Electronic Supplementary Information (ESI)

Ti^{3+}-defected and V-doped TiO_2 quantum dots loaded on MCM-41

Lun Pan,[a] Songbo Wang,[a] Ji-Jun Zou,[a] Zhen-Feng Huang,[a] Li Wang,[a] and Xiangwen Zhang[a]*

Key Laboratory for Green Chemical Technology of Ministry of Education, School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, China

Fax: (+) 86-22-27892340; E-mail: jj_zou@tju.edu.cn (J.-J. Zou)

Table of contents

	Captions	Page
	Experimental section	**S3**
Table S1	The element molar ratio of VTM*x*.	**S4**
Table S2	The surface area, pore volume and pore diameter of samples.	**S4**
Table S3	The area data of integrated EPR spectra.	**S4**
Fig. S1	V2p XPS of samples: (a) VTM30 and VTM20; (b) VTM10; (c), VTM5.	**S5**
Fig. S2	UV-vis DRS of samples.	**S6**
Fig. S3	Pore distributions of the as-prepared samples.	**S7**
Fig. S4	Si2p XPS of samples.	**S8**
Fig. S5	Low-angle XRD patterns of the as-prepared samples.	**S9**
Fig. S6	PL spectra of samples.	**S10**
Fig. S7	Photocatalytic degradation of RhB (a) and isomerization of NBD (c); (b) and (d) are the fitted lines by a pseudo-first-order kinetics.	**S11**

Experimental Section

Materials:

$VO(SO_4)$, Rhodamine B (RhB), tetrabutyl titanate (TBT) and ethanol were all reagent grade and purchased from Tianjin Guangfu Fine Chemical Research Institute. Deionized water was used in all experiments. MCM-41 was purchased from Tianjin Chemist Ltd. All the reagents were used as received.

Sample preparation:

The materials studied in this work were prepared *via* the direct hydrolysis of tetrabutyl titanate (TBOT) on MCM-41. 0.426 g TBOT was first adsorbed on the surface and pore channel of MCM-41 (1 g) in ethanol (60 mL). Into the mixture, 10 mL $VO(SO_4)$ aqueous solution ($Ti/V_{mol}=x$) was slowly dropwised. After that, the resulting gel was aged at room temperature for 24 h, then filtered, dried at 60 °C for 12 h and ultimately calcined at 500 °C for 5 h at a heating rate of 2 °C min^{-1}. The Ti/V_{mol} ratios of 5, 10, 20 and 30 were applied in this work. TiO_2/MCM-41 and V-TiO_2($Ti/V_{mol}=x$)/MCM-41were named as TM and VTM*x*, respectively.

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. The irradiation area was *ca.* 20 cm^2. Reaction conditions: temperature, 25± 0.2 ºC; C_0(RhB)= 20 μmol L^{-1}, TiO_2: 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.).

The photocatalytic isomerization of norbornadiene (NBD) was evaluated in a closed cylindrical quartz vessel with inner irradiation. A 400 W high-pressure xenon lamp (Ruisente Company, Tianjin) was positioned inside the vessel and cooled by circulating water jacket. To conduct the reaction, a mixture containing 5 mL NBD, 500 mL p-xylene and 0.1 g photocatalysts was suspended in the vessel under magnetic stirring. A sample was withdrawn at regular intervals and analyzed using a HP-4890 gas chromatography equipped with a BP-1 capillary column (25 m × 0.33 mm × 0.05 μm) and a FID detector.

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 N_2 adsorption/desorption isotherms using Micromeritics TriStar 3000 at –196 ºC, all samples were outgassed under vacuum at 300 ºC for 4 h. HR-TEM observations were carried out by a Tecnai G^2 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-5000 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 $BaSO_4$ as the reflectance sample. Electron Paramagnetic Resonance (EPR) studies were performed with a Bruker EMX-6/1 spectrometer under the temperature of 110 K. Steady-state photoluminescence (PL) spectra were measured by a Horiba JobinYvon Fluorolog3-21 with the excitation light at 325 nm.

Table S1. The element molar ratio of VTM*x*.

