

# A Fluoride-free Approach to Hierarchical Porous Anatase TiO<sub>2</sub> Composed of Ultrathin Oriented Graphene-liked Reactive Nanosheets

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**Abstract.** Hierarchical porous anatase TiO<sub>2</sub> is synthesis by a universal solvothermal reaction, However, most synthesis methods are usually carried out in the presence of environmentally unfriendly fluorides. In this study, hierarchical porous anatase TiO<sub>2</sub> composed of ultrathin oriented graphene-liked rich in (001) crystal facets were successfully synthesized under fluoride-free conditions. By adjusting the nitrogen doping content, the thickness of the nanosheets was controlled, and the crystals were characterized using X-ray diffraction, scanning electron and transmission electron microscopy, as well as electron spectroscopy.

**Keywords:** Fluoride-free; Hierarchical Porous; Anatase TiO<sub>2</sub>; Nanosheets.

## 1. Introduction

Mesoporous materials refer to materials containing pores with diameters between 2 and 50 nm. Their morphology and pore size and structure can be controlled, and their chemical composition can be adjusted [1]. As a result, mesoporous materials have found wide applications in adsorption separation [2], catalysis [3], energy [4], and other fields. As one of the most important oxide semiconductors, mesoporous TiO<sub>2</sub> single crystals with exposed (001) facets has been widely used in many applications in the field of energy [5]. Low-temperature is a method to obtain mesoporous TiO<sub>2</sub> with continuous framework structure [6], mesoporous structure can improve the surface area, continuous framework can improve the electron transport [7]. The anatase TiO<sub>2</sub> with well-defined morphology has high-performance facets, among which a high proportion of (001) facets is particularly important for understanding the relationship between performance and microstructure [8].

In addition, the emergence of two-dimensional materials such as graphene, which have ultra-thin flake-like morphologies and excellent electrical properties, has gained widespread attention in materials science research [9]. Nanosheets, due to their unique two-dimensional shape, provide many possibilities for constructing advanced materials [10]. The three-dimensionally self-organized architecture is thermally stable for ultrathin nanosheets [11], anatase TiO<sub>2</sub> film with continuous framework and porous structure is the desired, since it is the guarantee of fast electron transport and large surface area [12]. Hierarchical pore walls composed with ultrathin oriented nanosheets with a large percentage of reactive facets only have a high reactivity, but also can be beneficial to increase the surface areas [13].

However, the synthesis of anatase TiO<sub>2</sub> crystals, which are rich in (001) crystal facets, still requires the presence of fluoride, and they are highly toxic and corrosive in their gaseous or liquid state [14]. Therefore, it is still challenge to develop a new synthesis strategy for fluoride-free synthesis of anatase TiO<sub>2</sub> crystals that are rich in (001) facets. the formation of hierarchical porous structure assembled by the ultrathin anatase TiO<sub>2</sub> sheet dominated with (001) facets to increase the exchange. Nitrogen-dopping or metal-dopping to improve the utilization of visible light.

## 2. Experimental Section

The hierarchical porous anatase TiO<sub>2</sub> were achieved via a one-pot biphasic stratification approach by continuous growth using cationic surfactant CTAC as a template, tetrabutyl titanate

(TBOT) as a titanium source, diethanolamine (DEA) as a catalyst and organic solvent such 1-octadecene as an emulsion agent. At first, 24 ml of (25 wt %) CTAC solution and 0.18 g of DEA were added to 36 ml of water and stirred gently at 60 °C for 1 h in a 100 mL round bottom flask, then 20 mL of (20 v/v %) TBOT in 1-octadecene was carefully added to the water-CTAC-DEA solution and kept at 60 °C in an oil bath under a magnetic stirring. After it was stirred for 0.5 h, the above solution was transferred into a 50 mL sealed Teflon reactor, and the reaction was carried out at 180 °C for 24 h. After they were naturally cooled to room temperature in air, these obtained white precursors were washed with deionized water three times and then dried in a freeze-drying oven.

### 3. Results and discussion

The SEM and TEM images of the amorphous TiO<sub>2</sub> film prepared by direct coating of the colloid precursor solution obtained from CTAB/water/n-butanol/cyclohexane reverse micelle is shown in Figure 1. The amorphous TiO<sub>2</sub> film obtained from the reverse micelle exhibits an uneven morphology on the surface, which appears as continuous block-like structures. However, due to the high defect density, a uniformly porous film cannot be formed. It is precisely this microstructure that leads to poor film formation and uniformity of the TiO<sub>2</sub> film. As the particles of amorphous TiO<sub>2</sub> itself are amorphous and do not have a fixed crystal structure, unlike crystals, their shape depends entirely on the form of the reverse micelle formed by the surfactant molecules in the microemulsion. Therefore, it is necessary to ensure that the surfactant molecules in the oil/water system aggregate into a single spherical reverse micelle.

