Facile preparation of micro–mesoporous carbon-doped TiO_2 photocatalysts with anatase crystalline walls under template-free condition†

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A new low-temperature procedure has been used for preparing micro–mesoporous carbon-doped TiO_2 photocatalysts, with anatase pore wall and substitutional carbon occupying oxygen sites, which exhibit outstanding photocatalytic activity under visible light irradiation.

Mesoporous TiO_2 is attracting increasing attentions for the application as highly efficient photocatalysts and energy-converters due to high specific surface area.[1] However, more widespread applications of mesoporous TiO_2 as photocatalysts are encumbered by its wide band gap (3.2 eV for anatase). Shifting the optical response region of TiO_2 from the UV to visible light range means that more solar irradiation and even indoor illumination could be used as an effective excitation source. Although doping with nonmetals has been widely reported as a promising route for synthesizing TiO_2 with efficient visible light (Vis) photocatalytic activities,[2] only few reports on mesoporous TiO_2 doped with nonmetals have been presented to date.[3] Doping with nonmetals is generally performed at high temperature,[2a,e,f] while high-temperature treatment frequently results in partial collapse of the porous structure,[1a] which decreases the specific surface area of catalysts. Therefore, it will be very attractive for preparing TiO_2 Vis-photocatalysts with high specific surface areas to simultaneously realize doping with nonmetals, crystallization and formation of porous structures at low temperature.

On the other hand, carbon-doping is a promising approach for inducing effective Vis-absorption.[2a,e,f,4] The Vis-response features of C-doped TiO_2 strongly depends on the form of C existing in the TiO_2 lattice.[4] Carbon occupying O sites (C_{S-O}) is more favorable for the Vis-photocatalytic activity of C-doped TiO_2.[2a,4] However, C_{S-O} has been seldom observed in C-doped TiO_2 prepared by most of the reported synthesis routes.[2f–h,3c] Though the method presented by Khan *et al.* resulted in C_{S-O},[2e] the resultant rutile phase has a lower photocatalytic activity than the anatase phase.[5] It seems reasonable that using TiC as the starting material should potentially result in C_{S-O} in the TiO_2 lattice. In fact, Hashimoto and co-workers[6] synthesized C-doped anatase TiO_2 powders with C_{S-O} by a two-step oxidative annealing of TiC at high temperature. However, the low doping level of 0.32 atom% results in lower Vis-photocatalytic activity of C-doped TiO_2 than N-doped TiO_2 in their studies.[6]

Here we report a novel and simple method resulting in micro–mesoporous C-doped TiO_2 (MC-TiO_2) powders with anatase crystalline walls and high specific surface area. C_{S-O} was clearly detected by X-ray photoelectron spectroscopy (XPS). Moreover, the doping level of C_{S-O} is as high as 6.3 atom%. As a result, MC-TiO_2 powders exhibit outstanding Vis-absorbance and high Vis-photocatalytic activities for degradation of methylene blue (MB). This new method was carried out at a temperature as low as 60 °C and without special equipment requirements. It is thus an attractive route for industrial applications due to significantly reduced production cost and the ease of scaling up.

Nanocrystalline TiC powders (Hefei Kiln Nanometer Technology Development Co., Ltd, China), with an average grain size of 26 nm (Fig. S1, ESI†), were used as starting materials without further purification. In a typical synthesis, the treatment solution was prepared by mixing a 50 mL aqueous solution of 7 M nitric acid and 100 mL ethanol. Then, 2.5 g TiC powder was added into the treatment solution. After ultrasonically dispersing for 10 min, the suspension was kept at 60 °C under stirring for 12 h. The final gray powder was obtained after washing with deionized water and drying at 120 °C for 48 h.

Fig. 1 shows the nitrogen adsorption–desorption isotherm of MC-TiO_2. The adsorption hysteresis of the isotherm is close to the Type H4 according to the IUPAC classification.[7] This indicates the presence of slit-like pores.[7] The pore size distribution curve (inset of Fig. 1), calculated from the desorption branch of the isotherm by density functional theory (DFT) method based on a slit-pore model, shows a broad distribution from micropores to mesopores. This reveals the presence of a micro–mesoporous structure. The cumulative surface area curve (Fig. S2, ESI†) shows that large mesopores with pore size larger than 10 nm hardly contribute to the surface area. Such large mesopores may be ascribed to interparticle voids. The MC-TiO_2 powders have a high Brunauer–Emmett–Teller (BET) specific surface area of 238.3 $m^2\ g^{-1}$.