VTM*x*	Si/Ti (EDS)	Ti/V (EDS)	Ti/V (XPS)
TM	10.52	-	-
VTM30	10.25	33.25	31.02
VTM20	10.99	22.33	25.31
VTM10	10.76	9.52	5.52
VTM5	10.03	5.35	2.21

Table S2. The surface area, pore volume and pore diameter of samples.

Samples	S_{BET}/m^2g^{-1}	Pore Volume/cm^3g^{-1}
MCM-41	731.29	0.78
TM	658.95	0.70
VTM30	650.82	0.72
VTM20	651.12	0.73
VTM10	645.97	0.72
VTM5	651.72	0.72

Table S3. The area data of integrated EPR spectra.

Samples	O_v data of integrated EPR spectra/g	Ti^{3+} data of integrated EPR spectra/g
TM	3427912	0
VTM30	9603843	108513
VTM20	12765603	1641223
VTM10	2790295	0
VTM5	2985621	0

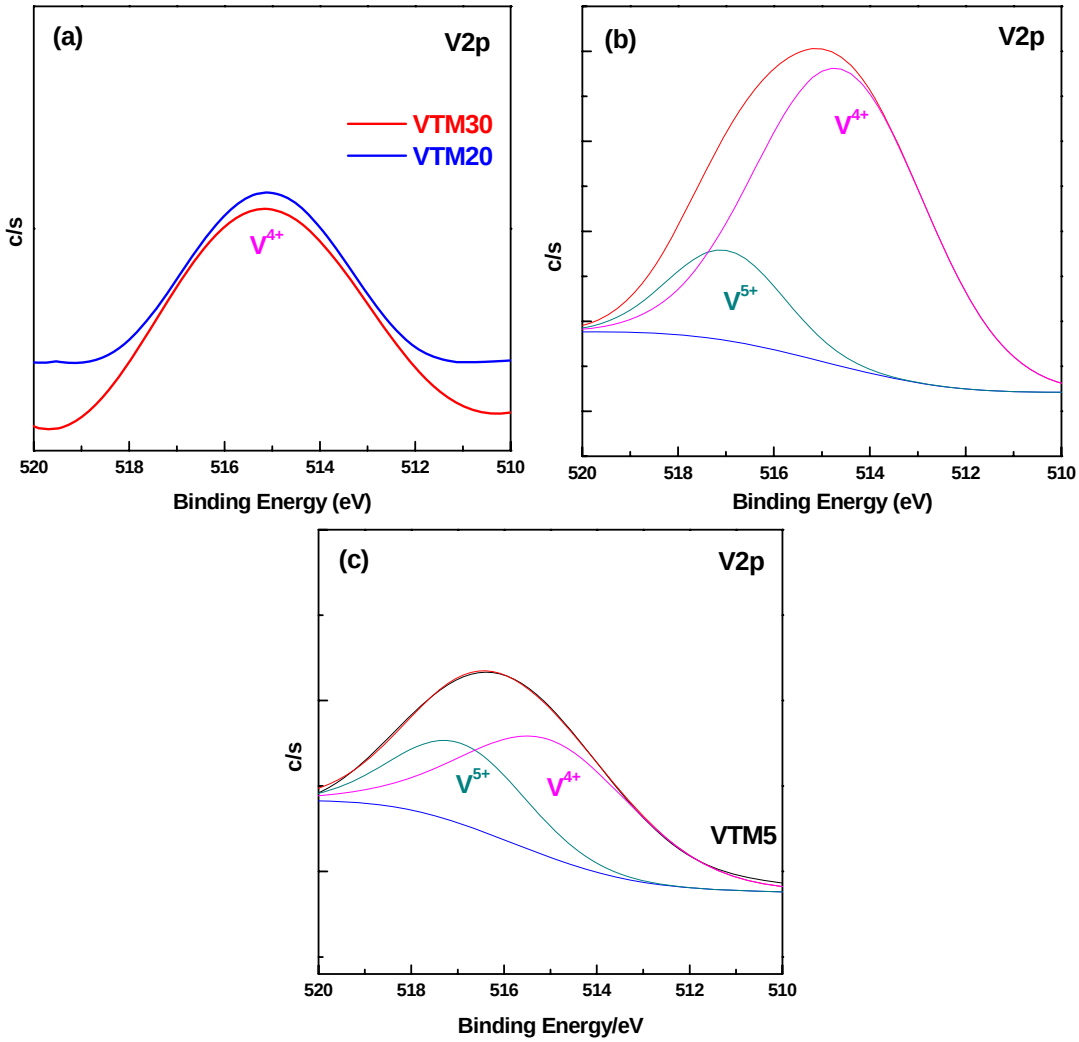

Fig. S1 V2p XPS of samples: (a) VTM30 and VTM20; (b) VTM10; (c), VTM5.