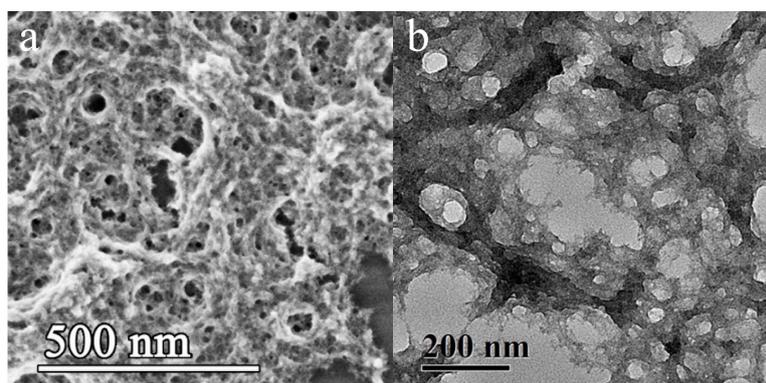


Figure 1 SEM & TEM images of uncrystallized TiO<sub>2</sub>

SEM and TEM were utilized to explore the morphology of the crystallized hierarchical porous TiO<sub>2</sub>. In the SEM images (Figure 2a, b, c), compared to the amorphous TiO<sub>2</sub>, the sample exhibits a uniformly thick layer of nanocrystals. As shown in Figure 2d, the TEM image reveals that the sample is composed of small stacks of nanosheets, and the lattice fringes with a spacing of 0.35 nm in Figure 2e may correspond to the (101) plane of the anatase TiO<sub>2</sub> phase. Due to the random stacking of nanosheets, many irregularly-shaped pores are formed, which increases the internal accessibility and enhances the permeation of the electrolyte. The selected area electron diffraction (SAED) pattern shown in Figure 2f corresponds to the (101), (103), (200), (105), and (213) diffraction rings of the anatase-type TiO<sub>2</sub> phase.

