



Room Temperature Synthesis of N-doped Urchin-like Rutile TiO₂ Nanostructure With Enhanced Photocatalytic Activity Under Sunlight

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PAPER INFO

Paper history:

Received 26 September 2015

Received in revised form 07 October 2015

Accepted 16 October 2015

Keywords:

Rutile TiO₂

Nanostructure

Nitrogen- doped

Room Temperature

Photocatalytic Activity

A B S T R A C T

We report the synthesis of nitrogen-doped urchin-like rutile TiO₂ nanostructure at room temperature without further heat treatment. The process was operated through hydrolysis of Ti(OC₄H₉)₄ employing the direct amination of the product. The samples characterized by x-ray diffraction (XRD), scanning electron microscopy (SEM), Transmission electron microscopy (TEM), Raman spectroscopy and Brunauer- Emmett- Teller (BET) for determination of surface area. Photocatalytic activity of the product was evaluated by degradation of Methylene blue under sunlight. This analysis demonstrated that obtained titanium oxide has an urchin- like form with rutile structure and high surface area is due to formation of nanospicules on the surface. N-TiO₂ exhibited excellent photocatalytic activity under sunlight due to their high surface area (148 m² g⁻¹) and the new absorption band in the visible region caused by nitrogen doping.

doi: 10.5829/idosi.ije.2015.28.10a.01

1. INTRODUCTION

Control over the static self-assembly of nano-architectures as an autonomous reorganization process with minimal energy penalty is common throughout nature [1, 2]. The inherent parameters affecting self-assembly, if exercised correctly, offer great simplicity and flexibility in achieving complex architectural design assisting tailor-making of the final structure for specific applications [1, 3-5]. To this end, many efforts have been focused on the self-assembly of semiconducting materials with engineered band gap of around 3 eV including TiO₂ and ZnO [6,7]. The indispensable exceptional electric properties of these materials enable their use for a diverse range of different technological applications including photocatalysis, solar cell applications, electrical switches, energy storage applications, etc. [8-10]. Among these applications, photocatalytic purification of polluted air and wastewater has attracted great attention as it shows great promise for literally green environmental

remediation [11]. However, conventional TiO₂ structures typically used for these applications although enjoy many unique properties such as environmental friendly nature, tuneable medium band gap, long-term stability and low cost compared to other semiconducting materials, suffer from a wide band gap (UV- range). This, in turn, severely limits their application due to the utilization of only about 4% of the solar energy [12].

A multitude of new strategies have been developed to address this issue. In the past, a wide range of metallic dopants, have been extensively studied to address this issue and extend the photocatalytic activity to visible light [13]. Although some very good advances have been made, there are still major drawbacks in terms of stability and reliability of these photocatalysts which make them ineffective for practical applications. Moreover, most of the work in this area is mainly focused on N-doped anatase phase [12, 14-17], while N-doped rutile phase is mainly neglected and just a few papers have addressed its role in optical activity [18-20]. Another promising strategy relies on the development of multi-modal porous architectures containing multi-scale porosity to improve mass-

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transfer of molecules in solid networks. These methods typically involve the combination of organic template synthesis with micromoulding technologies or guiding the self-assembly of TiO₂ during hydrothermal synthesis by use of a surfactant. However, the need for high temperature sintering of such architectures to remove the excess surfactants and enhance the crystallization of TiO₂ typically results in the loss of porosity and the final collapse of the structure rendering this strategy at its current state impractical for photocatalytic applications. Therefore, developing strategies to achieve highly porous photocatalytically active materials is becoming an urgent challenge to be addressed.

To meet such a challenge, we present a facile single step sol-gel approach towards the preparation of high surface area N-doped nanocrystalline rutile without any need for further calcination post-process. As there was no need to eliminate the sintering effects, we could also successfully omit the use of structural stabilizers (such as ZrO₂ or SiO₂) which are typically used for their anti-sintering effects. The as-prepared self-assembled structures showed high performance photocatalytic activity under visible light condition. Methylene blue was chosen as a probe of choice to monitor the photocatalytic activity of the structure because of its close structural relationship to some toxic volatile organic compounds.

