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Mesoporous titania microspheres composed of exposed active faceted nanosheets and their catalytic activities for solvent-free synthesis of azoxybenzenes<sup>†</sup>

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Mesoporous titania microspheres composed of nanosheets with exposed active facets were prepared by hydrothermal synthesis in the presence of hexafluorosilicic acid. They exhibited superior catalytic activity in the solvent-free synthesis of azoxybenzene by oxidation of aniline and could be used for 7 cycles with slight loss of activity.

Titanium dioxide (TiO<sub>2</sub>) has been intensively investigated in the last couple of decades due to its relatively low cost and wide application in many areas such as photocatalysis, energy conversion and storage, and as sensors, catalysts, and catalyst supports.<sup>1</sup> It is generally synthesized as nanoparticles and nano/microspheres. TiO2 with other morphologies, such as disks,<sup>2</sup> rods,<sup>3</sup> wires<sup>4</sup> and tubes,<sup>5</sup> is also produced, as these morphologies can endow unique properties to TiO<sub>2</sub>. Recently, TiO2 with highly exposed crystal facets and these exposed facet crystal-constructed hierarchical structures has attracted much attention. Various techniques have been developed to prepare these kinds of TiO<sub>2</sub>, mainly by hydrothermal or solvothermal treatment of titanium precursor solutions synthesized in the presence of a fluoric ion<sup>6,7</sup> and capping reagents such as ammonia,8 H2O2,9 alcohols,10 etc., or by hydrothermal treatment of titania powder, nanowires or nanotubes in acidic/basic solutions.<sup>11</sup> Further results demonstrate that exposure of {001}, {110}, {010}, {111}, {102}, {106} and {103} facets can enhance the reactivity of TiO2, especially in photocatalysis and dyesensitive solar cells (DSSCs).12 Similarly, TiO2 with exposed facet crystal-constructed V-shaped channels,13 nanosheet or nanorod assembly<sup>14,15</sup> and core-shell,<sup>16</sup> sphere-in-sphere,<sup>17</sup>

and dandelion-like<sup>18</sup> hierarchical structures exhibits outstanding performance in DSSCs, lithium ion batteries, and photocatalysis.

As a versatile catalytic material, TiO<sub>2</sub> is mostly used as a photocatalyst and a support of both metal and oxide catalysts in heterogeneous catalysis. A few studies used nano-sized TiO<sub>2</sub> as heterogeneous catalysts mainly for organic synthesis, such as Michael addition of indoles to  $\alpha,\beta$ -unsaturated ketones,<sup>19</sup> Mannich synthesis of  $\beta$ -aminocarbonyls,<sup>20</sup> synthesis of substituted 2-oxodihydropyrroles and bis(indolyl)methanes,<sup>21</sup> etc. It is interesting that there are limited studies on using TiO<sub>2</sub> as a catalyst for catalytic oxidation reactions, although titanium containing materials, such as titanium-substituted molecular sieves,<sup>22</sup> are good catalysts for this kind of reaction. Oxidations of amines with H<sub>2</sub>O<sub>2</sub> to oximes and azoxybenzenes are the main two reactions reported so far using the nano-sized TiO<sub>2</sub> as the catalysts in which solvents such as acetone, CH<sub>3</sub>CN, CH<sub>3</sub>OH, etc., are used to achieve good yields.<sup>23,24</sup> It would be of both academic and industrial interest to examine the catalytic oxidation activity of these TiO<sub>2</sub> with highly exposed crystal facets or with hierarchical structures.

Aromatic azo compounds are high-value intermediates for production of dyes, pigments, food additives, and drugs.<sup>25</sup> Reduction of nitroaromatics and oxidation of anilines are the main routes to prepare these compounds. Oxidation of anilines can be carried out with oxygen at high pressures or  $H_2O_2$  under mild conditions. From a practical viewpoint, a mild reaction is more favorable. As mentioned above, nanosized TiO<sub>2</sub> exhibits excellent catalytic activity in oxidation of anilines to azoxybenzenes; however, a solvent has to be used. Synthesis of azoxybenzene by oxidation of aniline with  $H_2O_2$ without a solvent provides a green and mild route and needs to be developed.