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† Electronic supplementary information (ESI) available: Wide-angle XRD pattern of TiC nanopowders and MC-TiO_2, A representative TEM overview image of MC-TiO_2 particles, XPS survey spectrum for MC-TiO_2, Ti 2p XPS spectrum for TiC nanopowders, the preparation procedure of R-TiO_2 and results on the reproducibility. See DOI: 10.1039/b800596f

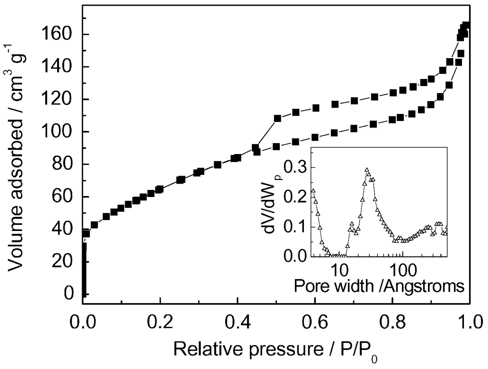

Fig. 1 Nitrogen adsorption–desorption isotherm and pore size distribution of MC-TiO_2.

The wide-angle X-ray diffraction (XRD) pattern of MC-TiO_2 is shown in Fig. S3, ESI.† All the diffraction peaks can be assigned to anatase TiO_2 (PDF No. 84-1286). No signals from the other allotropes of titania (rutile and brookite) and TiC are detected. This suggests that MC-TiO_2 has anatase crystalline walls. The average grain size of the pore walls is estimated as 3–5 nm by applying the Scherrer equation.

A representative TEM overview image (Fig. S4, ESI†) shows that the average particle size of MC-TiO_2 powders is about 0.6 μm. The magnified TEM image (Fig. 1(a)) of MC-TiO_2 particles demonstrates that particles have non-ordered wormhole-like pores with pore size less than 10 nm. The selected area diffraction (SAD) pattern (inset in Fig. 2(b)) exhibits a series of Debye–Scherrer diffraction rings, which can be completely indexed according to anatase TiO_2. The crystallinity of the pore walls is further confirmed by the HRTEM micrograph (Fig. 2(b)). It reveals clear lattice fringes and an average grain size of 3–5 nm, comparable to that from the XRD data.

The XPS survey spectrum (Fig. S5, ESI†) shows that MC-TiO_2 contains only Ti, O and C. The XPS spectrum of C 1s for MC-TiO_2 (Fig. 3(a)) consists of three peaks at 284.8, 281.9 and 288.6 eV. The C 1s peak at 284.8 eV is usually assigned to adventitious elemental carbon.[2f] The peak at 281.9 eV is very close to the C 1s peak of TiC.[8] Furthermore, the Ti 2p$_{3/2}$ peak (Fig. 3(b)) for MC-TiO_2 is composed of a single signal at 458.7 eV, typical of the Ti^{4+} oxidation state.[8] The shape and position of the Ti 2p signal clearly excludes the existence of other oxidation states. A Ti 2p signal at about 455 eV, characteristic of TiC (Fig. S6, ESI†),[8] was not detected for MC-TiO_2 powders. This further demonstrates the absence of the TiC phase in MC-TiO_2. Accordingly, the C 1s peak at 281.9 eV can be ascribed to C_{S-O} in the TiO_2 lattice.[6] The concentration of C_{S-O} was estimated at 6.3 atom% from the peak areas of C 1s associated with C_{S-O}, Ti 2p$_{3/2}$ and O 1s. The C 1s peak at 288.6 eV reveals that carbonate species were also formed during the controlled oxidation of TiC.[2f]

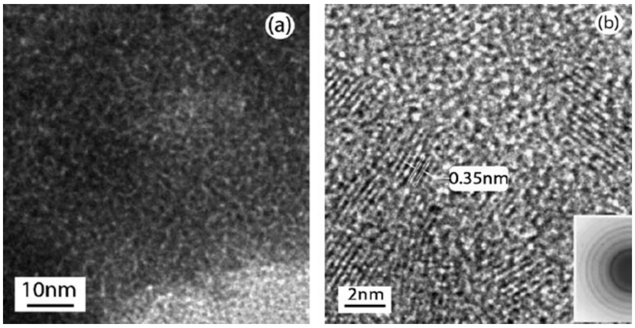

Fig. 2 (a) The magnified TEM image of MC-TiO_2; (b) HRTEM micrograph with the lattice fringes.

