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Visible Light Responsive Nitrogen Doped Anatase TiO_2 Sheets with Dominant {001} Facets Derived from TiN

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Anatase TiO_2 sheets with dominant {001} facets are becoming a hot research topic due to their promising high reactivity in heterogeneous reactions.[1] Since the first successful preparation of single crystal anatase TiO_2 sheets with 47% {001} facets synthesized by us,[2] several studies have extended this new route to synthesize more TiO_2 sheets as candidates for photocatalysis applications.[3] Very recently, the percentage of {001} facets in anatase TiO_2 sheets was improved to 64% by employing an alternative solverthermal route.[3a] Meanwhile, Wu et al.[3b] reported nanostructured anatase TiO_2 with high-energy {001} facets via a nonaqueous synthetic route, and Han et al.[3c] demonstrated the nanosized titania sheets with 89% {001} facets. Dai et al.[3d] reported truncated bipyramidal anatase nanocrystalline TiO_2 with a percentage of 9.6%. In all these cases, anatase TiO_2 sheets may have no visible light response due to the large band gap (3.2 eV) of TiO_2. However, from the viewpoint of utilizing solar light, visible light responsive TiO_2 photocatalysts are highly desired. Although nonmetal doping, in particular nitrogen doping,[4] has shown great potential in introducing visible light absorption of titania, it is challenging yet desirable to incorporate dopants into anatase TiO_2 sheets with dominant {001} facets. This is because well-faceted anatase TiO_2 sheets usually have very high crystallinity, making it hard or nearly impossible to incorporate dopants into them by mild post-treatment, while the addition of dopant precursors in the reaction medium may inevitably influence the nucleation and growth of anatase TiO_2 sheets so that no desirable TiO_2 sheets could be synthesized. Here, we report a facile and new route for one-pot synthesis of visible light responsive nitrogen doped anatase TiO_2 sheets with dominant {001} facets. Furthermore, we demonstrate that such TiO_2 sheets exhibit the capability for generating important photocatalysis active species of •OH radicals and splitting water into hydrogen under visible light irradiation. To the best of our knowledge, this is the first example demonstrating visible light photoactivity of anatase TiO_2 sheets with dominant {001} facets.

In a typical synthesis, 150 mM titanium nitride (TiN) solid powder with a particle size of several micrometers in 30 mL of 1 M hydrofluoric acid (HF) was hydrothermally treated at 180 °C in a Teflon-lined stainless steel autoclave. After hydrothermal treatment for 30 h, the product of anatase TiO_2 sheets was obtained. As shown in Figure S1, all X-ray diffraction (XRD) peaks of the synthesized TiO_2 can be indexed to anatase phase TiO_2 and no residual TiN phase can be detected. Scanning electron microscopy (SEM) images (Figure 1A and B) show that the typical morphology of most anatase TiO_2 particles made up of intersectional sheets.

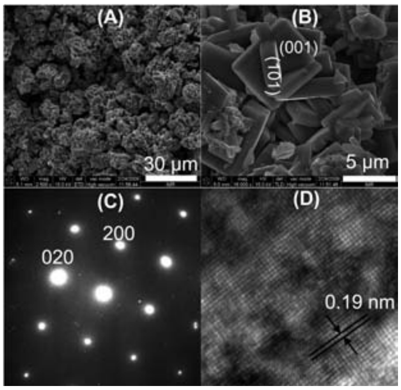

Figure 1. Low- (A) and high-magnification (B) SEM images of anatase TiO_2 sheets and SAED patterns (C) and high-resolution TEM image (D) recorded from single anatase TiO_2 sheet.

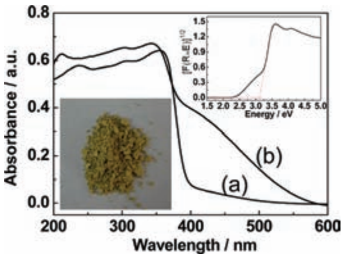

Figure 2. UV−visible absorption spectra of (a) pure anatase TiO_2 sheets and (b) nitrogen doped anatase TiO_2 sheets; the insets in the upper right and lower left corners are the plot of transformed Kubelka−Munk function vs the energy of light and optical photo of nitrogen doped anatase TiO_2 sheets, respectively.

