# **Supplementary Material for**

# Carbon dots-sensitized urchin-like Ti<sup>3+</sup> self-doped TiO<sub>2</sub> photocatalysts with enhanced photoredox ability for highly efficient removal of Cr<sup>6+</sup> and RhB

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### 2.1. Chemicals and materials

Titanium tetrachloride was purchased from Shanghai Macklin Biochemical Co., Ltd. (Shanghai, China). Acetone was obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Ethanol was purchased from Tianjin Guangfu Technology Development Co., Ltd. (Tianjin, China). K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> and 1, 5-diphenylcarbazide (DPC) were obtained from Aladdin Reagent Co., Ltd.

#### 2.2 Synthesis of TiO<sub>2-x</sub> and TiO<sub>2-x</sub>/CDs composites

#### 2.3 Characterization

The morphologies of the synthesized samples were characterized by transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) (JEM-2100, JEOL, Japan) at an accelerating voltage of 200 kV. X-ray diffraction (XRD) (D/max-2200VPC, Rigaku, Japan) was performed to determine the crystal structures of materials under Cu Ka radiation (40 kV, 30 mA) with a scanning range of 10–90° at a speed of 5°/min. Fourier transform infrared (FTIR) spectra were obtained using a Fourier-transform infrared spectrometer (iS10, Nicolet, USA) scanning from 4000-400 cm<sup>-1</sup> with a resolution of 4 cm<sup>-1</sup>. Surface element chemical compositions were analyzed by X-ray photoelectron spectroscopy (XPS) (PHI5700, Thermo Electron Corporation, USA) using non-monochromatic Al X-rays as the primary excitation. N<sub>2</sub> adsorption-desorption isotherms and pore-size distributions were studied using a nitrogen adsorption analyzer (ASAP2020, Micromeritics, USA). UV-vis diffuse reflectance spectra (UV-vis DRS) of samples were recorded using a double-beam ultraviolet-visible spectrophotometer (TU-1901, Beijing General Instrument Co., Ltd., China) using BaSO4 as a reference in the scan range of 200-800 nm. UV-vis spectra were acquired using a UV-vis spectrophotometer (TU-1900, Beijing General Instrument Co., Ltd., China). Photoluminescence (PL) spectra of solid powders were measured using a Cary Eclipse fluorescence spectrophotometer (Agilent Technologies, Australia) with an excitation wavelength of 380 nm. Electron paramagnetic resonance (EPR) and electron spin resonance (ESR) spectra were recorded at room temperature using a Bruker A200 EPR spectrometer with center field at 3398 G and X-band microwave frequency of 9.45 GHz. Electrochemical impedance spectra (EIS) and photocurrent transient response (I-t) were measured in a three-electrode system on an electrochemical workstation (CHI660E, Shanghai, China). Na<sub>2</sub>SO<sub>4</sub> aqueous solution (0.50 M, pH = 6.6) was used as the electrolyte. A Pt plate and Ag/AgCl electrode were used as the counter and reference electrode, respectively, while working electrodes were prepared by spreading a slurry of the as-prepared photocatalyst onto fluorine-doped tin oxide (FTO) glass.

#### 2.4 Evaluation of photocatalytic performance

To effectively assess the photocatalytic activity of the synthesized samples, the photocatalytic reduction of  $Cr^{6+}$  and degradation of RhB were performed under visible-light irradiation using a 300-W Xe lamp (Beijing Zhongjiao Jinyuan Technology Co., Ltd.) with a cut off filter ( $\lambda > 420$  nm). In a typical experiment, photocatalyst (50 mg) was placed in RhB (10 mg L<sup>-1</sup>) or Cr<sup>6+</sup> (40 mg L<sup>-1</sup>) aqueous solution (50 mL). For Cr<sup>6+</sup> photoreduction, the pH was controlled at about 3.0 using 0.2 M H<sub>2</sub>SO<sub>4</sub> solution. All experiments were conducted at room temperature under constant magnetic stirring. Prior to light irradiation, the reaction solution was stirred in the dark to reach adsorption–desorption equilibrium. During the photocatalytic process, 3.0-mL aliquots of the suspension were extracted at pre-set time intervals and filtered through 0.22-µm Millipore filter to remove the photocatalyst. Residual RhB in the solution was analyzed using a UV–vis spectrophotometer at the characteristic adsorption wavelength of 554 nm. The residual concentration of Cr<sup>6+</sup> was determined by the DPC method using a UV–vis spectrophotometer at 540 nm.