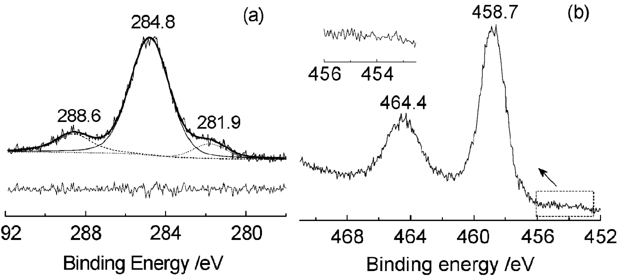

Fig. 3 (a) XPS spectrum of C 1s for MC-TiO_2; (b) XPS spectrum of Ti 2p$_{3/2}$ for MC-TiO_2.

Based on the above results, we propose that the controlled oxidation of nano-TiC by nitric acid results in the formation of anatase micro–mesoporous C-doped TiO_2. Due to the strong oxidation ability of nitric acid, TiC was oxidized into TiO_2 according to eqn (1):

$$TiC + 8HNO_3 \rightarrow TiO_2 + 8NO_2\uparrow + CO_2\uparrow + 4H_2O \quad (1)$$

The emission of gaseous products (NO_2 and CO_2) results in the formation of the micro–mesoporous structure. The nitric acid also acts as a catalyst for the crystallization of TiO_2,[1a] and aids crystallization of TiO_2 at low temperature. Most of C atoms in TiC are depleted by the gaseous product (CO_2) of the above reaction. However, some of C atoms were retained in the TiO_2 lattice due to the presence of ethanol occupying O sites or in interstitial positions of the TiO_2 lattice. As a result, carbon is incorporated into the lattice in the form of C_{S-O} and carbonate species.

Fig. 4 compares the UV-Vis absorption spectrum of MC-TiO_2 and that of the reference anatase TiO_2 (R-TiO_2). MC-TiO_2 shows a fundamental optical absorption threshold at 453 nm (2.73 eV). This means that MC-TiO_2 shows obvious narrowing of the band gap compared with anatase R-TiO_2. In MC-TiO_2, carbon exists in the TiO_2 lattice mainly in the forms

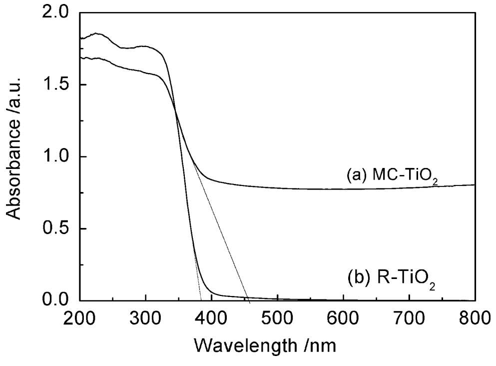

Fig. 4 UV-Vis absorption spectra of (a) MC-TiO_2 and (b) anatase R-TiO_2.

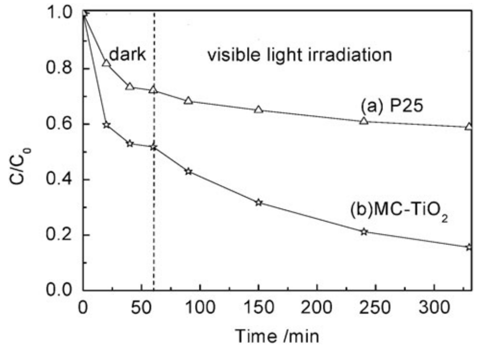

Fig. 5 Changes in the relative concentrations of MB under visible light irradiation ($\lambda > 420$ nm) catalyzed by (a) P25 and (b) MC-TiO_2.