Herein, we reported the preparation of mesoporous  $TiO_2$  microspheres (MTMs) with particle size of 2–15 µm composed of  $TiO_2$  nanosheets (side length of 10–20 nm, thickness of 4–6 nm) with exposed {101} facets (56%) by a simple

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hydrothermal synthesis. The microspheres exhibited superior catalytic activities in solvent-free oxidation of arylamines to azoxybenzenes rather than azobenzenes. To the best of our knowledge, no such application of exposed faceted crystal-constructed hierarchical  $TiO_2$  structures in heterogeneous catalysis has been reported.

The MTMs were hydrothermally synthesized at 180 °C for 48 h using a synthesis solution with a molar ratio of 1TBOT: 0.1H<sub>2</sub>SiF<sub>6</sub>: 1.5H<sub>2</sub>O prepared by adding a H<sub>2</sub>SiF<sub>6</sub> aqueous solution into TBOT under vigorous stirring (ESI<sup>+</sup>). Fig. 1a shows XRD patterns of the as-synthesized sample, indicating formation of pure anatase TiO<sub>2</sub> (tetragonal, I41/amd, JCPDS no. 21-1272). The diffraction peaks at  $2\theta$  of 25.3°, 37.8°, and  $48.5^{\circ}$  can be observed obviously, corresponding to (101), (004) and (200) faces of TiO<sub>2</sub>. The peak intensity at  $2\theta = 25.3^{\circ}$ is much stronger than those at 37.8° and 48.5°, implying the preferred growth along the (101) face.<sup>26</sup> The primary crystallite size calculated from the (101) peak of the XRD pattern using the Scherrer equation is about 14.7 nm. XRD patterns of the samples synthesized at 2-96 h (Fig. S1, ESI<sup>+</sup>) indicate that the intensity of the (101) face becomes stronger with increasing synthesis time and reaches the strongest at 48 h, indicating the highest crystallinity of the sample after synthesis for 48 h.

Fig. 1b shows an SEM picture of the MTMs. It exhibits spherical morphology with particle size of  $2-12 \ \mu m$  (inset in Fig. 1b). Close observation reveals that the microsphere is composed of compactly packed nanocrystals.

To elucidate the fine structure of nano-sized sheets, we examined the sample by TEM after grinding and ultrasound dispersing the sample. Analysis of a representative high-resolution TEM image of a single nanosheet (Fig. 1c)<sup>27</sup> reveals that these nanosheets are well-faceted nanocrystals with side length of 10–20 nm and thickness of *ca.* 4.6 nm.

Fig. 1 XRD pattern (a), SEM image (b), and TEM image (c) of the  $TiO_2$  microspheres composed of nanosheets, recorded from an anatase single nanocrystal with the corresponding fast-Fourier transform (FFT) pattern in the inset, and the nitrogen adsorption-desorption isotherm and the Barrett-Joyner-Halenda (BJH) pore size distribution plot of the MTM (d).

5 nm

ŝ

Absorbed

150

100

Volume A

0+ 0.0

0.2

0.4 0.6

Relative Pressure (P/P<sub>0</sub>)

0.8

The (-101), (101) and (002) atomic planes with lattice spacings of 0.35, 0.35 and 0.48 nm indicate that the top/bottom surface exposed by truncation is bound by a {001} facet.<sup>28,29</sup> The inset of Fig. 1c shows that the angle labeled in the corresponding fast-Fourier transform (FFT) image is  $68.3 \pm 0.3^{\circ}$ , which is identical to the theoretical value for the angle between the {101} and {001} facets.<sup>28</sup> These facets prove that the anatase single crystals exhibit flat facets of {101} and {001}. On the basis of the above structural information, the percentage of {001} facets in the TiO<sub>2</sub> nanosheets shown in Fig. 1c is estimated to be 44% according to eqn (1).<sup>30</sup> Correspondingly, the percentage of {101} facets is 56%.

$$\frac{a^2}{\left(b^2 - a^2\right)} \times 100\% \tag{1}$$

where, *a* is the side length of the {001} facet, *b* the bottom edge of the {101} facet and  $\theta$  the value for the angle between the {101} and {001} facets.