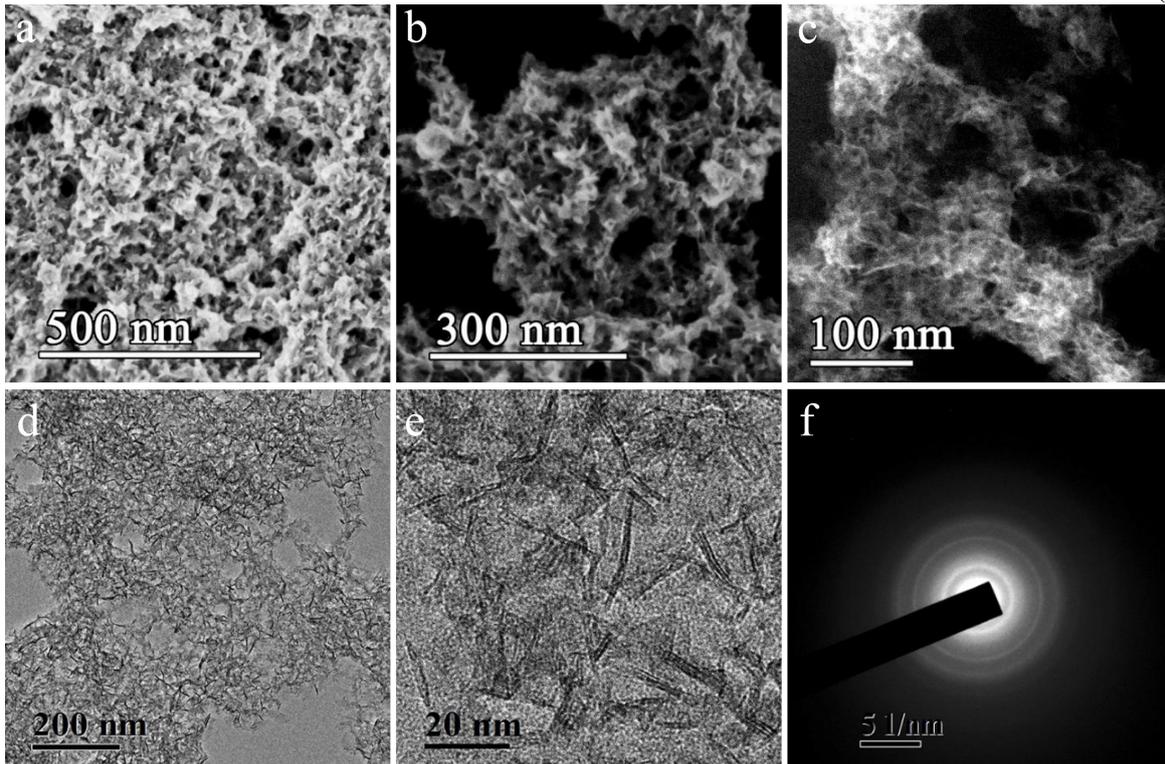


Figure 2 SEM & TEM images of Crystallized Hierarchical Porous TiO<sub>2</sub>

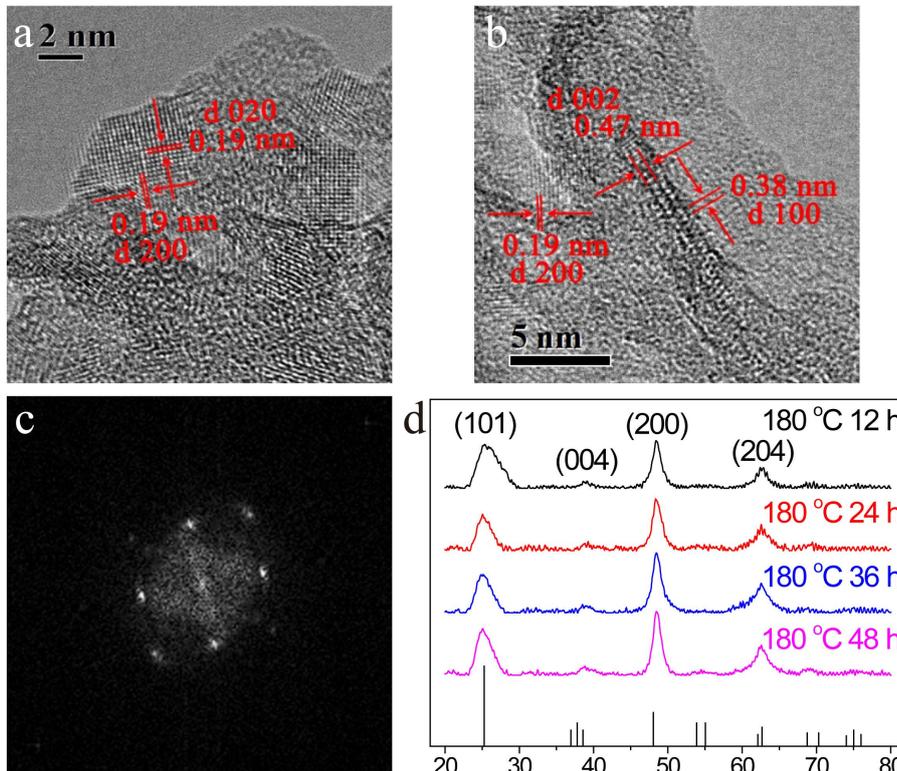


Figure 3 TEM images & XRD of Crystallized Hierarchical Nitrogen Doped Porous TiO<sub>2</sub>

Transmission electron microscopy (TEM) images and the selected area electron diffraction pattern confirmed that crystal exhibits single-crystal features (as shown in Figure 3a, b, c). The high-resolution TEM images (Figure 3a, b) show the (200) and (020) atomic planes with a lattice spacing of 0.19 nm. The selected area electron diffraction pattern can be indexed to the (001) diffraction point. Further confirmation of the crystal structure of the sample was obtained through XRD measurement. As shown in Figure 3d, the diffraction peaks at 25.4°, 37.9°, 48.1°, 54.1°, 55.1°, 62.9°, 68.9°, and 70.4° corresponded to the (101), (004), (200), (105), (211), (204), (116), and (220)

crystal planes, respectively. According to the Scherrer equation, based on the peak at (101), the estimated average crystallite size of the nanoparticles is about 10 nm. As crystallization proceeds, the peaks at (101) and (204) become sharper, indicating stronger crystallinity. And the peak area of (101) is the largest.