of C_{S-O} and carbonate species. It has been reported that the carbonate species in the TiO_2 lattice hardly results in an obvious red-shift of the fundamental optical absorption edge for C-doped TiO_2.[2f,g,3c] Therefore, band-gap narrowing of MC-TiO_2 can be attributed to the high concentration of C_{S-O}, which results in the upward shift of the valence band top.[2a,4b]

Another feature of the UV-Vis absorption spectrum of MC-TiO_2 is a strong absorption in the visible region up to 800 nm. The mechanisms resulting in this feature are complicated. The theoretical calculation has indicated that the interstitial C (C_I) can induce the Vis-absorption of TiO_2, while carbon occupying Ti sites (C_{S-Ti}) does not.[4] It has been reported that the carbonate species in C-doped TiO_2 causes an obvious long-tail absorption in the visible region.[2f,g,3c] Therefore, it seems more reasonable that C associated with the carbonate species mainly exists at interstitial positions of the TiO_2 lattice.[4b] C_I in MC-TiO_2 results in the impurity states (S_I) below the bottom of conduction band (CB),[4b] which partially contributes to the Vis-absorption (453–800 nm) of MC-TiO_2. Furthermore, some of the impurity states (S_{S-O}) induced from C_{S-O} lie above the Fermi energy and are unoccupied.[4a] The Vis-absorption partially results from transitions from the valence band to the unoccupied S_{S-O}. The micro–mesoporous structure may facilitate further absorption in the visible region by repeatedly scattering within pores.

The Vis-photocatalytic activity of MC-TiO_2 was evaluated by measuring the decomposition of methylene blue (MB) under Vis-irradiation ($\lambda > 420$ nm).[9] P25 (DeGussa), as a typical reference TiO_2 for the evaluation of TiO_2 photocatalyst activity, was used for comparison. Fig. 5 shows changes of the relative concentrations of MB with irradiation time. The decrease of the concentration of MB in the dark reveals that MC-TiO_2 has good adsorbability due to the micro–mesoporous structure.[1e] Under Vis-irradiation, MC-TiO_2 showed high Vis-photocatalytic activity compared with P25. As shown above, C incorporated into the anatase lattice of MC-TiO_2 results in an obvious red-shift of the fundamental optical absorption edge and a strong absorption in the visible region up to 800 nm. This provides MC-TiO_2 with effective Vis-photocatalytic activity. The activity is further enhanced by the high specific surface area of MC-TiO_2. We evaluated the reproducibility of the synthesis method by five batches of samples, prepared under the same conditions as described above. The BET specific surface areas and Vis-photocatalytic activities of these samples are listed in Table S1 (ESI,†). The results clearly show that the synthesis method is well-reproducible.

In conclusion, the method here reported successfully gives rise to micro–mesoporous C-doped TiO_2 with anatase pore walls and high specific surface area. C-doping, crystallization and the formation of porous structures have been simultaneously achieved at low temperature. C incorporated into the lattice exists in the forms of substitutional C occupying some of oxygen sites and carbonate species. The synthesized catalyst has outstanding Vis-photocatalytic activity. This well-reproducible method may provide a general industrial route for synthesizing micro–mesoprous nonmetal-doped TiO_2 catalysts with high Vis-photocatalytic activities due to reduced production cost and the ease of scaling up.

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9 The Vis-photocatalytic activity of MC-TiO_2 was evaluated by measuring the decomposition of methylene blue under visible light irradiation. A 400W xenon lamp was used as the visible light source. A colored glass filter (JB420, EOLFH, China) with cut-off wavelength of 420 nm was used for eliminating UV light. For a photocatalytic experiment, Catalysts (100 mg) were ultrasonically dispersed into 100 mL aqueous solution of 0.01 mM MB in a beaker. The distance between the beaker and the light source is about 25 cm. Before irradiation, the suspensions containing MB and catalysts were magnetically stirred for 60 min in the dark in order to reach an absorption–desorption equilibrium. The absorbance of MB solution was determined by UV-Vis spectrometry at 661.0 nm. The concentration of MB was obtained according to the linear relation between the absorbance and the concentration of MB solution.