The nitrogen adsorption-desorption isotherm was measured to determine the specific area and pore volume of the MTM. The corresponding results are presented in Fig. 1d. The pore size distribution, derived from desorption data and calculated using the BJH model, indicated that the average pore of such a sample is around 10.2 nm. The Brunauer-Emmett-Teller (BET) specific surface area of the sample calculated from N<sub>2</sub> adsorption is 117 m<sup>2</sup> g<sup>-1</sup>, which is larger than that of conventionally prepared TiO<sub>2</sub> microspheres.<sup>13,15</sup> The much higher BET surface area of the MTM may provide the possibility of contacting the active center more effectively.

To investigate the elemental compositions and the binding states of the MTM, the sample was analyzed by XPS (Fig. S3, ESI<sup>†</sup>). Sharp photoelectron peaks appear at binding energies of 458 (Ti 2p) and 531 eV (O 1s). An 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) are found after the MTM was calcined at 600 °C, implying that all F<sup>-</sup> are physically adsorbed on the surface of the MTM and do not substitute oxygen in the TiO<sub>2</sub> lattice. The binding energy of Ti 2p3/2 is equal to 458.7 eV and the binding energy of Ti 2p1/2 is equal to 464.4 eV, which are identical to those in the reported literature.<sup>31</sup> These results confirm that titanium exists as a 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<sub>2</sub>SiF<sub>6</sub> does not enter or is not adsorbed on the MTM.

The MTM shows quite high catalytic activity in the catalytic oxidation of arylamines with  $H_2O_2$  to azoxybenzenes. In particular, no solvent is used in these reaction systems, unlike the reported system for conversion of aniline using  $H_2O_2$  to azoxybenzene, in which acetone,  $CH_3CN$  and  $CH_3OH$  are usually used as solvents,<sup>23,24</sup> implying a green catalytic synthesis route. Table 1 lists the reaction results of oxidation of some arylamines with  $H_2O_2$ . It is observed that aniline

а

ntensity(a.u)



40 50 60 2θ / degree

Table 1 Oxidation of arylamines to azoxybenzenes in the presence of a  $TiO_2/H_2O_2$  system<sup>*a*</sup>

Entry	Arylamine	Time (h)	Conversion (%)	Yield (%)
1		0.75	97.8	95.6
2	CH3	2	98.7	94.5
3	H <sub>2</sub> N CH <sub>3</sub>	4.5	91.0	86.5
4	H3CO-NH2	4.5	85.4	81.3
5		6.0	80.8	75

 $^a$  Catalyst = 25 mg; arylamines = 0.02 mol; arylamines/H2O2 molar ratio = 1 : 1.7; temperature = 333 K.

results in a good yield of azoxybenzene within a shorter reaction time when compared with substituted anilines, while toluidines are more reactive than chloro or methoxy substituted anilines. This may be attributed to the smaller size of toluidine atoms, which would allow the reactant molecules to gain closer proximity to the active centers of the titanium peroxo species compared to the larger chlorine atoms or methoxy groups. However, the differences in the reactivity of various substituted anilines are dependent on the synergetic effect of the molecular parameters such as the mesomeric (+M), the inductive (+I/-I) and the steric effect of the substituents.<sup>24</sup> Furthermore, it should be noted that no obvious difference was observed on the conversion of aniline and the yield of azoxybenzene when the reaction was conducted with or without sunlight irradiation, clearly suggesting that the MTM does not act as a photocatalyst in the present reaction.

To compare the catalytic property of the  $TiO_2$  microspheres with  $TiO_2$  powder P25 (Degussa), we conducted timedependent kinetics of aniline with  $H_2O_2$  using the MTM and P25 as the catalysts. A blank test without a catalyst was also conducted. The reaction results shown in Fig. 2 clearly demonstrate that this reaction proceeds at a quite slow reaction rate with low conversion of aniline without a catalyst. Increasing the reaction time directly increases the aniline conversion using the MTM and P25. The reaction rate of the MTM is significantly greater than that of P25. The yield of azoxybenzene increases smoothly with the reaction time for 30 min to 45 min. After 45 min, aniline conversion reaches a maximum value of 97.8% and the yield of azoxybenzene is up to 95.6%, which are much higher than those by P25.

