

Supporting Information

**Enhanced Photoreduction of Cr(VI) and Photooxidation of
NO over TiO_{2-x} Mesoporous Single Crystals**

*Yi Zhou^a, Wenzhang Fang^a, Yuanxin Deng^a, Lihan Pan^a, Bin Shen^a, Hexing Li^b, Yun Hu^c,
Haijun Chen^d, Mingyang Xing^{a,*} and Jinlong Zhang^{a,*}*

^a Key Laboratory for Advanced Materials and Institute of Fine Chemicals, School of Chemistry and Molecular Engineering, East China University of Science and Technology, 130 Meilong Road, Shanghai 200237, P.R. China

^b Education Ministry Key Lab of Resource Chemistry and Shanghai Key Laboratory of Rare Earth Functional Materials, Department of Chemistry, Shanghai Normal University, Shanghai 200234, PR China

^c School of Environment and Energy, South China University of Technology, Guangzhou 510006, P. R. China

^d Department of Electronics and Tianjin Key Laboratory of Photo-Electronic Thin Film Device and Technology, Nankai University, Tianjin, 300071, P. R. China

Corresponding Author

*Email: mingyangxing@ecust.edu.cn; jlzhang@ecust.edu.cn

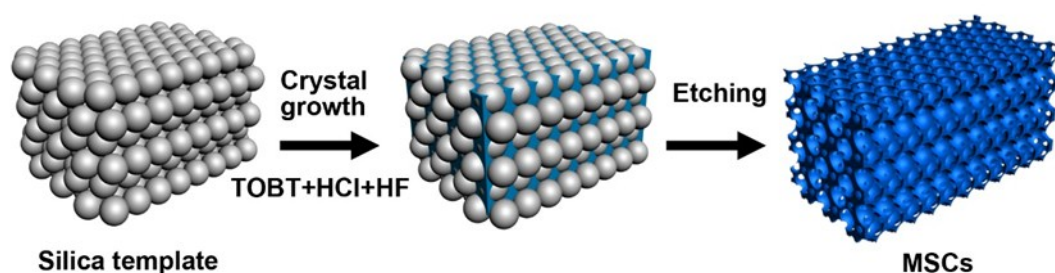
1. MATERIAL AND METHODS

1.1. Chemical Reagents.

All chemicals, including ethanol, tetraethoxysilane (TEOS), ammonium hydroxide (NH_4OH), TiCl_4 , titanium butoxide (TBOT) are purchased from Sigma-Aldrich and Adamas-beta®. Sodium hydroxide (NaOH), hydrochloric acid (HCl) and hydrofluoric acid (HF) are obtained from Sinopharm chemical reagent Co., China without further purification.

1.2. Preparation of catalysts

Scheme S1 illustrates the synthetic process of titanous doping mesoporous single crystal (Ti^{3+} -MSCs) by a simple hydrothermal treatment, with some modification on the method we previously reported.¹ Following the preparation of silica template, the seeds of TiO_2 crystals are insetted into the closely packed silica spheres. During the subsequent hydrothermal treatment, the crystal seeds grew gradually using tetrabutyl titanate as the titanium precursor, leading to the formation of defective inverse opal structure single crystal in the presence of HF. Then, silica templates are removed by etching process with sodium hydroxide solution. As a result, the Ti^{3+} -MSCs are successfully synthesized. Specific experimental steps are as follows.



Scheme S1. Schematic illustration of the growth pathways of Ti^{3+} -MSCs

Preparation of ~50 nm SiO_2 sphere. The silica spheres were synthesized by the Stöber method.² 28.8 mL water and 4.0 mL ammonium hydroxide solution were

mixed with 167.2 mL absolute ethanol in a beaker. The above mixture was stirred to blend well at room temperature. Simultaneously, 18.0 mL tetraethoxysilane (TEOS) was mixed up with 182.0 mL absolute ethanol at room temperature. The TEOS solution was stirred for few minutes. Then it was added into the above solution containing ammonia under vigorous stirring. The transparent and colorless precursor liquid turned pale blue solution in 4 h and it was kept stirring for 24 h. Finally, a suspension of silica colloids was obtained.

Preparation of TiO₂ seeded silica templates. Silica colloids were centrifuged at 12500 r.p.m for 1 h to obtain translucent solid. The solid was dried at 60 °C for 12 h and calcinated at 500 °C for 30 min to obtain the silica hard templates. Then the silica hard templates were seeded by using titanium tetrachloride (TiCl₄ 0.05 M) at 70 °C for 1 h. And the template was rinsed with 1 litre distilled water. The solids were calcinated at 500 °C under air (ramping time 240 min), which was denoted as Ti-SiO₂.