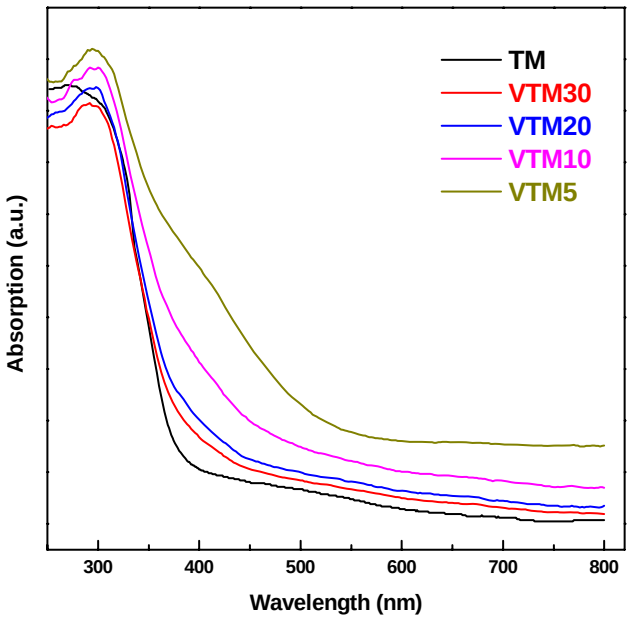

Fig. S2 UV-vis DRS of samples.

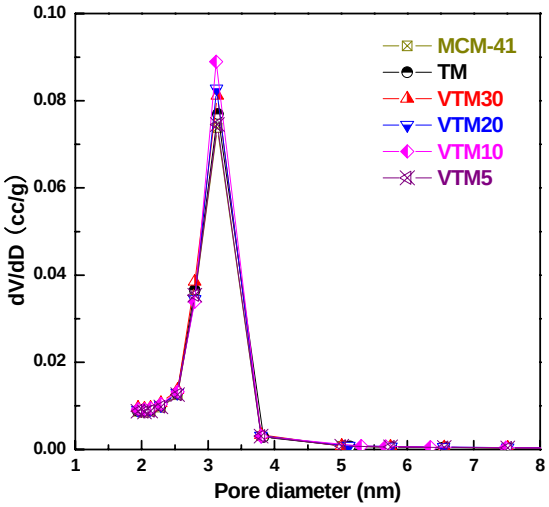

Fig. S3 Pore distributions of the as-prepared samples.

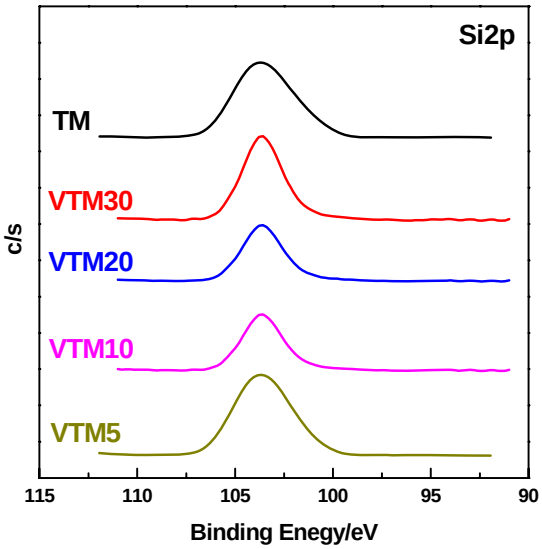

Fig. S4 Si2p XPS of samples.

