Supplementary Information

Ultrafine ZnO quantum dots modified TiO₂ composite photocatalysts: the role of

quantum size effect in heterojunction-enhanced photocatalytic hydrogen

evolution

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Synthesis of ZnO QDs and bulk ZnO.

Synthesis of ZnO QDs. ZnO QDs were prepared according to the literature.¹ In a typical procedure, 26.3 mg of DEA were dissolved into 50 mL of distilled water to obtain a 5.0 mM DEA solution, and 37.2 mg of zinc nitrate hexahydrate were dissolved into 50 mL of distilled water to form a 2.5 mM zinc nitrate solution; the above two solutions and 0.35 mmol of OA were added into a reactor together. After the mixture stirred at room temperature for 30 min and the temperature was increased to 80 °C with continuous stirring for another 2.0 h. The as-prepared dispersion was filtered, centrifuged and washed with 1-butanol, 1-propanol, and ethanol to remove any unreacted molecules. Finally, the QDs were obtained by centrifugation and then dispersed in water for further characterization.

Synthesis of ZnO Nanoflakes. In a typical procedure, 250 mL solution of zinc acetate dehydrate (0.1 M) in methanol was dropwise added to 250 mL NaOH solution (0.1 M) at 60 ° C and stirred for 12 h. The resulting milky precipitate was collected and washed with ultrapure water and ethanol for several times, and finally dried at 60 °C for further characterizations.

Samples	Zn element wt%	ZnO QD	ZnO QDs wt%	
	ICP-AES results	Theoretical content	Actual content	
TZ-0.3%	0.28%	0.30%	0.34%	
TZ-0.6%	0.54%	0.60%	0.68%	
TZ-0.9%	0.80%	0.90%	1.00%	
TZ-1.2%	1.09%	1.20%	1.30%	

 Table S1 ICP-AES analysis results of TZ-x% samples.

 Table S2 BET surface areas of P25 and TZ-x% samples.

Samples	P25	TZ-0%	% TZ-0.3%	TZ-0.6%	TZ-0.9%	TZ-1.2%
BET surface area (m ³ /g)	49.5342	204.43	1 187.8518	192.9511	191.6541	185.6265
BJH desorption average pore width (nm)	13.8721	15.992	8 16.5429	16.3996	17.5757	16.6522
(a1)			a2)			
		NA PAR		E.		
E.		200.00	STAL	100mm		
(b1)		(1	b2)			
				-		
			3AP			
		<u>200nm</u>	181-1	00nm		

Fig. S1 SEM images of (a1, a2) potassium titanate NWs and (b1, b2) protonated titanate NWs.



Fig. S2 N₂ adsorption/desorption isotherms of P25 and TZ-x% samples.



Fig. S3 (a) Raman spectra and (b) partially magnified Raman spectra of TZ-0% and TZ-0.6%.



Fig. S4 Photocatalytic H_2 evolution on P25 and TZ-0.6% as a function of time under 300 W Xe lamp equipped with a band-pass filter of 380nm. The insert shows the apparent quantum yield of

P25 and TZ-0.6%. All samples were loaded with 1wt% Pt as co-catalyst before measurement. The light intensity was fixed at 4.61 mW cm⁻².



Fig. S5 (a) UV-vis DRS spectra of P25 and TZ-x% samples and (b) the plots of the transformed Kubelka–Munk function versus the energy of exciting light of TZ-0% (TiO₂ NWs).

In our work, bulk ZnO and QDs were specifically prepared and characterized thoroughly, of which the results are displayed below. As shown in Fig. S6, the main diffraction peaks of bulk ZnO and QDs agree well with the standard card of ZnO (JCPDS *No.* 21-1486). In the XRD patterns of ZnO QDs, the pronouncing broadening of all peaks indicates the extremely small size of as-prepared ZnO QDs, which is in consistent with the XRD results reported in the reference 1. And the morphology features of bulk ZnO and ZnO QDs were characterized by SEM and TEM, respectively (Fig. S7). As shown in Fig. S7a, ZnO QDs (marked out with yellow dashed circles) has a narrow size range, the particle size of which is about 2~3 nm. The as-prepared bulk ZnO has a regular hexagonal nanoflake structure, the thickness is about 100 nm, while the radial length is about 700~800 nm.



Fig. S6 XRD patterns of bulk ZnO and ZnO QDs.



Fig. S7 (a) TEM image of ZnO QDs and (b) SEM image of bulk ZnO.

For a more intuitive explanation of photocatalytic mechanism, the specific band gap energies, position of conduction and valence band potentials of TiO₂ NWs, bulk ZnO and QDs were acquired via the measurements of their UV-Vis DRS spectra (Fig. S5 and S8) and Mott-Schottky plots (Fig. S9), respectively. It can be clearly observed from Fig. S8a that both ZnO QDs and bulk ZnO exhibit intense absorption within ultraviolet light region, but negligible optical response in visible light region. And the plots of the transformed Kubelka–Munk function versus the energy of exciting light (Fig. S7b) confirm that the band gap energy of ZnO QDs and bulk ZnO are 3.65 and 3.29 eV, respectively. Similarly, the band gap energy of TiO₂ NWs is 3.30 eV as estimated by Fig. S5b.



Fig. S8 (a) UV–vis diffuse reflectance spectra and (b) the plots of the transformed Kubelka–Munk function versus the energy of exciting light of ZnO QDs and bulk ZnO.

Then, the Mott-Schottky plots were applied to analyze the flat-band potential of TiO₂ NWs, bulk ZnO and QDs (Fig. S9). Both of them display n-type semiconductor characteristics on account of the positive slope. In general, for n-type semiconductors, the flat-band potential is approximately at the conduction band potential. Therefore, the real values of conduction band and the calculated valence band potentials could be obtained according to band gap energies and flat-band potentials. As a result, the specific conduction band and valence band potential diagram could be drawn as shown in Fig. S9d.



Fig. S9 Mott-Schottky plots of (a) TiO_2 NWs, (b) bulk ZnO and (c) ZnO QDs. (d) schematic

drawing of conduction band and valence band potential of TiO₂ NWs, bulk ZnO and ZnO QDs.



Fig. S10 Spectrum range of light source used in experiments: (a) 300 W Xe lamp, (b) 300 W Xe lamp equipped with a band-pass filter of 380nm.

Reference

1. Y. Fu, X. Du, S. Kulinich, J. Qiu, W. Qin, R. Li, J. Sun and J. Liu, *J. Am. Chem. Soc.*, 2007, **129**, 16029-16033.