Figure 4 shows the XPS full spectra of TiO<sub>2</sub> before and after nitrogen doping. From Figure 4b, it can be observed that an electron peak of nitrogen appears at 400.65 eV in the XPS full spectrum of N-Ti, indicating the presence of nitrogen in the doped TiO<sub>2</sub> sample. The high-resolution XPS spectra of Ti 2p are shown in Figure 4c, the bands at 459.6 and 465.3 eV are assigned as the Ti 2p<sub>3/2</sub> and Ti 2p<sub>1/2</sub>, respectively, which indicates the presence of the Ti<sup>4+</sup> in TiO<sub>2</sub>. The high resolution XPS spectrum of O 1s in Figure 4d can be fitted to three sub-peaks at 533.4, 532.0 and 530.3 eV, which can be assigned to the H–O–H bond from the adsorbed H<sub>2</sub>O molecules, the surface oxygen vacancy and the Ti–O lattice bond, respectively. This further confirms the presence of nitrogen in the sample and the successful synthesis of N-TiO<sub>2</sub> powder.

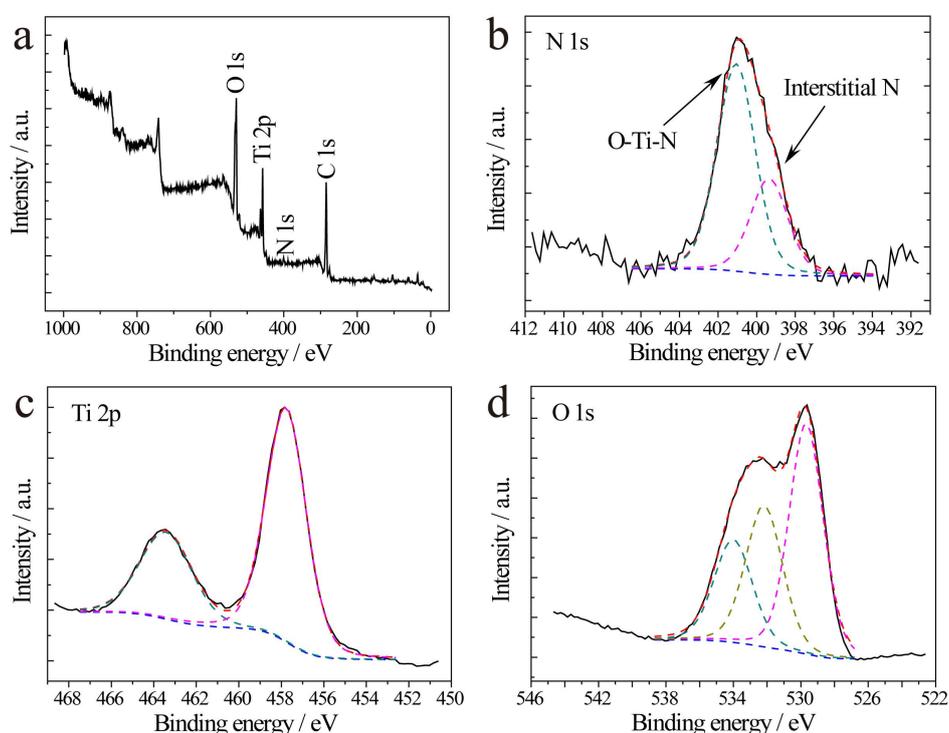


Figure 4 XPS of the crystallized hierarchical porous nitrogen doped anatase TiO<sub>2</sub>

In order to further investigate the effect of different nitrogen doping levels on Anatase TiO<sub>2</sub>, different amounts of diethanolamine (DEA) were doped into layered porous TiO<sub>2</sub>. TEM images show that with the increase of DEA amount, the black areas gradually decrease (Figure 5a, b, c). According to the theory of transmission electron microscopy contrast between materials thickness, this is caused by the difference in region thickness. Therefore, it can be inferred that as the nitrogen content increases, the thickness of anatase TiO<sub>2</sub> will gradually decrease. High-resolution TEM images (Figure 5d, e, f) clearly show lattice fringes, and the XRD spectra (Figure 5d) show no significant changes in the diffraction patterns with the addition of different amounts of DEA. Therefore, it can be concluded that nitrogen doping has no effect on the crystallinity of Anatase TiO<sub>2</sub>. In addition, the BET curve and pore size distribution curve show that the doping amount of DEA has no significant effect on the surface area, and the pore size is 2.1 nm (Figure 5h, i).

