Electronic Supplementary Material (ESI) for CrystEngComm

Electronic Supplementary Information

Mesoporous titania microspheres composed of exposed active faceted nanosheets and their catalytic activities for solvent-free synthesis of azoxybenzenes

Liuliu Yang,[a] Guodong Shi,[a] Xuebin Ke,[b] Ruwei Shen[a] and Lixiong Zhang*[a]

[a] *State Key Laboratory of materials-oriented Chemical Engineering, College of Chemistry and Chemical Engineering, Nanjing University of Technology, Nanjing, China. Fax: +86 25 83172263; Tel: +86 25 83172265; E-mail: lixiongzhang@yahoo.com.*
[b] *School of Chemistry, Physics and Mechanism Engineering, Queensland University of Technology, Brisbane, Qld 4001, Australia.*

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Experimental Detail:

Synthesis. Tetrabutyl titanate (98% $Ti(OBu)_4$, Shanghai Lingfeng Chemical Reagent Co., Ltd.) and hexafluosilicic acid (35% H_2SiF_6, Sinopharm Chemical Reagent Co., Ltd.) were used in synthesis of the anatase mesoporous TiO_2 microsphere (MTM). In a typical experimental procedure, a H_2SiF_6 aqueous solution was added into TBOT under vigorous stirring. The molar composition was 1TBOT: $0.1H_2SiF_6$: $1.5H_2O$. After magnetic stirring for 30 min, the reaction mixture was transferred into a 75 mL Teflon-lined stainless steel autoclave and heated in a conventional oven at 180 °C for 48 h. Afterward, the reaction mixture was filtered, washed with anhydrous ethanol and deionized water, and dried at 80 °C overnight to obtain the MTM.

Characterization. The X-ray diffraction (XRD) patterns were collocted on a Bruker D8-Advance powder diffractometer with Ni-filtered Cu Kα radiation source at 40 kV and 40 mA. The samples were scanned in the 2θ range of 20-80° with a Braun position sensitive detector at a scan rate of 5 °/min and step size of 0.05 ° to determine the structure and crystallinity of the samples. The percentage of {001} facets in the TiO_2 nanosheets was calculated according to eq. 1.[s1] [s1 Y. B. Zhao, W. H. Ma, Y. Li, H. W. Ji, C. C. Chen, H. Y. Zhu and J. C. Zhao, *Angew. Chem. Int. Ed.,* 2012, **124**, 3242.]

$$\frac{a^2}{\frac{(b^2-a^2)}{\cos\theta}+a^2}\times 100\% \qquad (1)$$

Where, a is the side length of {001} facet, b the bottom edge of {101} facet and θ the value for the angle between the {101} and {001} facets.

The morphology of samples was observed on a Field Emission scanning electron microscopy (FESEM, HITACHI S-4800). The high-resolution transmission electron microscopy (HRTEM) observation was performed on a JEOL JEM-2010UHR instrument at an acceleration voltage of 200KV.

X-ray photoelectron spectroscopy (XPS) measurements were conducted on a VG ESCALAB 210 electron spectrometer with an Al Kα (1486.6 eV) X-ray source and a charge neutralizer; all the binding energies were calibrated to C 1s peak at 284.6 eV.

The nitrogen adsorption-desorption isotherms were measured on a Micromeritics ASAP 2020 instrument at the liquid nitrogen temperature. The pore size distribution was calculated using the

BJH model from desorption data.

Aniline oxidation reaction to azoxybenzene. The reaction was carried out in a 50 mL tube reactor containg 0.025g of MTM, 1.86 g of aniline and 3.5 mL H_2O_2 (30%). The reactor was heated in a jacket at 60 °C with magnetical stirring. After reaction, the product was extracted with trichloromethane. The organic phases were combined, dried over Na_2SO_4. The quantities of organic phases were analysed by a gas chromatograph (SHIMADZU, GC-2014) equipped with a flame ionization detector (FID), an AOC-20i autoinjector, and a HP-INNOWAX column (30 m × 0.32 mm × 0.25 μm). The crude product was purified by column chromatography on silica gel (100-200 mesh) to give pure product. The obtained product was analysed by ^{1}H NMR spectroscopy (AV400D).