2. MATERIALS AND METHOD

All chemicals were purchased from Merck (Germany) and used without any further purification.

Nanocrystalline urchin-like rutile TiO₂ powders were prepared by the reaction of tetraethyl orthotitanate (purity 95%) in isopropyl alcohol (purity 99.8%) and nitric acid 65% at pH<1 using the sol-gel method in a similar way to the previous work [21]. The resulting white precipitates were filtrated without further washing and were dried in air at room temperature. The same procedure was applied to prepare N-doped TiO₂ powders except that NH₄NO₃ (99%), as a source of nitrogen, with the same molar ratio of TiO₂ was added in the hydrolysis step.

The final products were characterized using X-ray diffractometry (Siemens D-500, Philips) with CuK α X-ray tube at 1.54 Å, transmission electron microscopy (TEM, CEM902A, ZEISS), scanning electron microscopy (SEM, Streoscan 360, Leica Cambridge) and UV-visible spectrophotometry (optical absorption, Agilent 8453) techniques. The specific surface area was determined using the Brunauer-Emmett-Teller (BET) method (Belsorp mini II Japan). The photocatalytic activity of pure and N-doped TiO₂ powders under sunlight was evaluated by the photodegradation of 4 mg as prepared powder. The powders were added to a 10 ml aqueous methylene blue (MB) solution (2.0×10^{-4} M)

which was placed under sunlight on a winter's day. Thus, all the experiments were carried out under sunlight for 60 min, from 12.00 p.m. to 1.00 p.m. (noon). The change in MB concentration was monitored using a UV-Vis spectrophotometer at a wavelength of 665 nm.

3. RESULT AND DISCUSSION

The search for new strategies to overcome the classical shortcoming of archetypical semiconductors such as TiO₂ has led to the development of new approaches to increase the photocatalytic reaction sites and hence photocatalytic reaction rate while simultaneously increase the stability of these materials. A promising solution is the use of rutile TiO₂ phase as the most stable phase of titania which exhibits unique properties distinguishing it from other traditional semiconductors [22]. First and foremost, the direct bandgap of rutile lies in lower energy levels which results in extended photoresponse range [23]. Thus, the loss in some part of frequency spectrum can be engineered. Moreover, the higher refractive index of rutile compared to anatase results in slower time of travel of light inside the material providing increased photocatalytic reaction sites, and enhanced charge transportation and separation efficiency simultaneously. Therefore, employing rutile can potentially serve as a facile and straightforward strategy for the fabrication of efficient and stable photocatalysts. However, to use such structures to their full potential, scalable systems with high throughput are required to serve as platforms for improved visible-light driven photocatalytic properties.

To this end, we prepared N-doped rutile phase via a simple sol-gel method as described in the experimental part. It should be noted that although rutile is the most thermodynamically stable polymorph of TiO₂, under normal hydrolysis condition the formation of this phase is not kinetically favourable. Therefore, to achieve the rutile phase one needs to control the formation of TiO₆ octahedra blocks. In general, TiO₆ moieties should be able to rearrange themselves into rutile polymorph. Such phase transformation can take place by adjusting the hydrolysis rate which is regulated by the presence of acids. Acids have been reported to play the role of a chemical catalyst to change the crystallization mechanism resulting in a notable decrement of activation energy for the rutile formation. The formation of rutile can thus be determined by the kinetic behaviour of TiO₂ clusters upon nucleation and growth. NO₃⁻ anions in nitric acid have very weak affinity for titanium and therefore can facilitate the rearrangement of TiO₆. Therefore, in acidic conditions anatase phase can be formed as we had previously reported. Increasing the concentration of NO₃⁻ anions through going to extremely acidic conditions can further facilitate the

rearrangement of TiO_6 basic building blocks resulting in much larger repulsion from H_3O^+ ions promoting the slower formation of aggregates or clusters. This, in turn, provides enough reaction time for the formation of the rutile phase which is thermodynamically favourable [24]. In other words, the condensation rate is slow enough to produce rutile TiO_2 phase at lower temperatures. Therefore, the use of HNO_3 facilitates the formation of pure rutile phase.