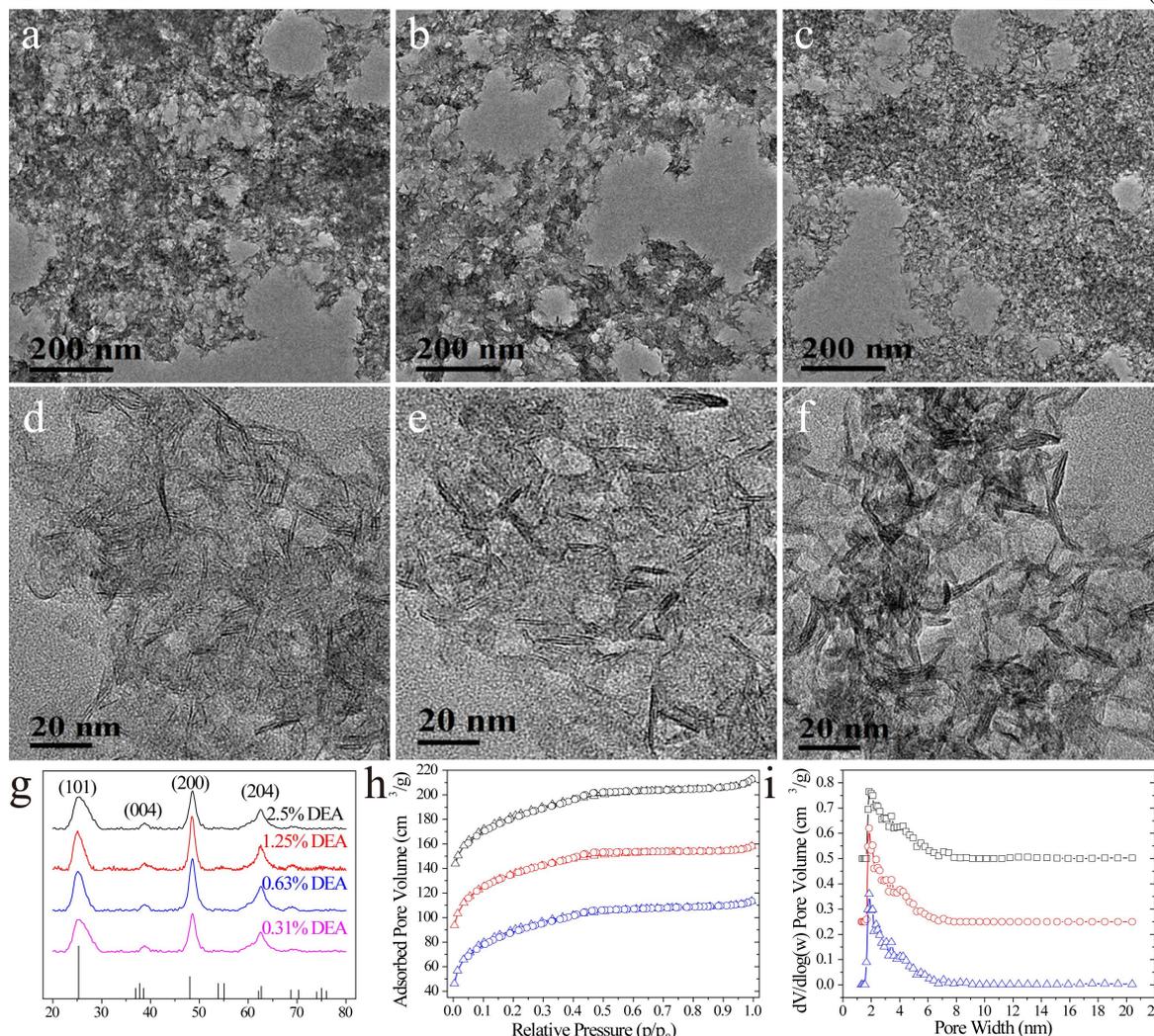


Figure 5 (a-f) TEM images, (g) XRD, (h) BET and (i) pore size distribution curve of Crystallized Hierarchical Porous Titania with different Nitrogen Doped contents

## 4. Conclusion

In summary, we successfully synthesized layered porous TiO<sub>2</sub> crystals with rich (001) crystal facets under fluoride-free conditions in the presence of DEA. The layered porous TiO<sub>2</sub> crystals exhibit excellent internal accessibility, which can greatly enhance the transfer of electrolyte inside. By using DEA-controlled synthesis, porous nanosheets with different thicknesses can be obtained, which has potential significance for the design and preparation of functional oxide materials in the future.

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