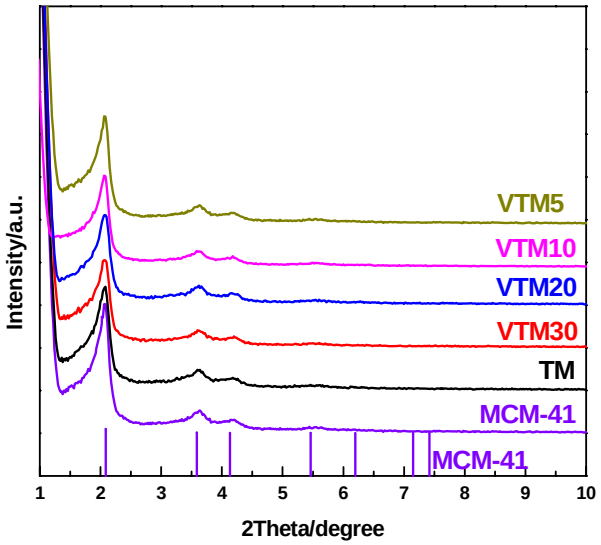

Fig. S5 Low-angle XRD patterns of the as-prepared samples.

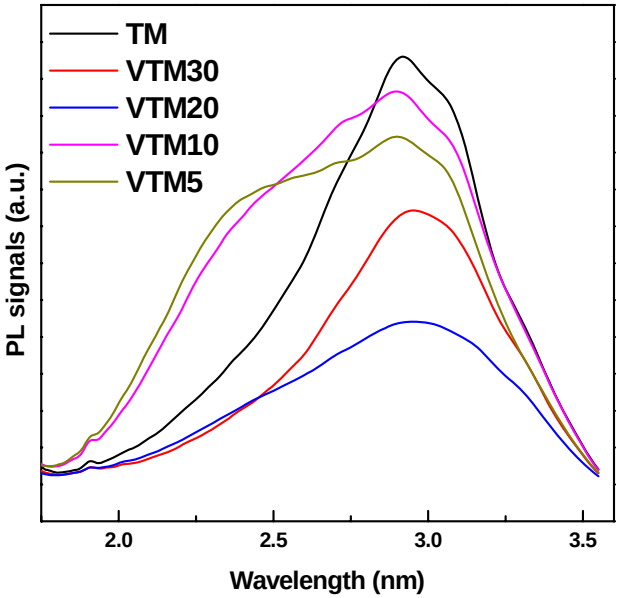

Fig. S6 PL spectra of samples.

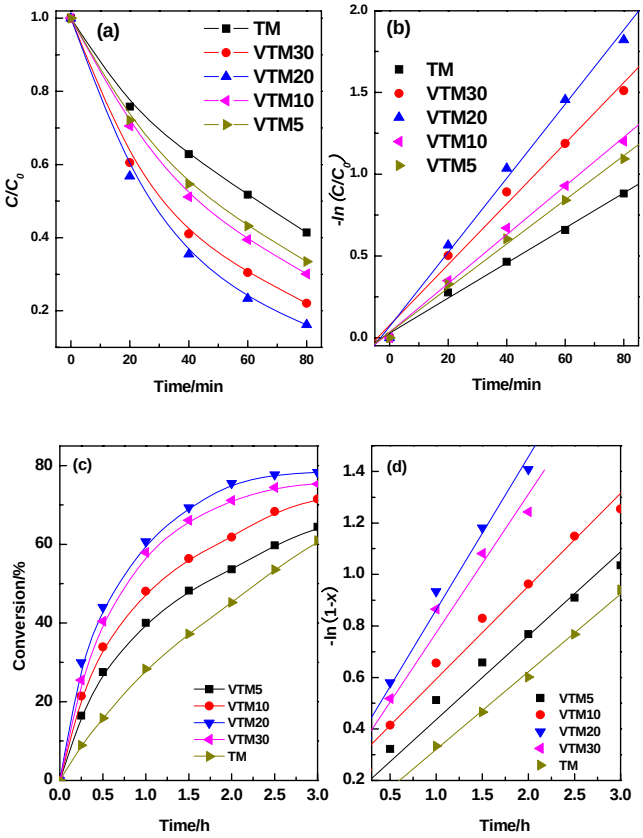

Fig. S7 Photocatalytic degradation of RhB (a) and isomerization of NBD (c); (b) and (d) are the fitted lines by a pseudo-first-order kinetics.