XRD patterns of the MTM:

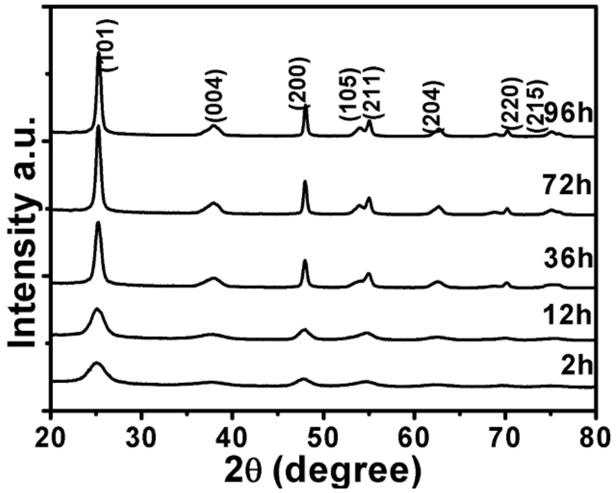

Figure S1. XRD patterns of the TiO_2 microspheres obtained after synthesis for 2, 12, 36, 72 and 96 h.

SEM and TEM images of the MTM:

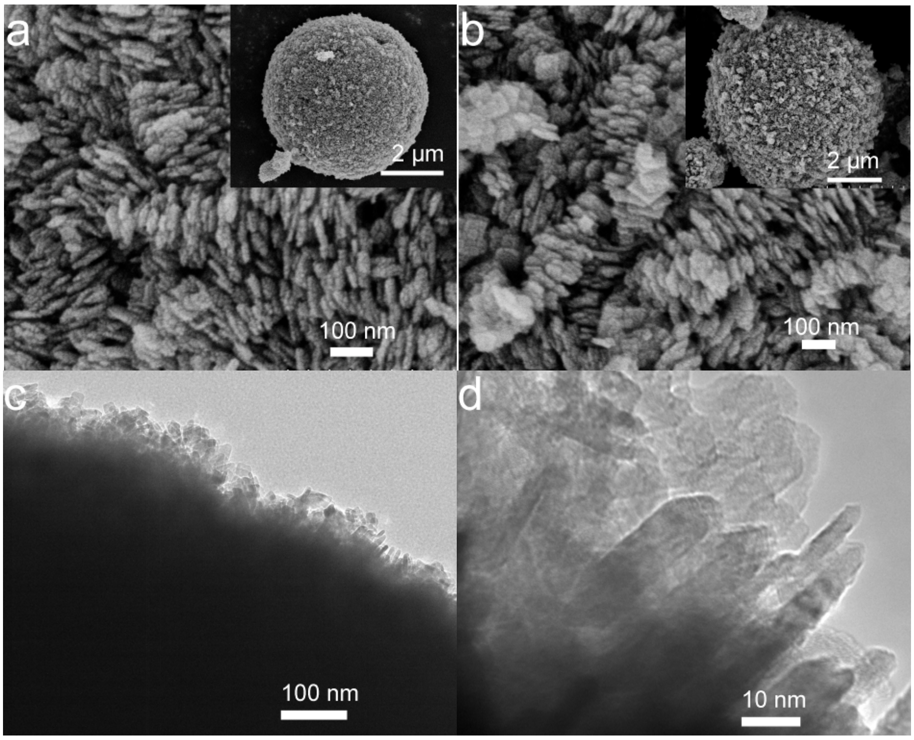

Figure S2. a, b shows the SEM images of the MTM[a], MTM[b] synthesized at 72 and 96 h, c and d low-resolution TEM images of the MTM synthesized at 48 h.

XPS spectra of the MTM:

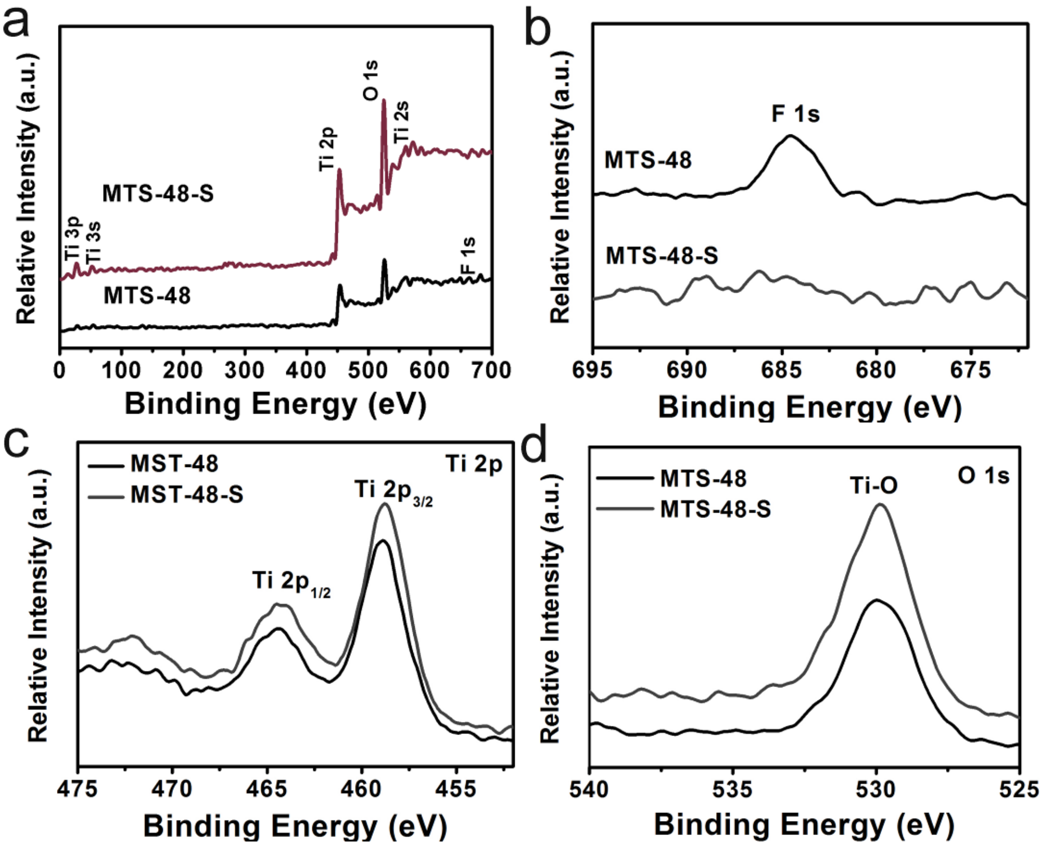

Figure S3. XPS spectra of the MTM. (a) survey XPS spectrum and (b, c and d) high resolution spectra of the F 1s, Ti 2p, O 1s regions. Sharp photoelectron peaks appear at binding energies of 458 (Ti 2p) and 531 eV (O 1s). The F 1s peak at 684.5 eV is observed due to surface fluorination. High-resolution XPS was used to detect the surface F 1s, Ti 2p, and O 1s core levels. No signals for F^- in the lattice (BE =688.5 eV) is found after the MTM was calcined at 600 °C, implying that all F^- is physically adsorbed on the surface of the MTM, and does not substitute of oxygen in TiO_2 lattice. The binding energy of Ti 2p3/2 equals to 458.7 eV and the binding energy of Ti 2p1/2 equals to 464.4 eV, which are identical to the reported literature.[1] These results confirm that titanium exists as Ti (IV) state. The O 1s peak at 530.2 eV indicates oxygen in Ti–O–Ti. No Si peak (101.8 eV) is observed, suggesting that Si in H_2SiF_6 does not enter into or adsorb on the MTM.

1 (a) J. C. Yu, J. G. Yu, W. K. Ho, Z. T. Jiang and L. Z. Zhang, *Chem. Mater.,* 2002, **14**, 3808; (b) D. Li, H. Haneda, S. Hishita and N. Ohashi, *Chem. Mater.,* 2005, **17**, 2596.

Table S1. Oxidation of aniline to azoxybenzene catalyzed by MTM in different solvents

Entry	Solvent	Reaction time	Conversion (%)	Yeild (%)
1	no solvent	0.75 h	97.8	95.6
2	H_2O	1 h	98	93
3	*t*-BuOH	2 h	90.3	89.2
(Conditions: MTM =25 mg; arylamines = 0.02 mol; arylamines/H_2O_2 molar ratio=1: 1.7; temperature=333 K)				