Fig. S1. The optical photograph of (a) pristine TiO<sub>2-x</sub>, (b) TiO<sub>2-x</sub>/CDs-1wt%, (c) TiO<sub>2-x</sub>/CDs-2wt%,
(d) TiO<sub>2-x</sub>/CDs-4wt% and (e) TiO<sub>2-x</sub>/CDs-6wt%.



Fig. S2. (a) XPS spectrum and (b)  $N_2$  adsorption-desorption isotherm of TiO<sub>2-x</sub>/CDs-4wt%. The insert indicated pore size distribution curve of TiO<sub>2-x</sub>/CDs-4wt%.



Fig. S3. Pseudo-first-order kinetic curves of the photocatalytic reduction of (a)  $Cr^{6+}$  and oxidation of (b) RhB with different photocatalysts.



Fig. S4. High-resolution XPS spectrum of Cr2p of  $TiO_{2-x}/CDs-4wt\%$  composite after photocatalytic reaction.



Fig. S5. The (a) TEM of  $TiO_{2-x}/CDs-4wt\%$  photocatalyst after the photocatalytic reaction.



Fig. S6. (a) XRD patterns and (b) FT-IR spectra of  $TiO_{2-x}/CDs-4wt\%$  photocatalyst before and after the photocatalytic reaction.



Fig. S7. ESR spectra of (a) DMPO  $\cdot O^{2-}$  in methanol solution and (b) DMPO  $\cdot OH$  in aqueous solution recorded with TiO<sub>2-x</sub>/CDs-4wt% composite.

Table S1 Comparation of the removal efficiency of  $Cr^{6+}$  photoreduction and the photooxidation of S-7

organic pollutants/dyes.

Catalysts	Dosage	Solutions/	Time	Removal	References
	(g/L)	Contentions	(min)	Rate (%)	
		(mg/L)			
(Fe <sup>0</sup> ) doped g-C <sub>3</sub> N <sub>4</sub> /MoS <sub>2</sub> (GCNFM)	0.3	RhB/20	120	98.2%	1
		Cr <sup>6+</sup> /20	120	91.4%	
BiOCl/Fe <sub>2</sub> O <sub>3</sub>	0.2	RhB /10	120	99.5%	2
	0.2	MB/10	30	100%	
	1	Cr <sup>6+</sup> /100	300	46.5%	
PANI/MgIn <sub>2</sub> S <sub>4</sub>	1	Cr <sup>6+</sup> /50	30	Nearly100%	3
	0.5	MB/10	50	97.0%	
CNNS/CDs/BiOBr	0.4	RhB/4.8	30	100%	4
		MB/3.2			
		MO/3.3			
CNNS/CDs/BiOBr	0.4	Cr <sup>6+</sup> /100			
ZnIn <sub>2</sub> S <sub>4</sub> /CQDs	0.2	RhB/20	30	95.0%	5
	0.3	MO/20	80	96.0%	
	0.5	Cr <sup>6+</sup> /80	40	93.0%	
β-Bi <sub>2</sub> O <sub>3</sub> @Bi <sub>2</sub> S <sub>3</sub>	0.5	RhB/10	90	99.7%	6
	0.5	Cr <sup>6+</sup> /20	60	98.7%	
MoS <sub>2</sub> /RP	0.5	RhB/10	80	97.5%	7
		Cr <sup>6+</sup> /40	80	72.7%	
$TiO_2$ -based nanorods-g- $C_3N_4(TNRs-C_3N_4)$		RhB/20	70	98.9%	8
		Cr <sup>6+</sup> /50		94.7%	
RP-MoS <sub>2</sub> /rGO	0.4	RhB/20	30	99.3%	9

		$Cr^{6+}/40$		98.0%	
	0.4	MB/20	30	96.9%	
		Cr <sup>6+</sup> /40		89.7%	
Al <sub>4</sub> SiC <sub>4</sub> /rGO	0.7	Cr <sup>6+</sup> /10	60	98.0%	10
	0.7	RhB/10	60	45.0%	
		Cr <sup>6+</sup> /10	60	96.0%	
		MB/10	120	52.0%	
		Cr <sup>6+</sup> /10	120	91.0%	
TiO <sub>2-x</sub> /CDs	1	RhB/10	30	99.7%	This work
	1	Cr <sup>6+</sup> /40	100	98.3%	

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