According to the symmetries of anatase TiO_2, two flat and square surfaces in the crystal structure of anatase TiO_2 sheets can be ascribed to (001) and the eight isosceles trapezoidal surfaces are {101} facets of the anatase TiO_2 crystal.[2] The percentage of {001} facets was estimated to be ca. 60%. Selected area electron diffraction (SAED) patterns in Figure 1C and the high resolution transmission electron microscopy (TEM) image in Figure 1D of a single sheet of anatase TiO_2 show the diffraction spots of the [001] zone and a (200) atomic lattice spacing of 0.19 nm.[2]

Figure 2 shows the UV−visible absorption spectra of the synthesized anatase TiO_2 sheets. Interestingly, in contrast to the undoped anatase sheets, an additional high visible light absorption band appears from 400 nm to ca. 570 nm, which is consistent with the yellow color of the sample (The inset in Figure 2). Derived from the plot of the Kubelka−Munk function versus the energy of the light absorbed (The inset) assuming titania as indirect semi-

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conductor, the bandgap of the obtained anatase TiO_2 sheets is extrapolated to be 3.11 eV, which is nearly identical to that of pure bulk anatase TiO_2. This means that the intrinsic bandgap of the TiO_2 sheets is not changed and only some localized states are introduced in the bandgap of TiO_2.[4c,5]

X-ray photoelectron spectra of F 1s, N 1s, Ti 2p, and O 1s for the anatase TiO_2 sheets are shown in Figure S2. The binding energy of F 1s core electrons is 684.2 eV, which belongs to the typical surface Ti−F species.[2,6] Two bonding states of nitrogen species are evidenced with their N 1s binding energies of 399.5 and 401.0 eV. The former is attributed to the incorporated nitrogen dopant in titania as interstitial N or O−Ti−N,[4c,g,h] and the latter is probably originated from surface adsorbed or contaminated nitrogen species.[4a,d,5] The amount of N dopant is ca. 0.67 at %. In contrast to undoped anatase TiO_2 sheets, nitrogen doped anatase TiO_2 sheets have a binding energy shift toward high energy by 0.15 eV for Ti 2p and O 1s due to nitrogen doping (Figure S2). It is known that fluorine doping itself cannot introduce visible light absorption but can be favorable for enhancing photocatalytic activity.[6,7] The visible light absorption band as evidenced in Figure 2 can be reasonably thought to arise from the localized states of N 2p above the valence band[8a] and also concomitant oxygen-vacancy states below the conduction band.[8b] Further depth profiling analysis of N element confirms the existence of nitrogen dopant in the bulk of the doped TiO_2 (Figure S3).

Direct thermal oxidation of TiN powder in air can only lead to nitrogen doped *rutile* titania.[9] Yet, our wet-chemistry oxidation process in HF solution results in not only nitrogen doped TiO_2 with *anatase* phase but also a large percentage of {001} facets induced by surface Ti−F bonds (see Figure S2).[2]

The photoactivity of the nitrogen doped anatase TiO_2 sheets was estimated by detecting the generated amount of the important photocatalysis active species of •OH radicals.[5] As shown in Figure S4A, obvious fluorescence spectra associated with 2-hydroxy terephthalic acid (TAOH) are generated upon irradiation of the nitrogen doped anatase TiO_2 sheets suspended in terephthalic acid (TA) solution within 220−770 nm for different irradiation times. The nearly linear relationship between fluorescence intensity and irradiation time does confirm the stability of our developed TiO_2 sheets as photocatalyst, and more importantly, the synthesized anatase TiO_2 sheets can generate the photocatalytic •OH radicals under 420−770 nm as illuminated in Figure S4B. Only neglectable •OH radicals can be formed for undoped anatase TiO_2 sheets under visible light irradiation (Figure S4D).

We further measured the efficiency for hydrogen evolution of the nitrogen doped anatase TiO_2 sheets loaded with 1 wt % Pt from photochemical reduction of water in the presence of methanol as a scavenger. The doped anatase TiO_2 sheets show a hydrogen evolution rate of 1483 and 81 $\mu mol \cdot h^{-1} \cdot m^{-2}$ under 220−770 nm and 420−770 nm, respectively. However, the corresponding rate for pure anatase TiO_2 sheets with a comparable particle size and percentage of {001} facets is 1333 and 0 $\mu mol \cdot h^{-1} \cdot m^{-2}$ under the same measurement conditions. It was also found that nitrogen doped anatase TiO_2 sheets show a more superior hydrogen evolution rate to nitrogen doped anatase TiO_2 without dominant {001} facets (see Supporting Information). In addition, our nitrogen doped TiO_2 sheets show good stability upon light irradiation (Figure S5) as a result of bulk N doping.

In summary, we have developed a facile and new route for one-pot synthesis of nitrogen doped {001} dominant anatase TiO_2 sheets. Such TiO_2 shows a significantly enhanced stability of high visible light absorption by bulk N doping and good photooxidation and photoreduction activity. The developed route has the merits of being simple, reproducible, and easy to scale-up. This work can also have some important implications on developing other nonmetal doped anatase TiO_2 sheets with dominant {001} facets.

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Supporting Information Available: Experimental details, XPS and photoactivity data. This material is available free of charge via the Internet at http://pubs.acs.org.

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