Preparation of TiO_{2-x} mesoporous single crystals (Ti³⁺-MSCs). TiO_{2-x} mesoporous single crystals were prepared by following a synthesis procedure with some modifications. 14 mL distilled water was mixed with 14 mL of HCl and stirred for 10 min at the room temperature. And 350 µL tetrabutyl titanate (TBOT) was injected into above mixture under magnetic stirring for another 10 min. Then 30 µL HF were added into the solution by the pipette and stirred for another 10 min. Afterwards, 0.5 g Ti-SiO₂ templates were added in the solution and then transferred to a teflon-inner-linear stainless steel autoclave. The autoclave was kept in an oven at 180 °C for 12 h. Then, the precipitate was rinsed with distilled water for several times and was etching with NaOH solution (2M) at 80 °C for 1 h. After the silica etching, the remaining titanium dioxide products were collected by centrifugation and washing with water and ethanol for several times. The sediments were dried at 60 °C for 12 h, which were denoted as Ti³⁺-MSCs.

Preparation of TiO_{2-x} mesoporous single crystals (MSCs). TiO₂ mesoporous single

crystals without Ti^{3+} doping were prepared by following procedure. 0.1 g MSCs were calcined at 500 °C for 1h in air using a heating rate of 2 °C/min. After being naturally cooled to room temperature, white TiO_2 mesoporous single crystals was obtained. The products were denoted as MSCs.

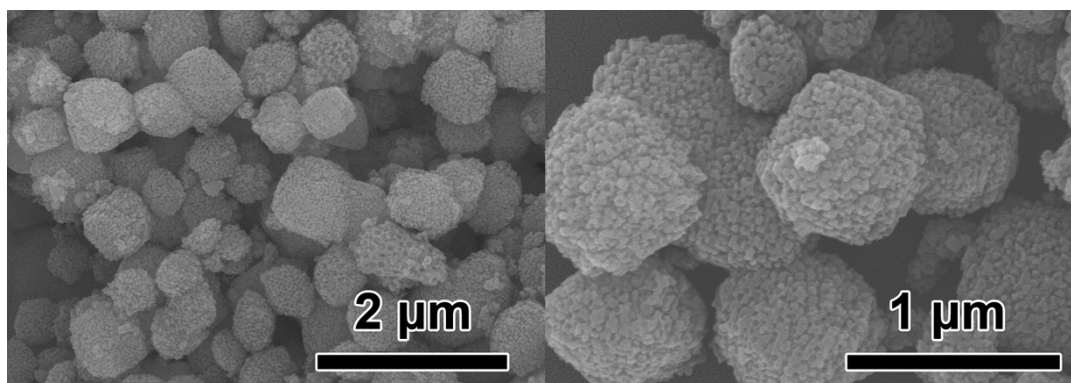


Figure S1. FESEM images of Ti^{3+} -MSCs

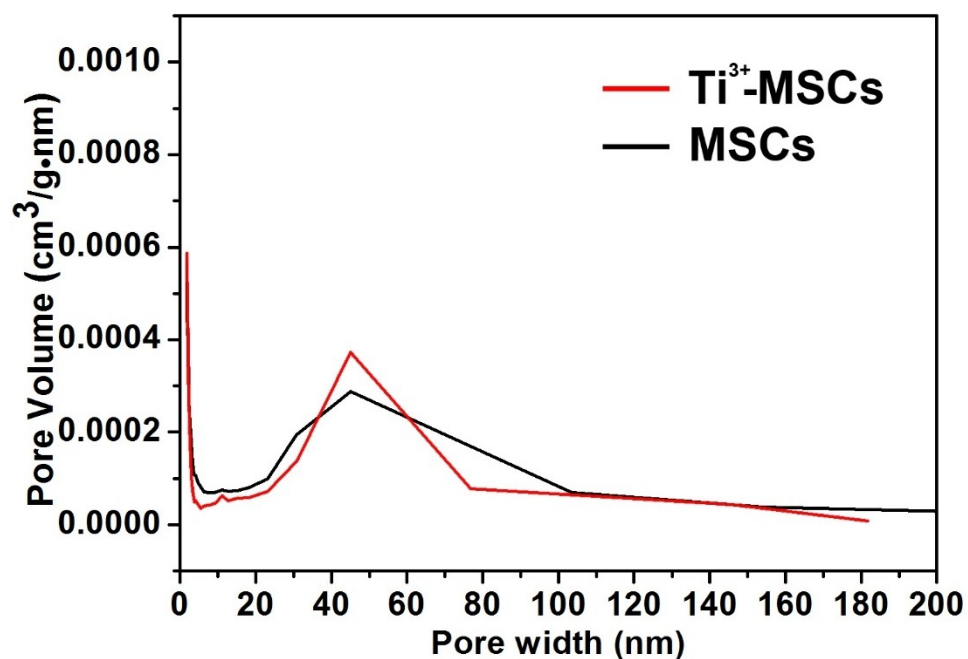


Figure S2. The pore size distribution curves of MSCs and Ti^{3+} -MSCs.

References:

- (1) Y. Zhou, Q. Yi, M. Xing, L. Shang, T. Zhang and J. Zhang, *Chem. Commun.*, 2016, **52**,

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(2) W. Stöber, A. Fink and E. Bohn, *J. Colloid Interface Sci.*, 1968, **26**, 62-69.