Fig. 3 shows that after 6 recycling uses, the activity of the MTM remains above 93.3% with selectivity of azoxybenzene being 95.6%, which indicates that the exposed crystal facets of  $TiO_2$  microspheres have high catalytic stability in the oxidation of arylamine. A slight loss in the catalytic activity was observed in the 7th recycling use (conversion: 91.2%, selectivity: 94.3%).

To identify the contributions of the  $\{101\}$  facets and the hierarchical structure of the MTM on aniline oxidation, diverse samples with varying percentages of exposed  $\{101\}$ 



30

t (min)

40

50

**Fig. 2** Effect of reaction time on aniline conversion and azoxybenzene yield with MTM and P25 and without a catalyst (catalyst = 25 mg; aniline = 1.86 g; aniline/H<sub>2</sub>O<sub>2</sub> molar ratio = 1:1.7; temperature = 333 K).

20

10

0

Conversion (%)



Fig. 3 Cycling curve for aniline oxidation with the MTM as the catalyst.

facets were prepared by changing the synthesis time, and the results of aniline oxidation to azoxybenzene on these samples are listed in Table 2 (entries 1 and 2). By extending the synthesis time to 72 and 96 h at 180 °C, the percentages of {101} facets of the MTM are 47% to 37%, respectively. This is similar to the result reported by Yang, *et al.*<sup>6a</sup> The conversion of

Table 2         Oxidation of aniline to azoxybenzene using different catalysts									
Entry	Catalyst	Conversion (%)	Yield (%)	P(101) (%)	Hierarchical structure				
1	MTM <sup>a</sup>	94.5	90.9	47	Yes				
2	$MTM^{b}$	93.6	89.6	37	Yes				
3	MTM <sup>c</sup>	91.4	89.3	56	No				
4	ATNM	22.6	21.0	94	Yes				
5	ATNHS	61.8	58.4	10	Yes				
6	NS	87.3	85.4	20	No				

 $^a$  The MTM sample synthesized at 180 °C for 72 h.  $^b$  The MTM sample synthesized at 180 °C for 96 h.  $^c$  The MTM sample synthesized at 180 °C for 48 h and ground into mostly nanosheets. The reaction time is 0.75 h.

aniline and the yield of azoxybenzene are slightly decreased, suggesting possibly more active sites on the MTM with a higher percentage of {101} facets. To examine the effect of the hierarchical structure of the MTM on aniline oxidation, we ground the MTM sample to form mostly nanosheets. Even with an increase in the percentage of  $\{101\}$  facets (56%), the conversion still decreases slightly (entry 3), possibly due to a lack of hierarchical structure. To further elucidate the effect, anatase TiO<sub>2</sub> nanosheet-based microspheres (ATNM)<sup>15</sup> and anatase TiO<sub>2</sub> nanoparticle-based hierarchical spheres (ATNHS),<sup>29</sup> as well as titania nanosheets  $(NS)^7$  were also prepared, with  $\{101\}$ facet percentages of 94%, 10%, and 20%, respectively. The results indicated that the samples with hierarchical structures and both very high or low {101} facet percentages (entries 4 and 5) exhibit quite low conversions and yields, while the sample with a very low {101} facet percentage shows slightly low conversion and yield (entry 6), compared with those for the MTM. These results suggested that both the {101} facet percentage and the hierarchical structure of the MTM play significant roles in the oxidation of aniline. To obtain much higher catalytic activity,  $TiO_2$  catalysts with intermediate {101} facet percentages as well as hierarchical structures have to be used (entries 1 and 2 in Table 2).

In conclusion, we developed a new approach to synthesize anatase mesoporous  $TiO_2$  microspheres composed of nanosheets with exposed {101} facets (56%) by a simple hydrothermal synthesis using  $H_2SiF_6$ . The microsphere shows high conversion and yield in the oxidation of arylamines to azoxybenzenes with  $H_2O_2$  without a solvent under mild conditions. Both the appropriate proportion of {101} and {001} facets and the hierarchical structure of the MTM contribute to the high reaction activity. The MTM provides an environment-friendly and easily recyclable heterogeneous catalytic route for the preparation of azoxybenzenes.

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