XRD patterns presented in Figure 1a further prove the formation of pure rutile phase. XRD patterns of both the sample doped with nitrogen and the undoped sample both show no traces of anatase or brookite structure. By applying the Scherrer's equation, the average crystallite sizes were estimated to be 14.9 and 15.5 nm for the undoped and N-doped TiO_2 , respectively. As depicted in the pattern, due to low concentration of doped nitrogen in TiO_2 crystal structure, there is no observable dopant related peaks such as TiN [25].

Raman spectroscopy was also used to further investigate the structure of the doped sample (Figure 1b). In a tetragonal structure, the E_g mode (located at $\sim 440 \text{ cm}^{-1}$) is more sensitive to oxygen deficiencies compared to other modes such as Ti-O stretching modes due to the out-of-phase motion of oxygen atoms along the c-axis [26,27]. However, the change in Raman shift observed in the E_g mode of the as-prepared n-doped rutile is subtle which serves as a direct evidence that there is no to little oxygen vacancy present in the system [27]. Furthermore, as the frequency of the Raman shift doesn't change substantially, it can be deduced that nitrogen atoms have not replaced oxygen atoms, as any substitution can dramatically change the Raman shift value. On the other hand, the Ti-O stretching mode (a_1g) located at 610 cm^{-1} , which is sensitive to Ti-O bond lengths, shows a substantial Raman shift of $\sim 10 \text{ cm}^{-1}$. The downshift of Ti-O stretching mode most likely arises from the presence of interstitial N atoms which results in the phonon confinement in the Brillouin zone. The broad Raman band observed around 231 is also assigned to three and four coordinate oxygen (O-O) interactions [27, 28].

There are a large number of studies done on the grain growth process of TiO_2 [29-32]. These findings systematically show that rutile's inherent growth is along (001) because the (001) surface has the highest energy among the considered surfaces [33]. The diffraction peaks in the XRD pattern presented in Figure 1a can be well indexed to tetragonal rutile TiO_2 .

Such structural changes can have profound effect on the morphology of the final architecture. To better understand these effects, High-resolution field emission SEM (FESEM) analysis was performed on the doped structure (Figure 2). The final architecture exhibited a solid core with spicules protruding out of the surface.

