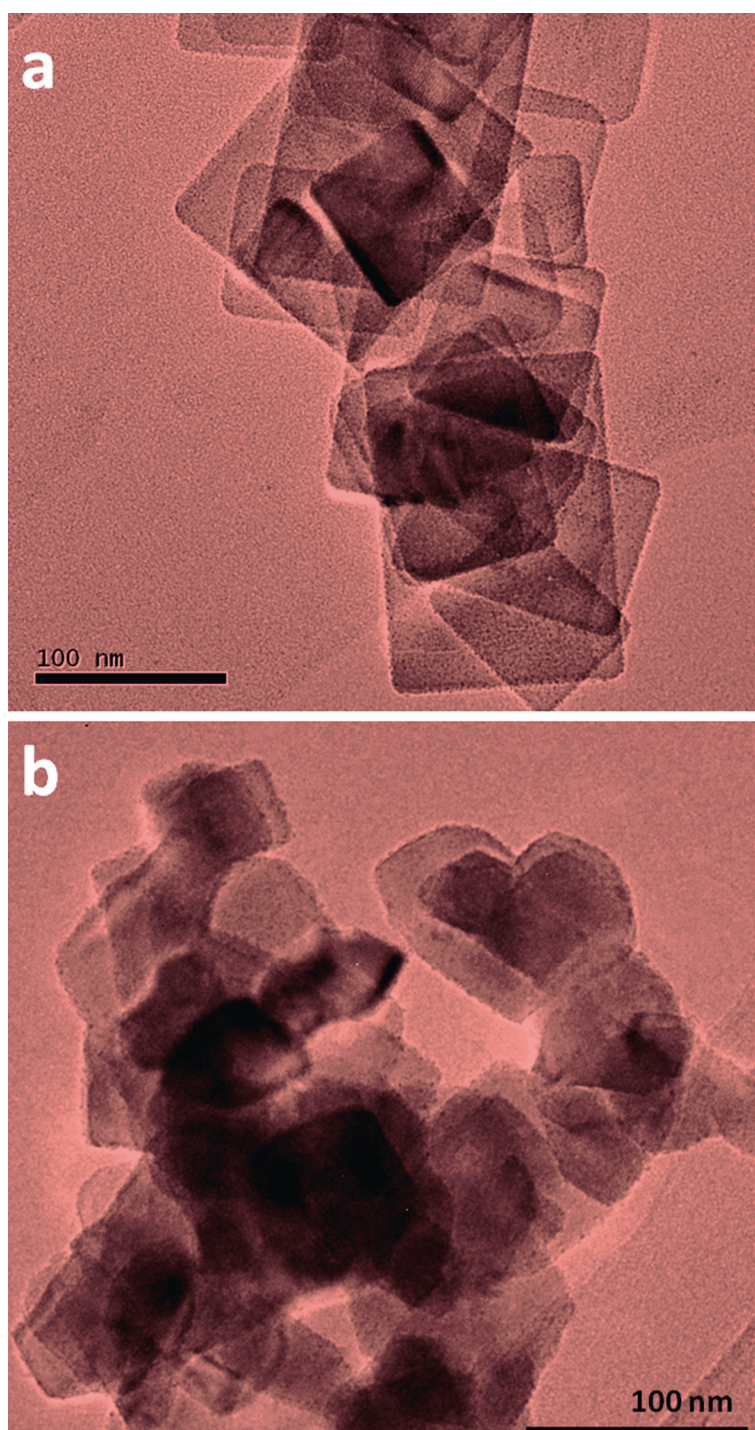


Fig. S5 TEM images of A-168H (a) and A-168C (b).

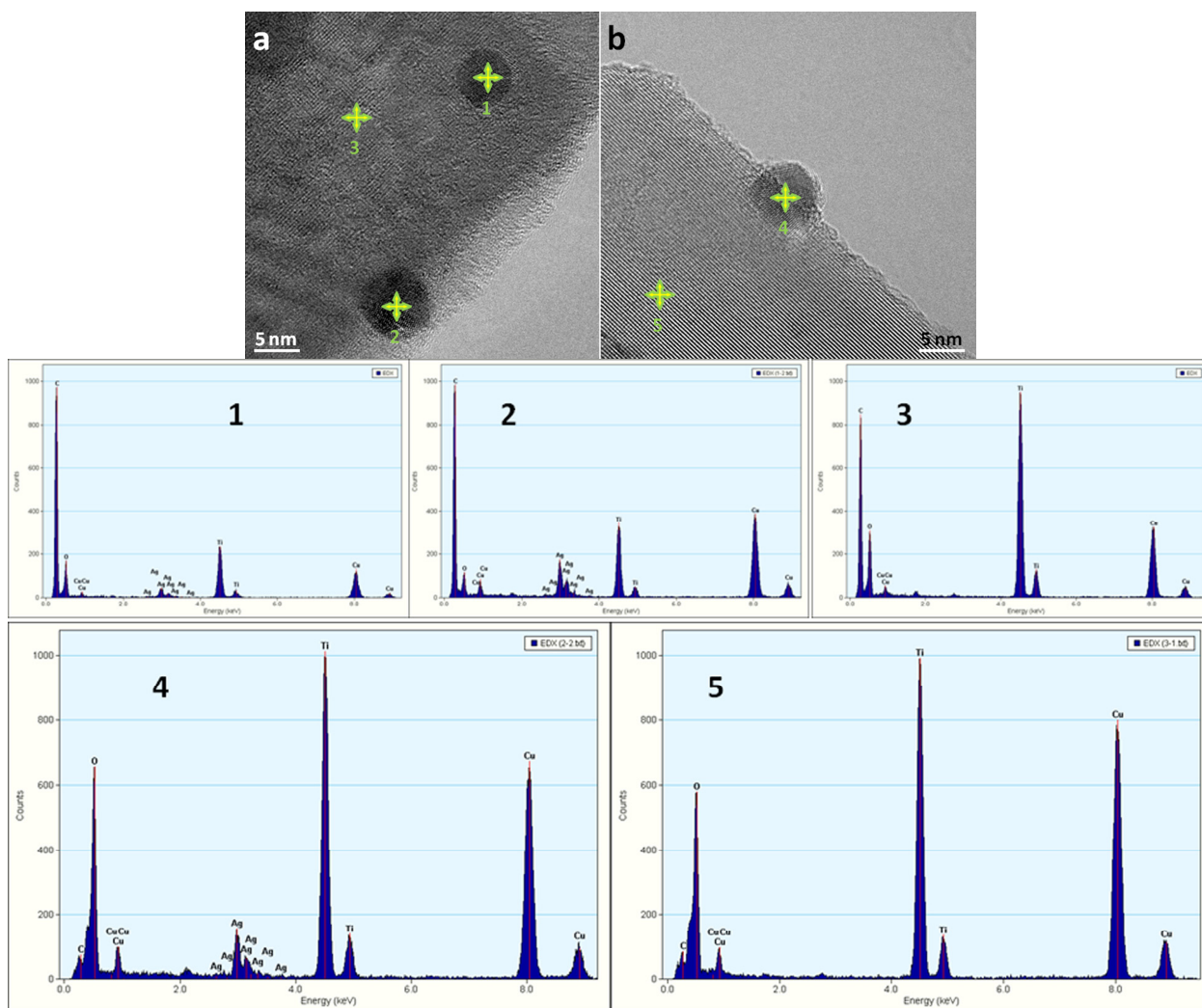


Fig. S6 HR-TEM images of Ag-loaded A-168H (a) and A-24 (b). The below data are the selected-point EDS results from (a) and (b).