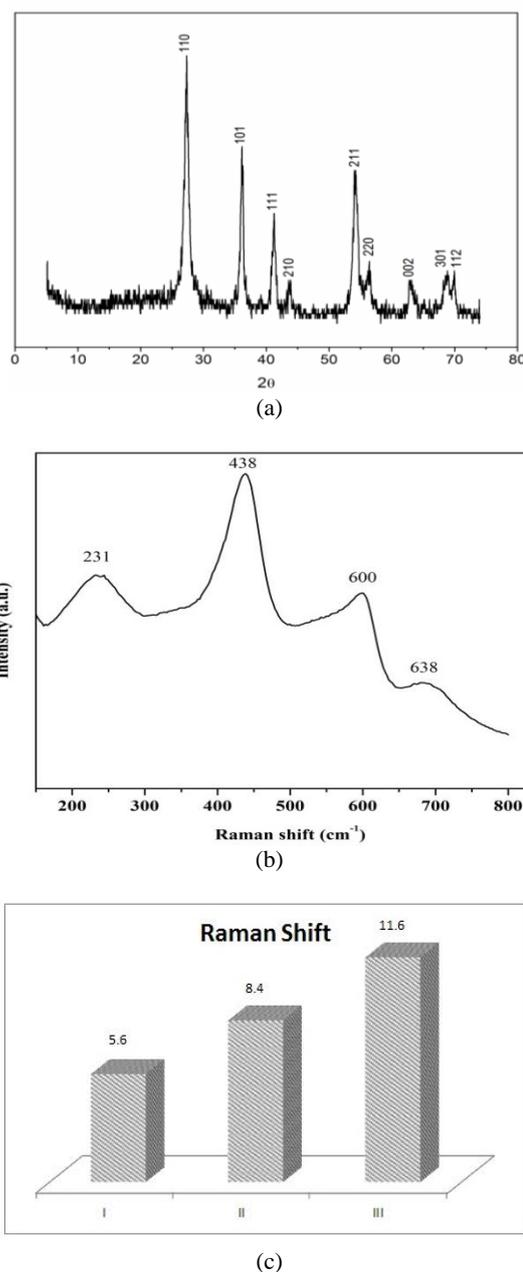


Figure 1. (a) XRD peaks of N-doped urchin TiO_2 , (b) Raman spectra and (c) Raman Shift of the rutile Raman Band (The raman bands located at $\sim 145, 237, 447,$ and 612 cm^{-1} are attributed to the rutile phase)

The existence of plate like specules resulted in a higher surface to volume ration consequently leading to an extremely high surface area of $148 \text{ m}^2 \cdot \text{g}^{-1}$ which is about three times greater than that of P25- TiO_2 ($52.2 \text{ m}^2 \cdot \text{g}^{-1}$) and is even comparable with ultra-high surface area powders produced by spray pyrolysis method. The specular architecture can act as an indispensable reaction surface for extraordinary light harvesting properties.

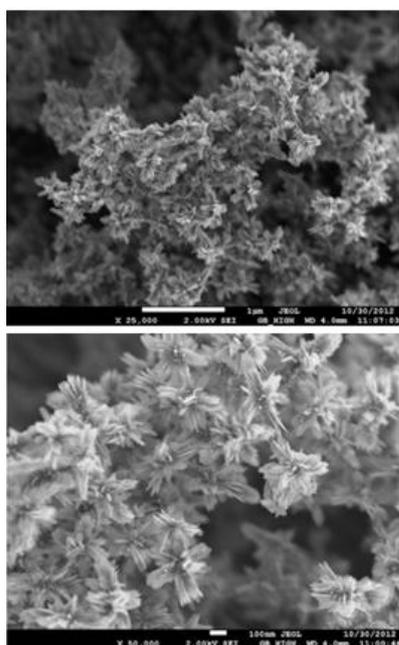


Figure 2. FESEM images of N-doped urchin TiO₂

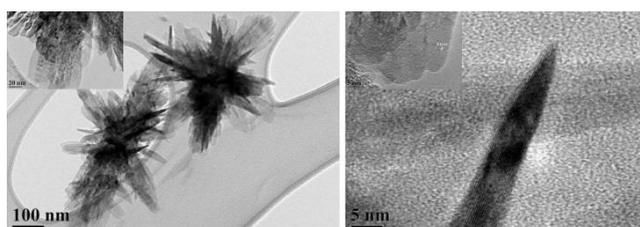


Figure 3. TEM images of N-doped TiO₂ nanospicules

Furthermore, the specules can act as optical fibers being able to trap and harvest light. The individual finely divided architecture also enables higher access of electrolytes or other materials to the surface sites of TiO₂ which can have profound effect on applications in which high access of ions or electrolytes to the surface play an important role such as photocatalytic and energy storage applications.

To further investigate the structure, we performed high resolution TEM analysis on the as-prepared doped architecture. TEM observations in Figure 3 show that the urchin-like N-doped rutile TiO₂ powders are not just bundles of small crystallites, but they are composed of nanospicules growing concentrically. At first, the small rutile nanospicules aggregate to produce small bundles of nanospicules and eventually coalesce through “oriented attachment” mechanism [34] to form larger size spicules. Finally, the resultant nanospicules self-organize to produce the urchin like morphology. Fusing the nanospicules causes the surface energy reduction. Small nanospicules fused with each other are demonstrated with arrows in Figure 3. Further observation shows that the fully formed final spicule is

composed of a single faceted crystal with a plate-like morphology which is extremely thin. The distance between lattice fringes in one spicule was measured using high resolution transmission electron microscopy (HRTEM). These fringes which extend through the whole spicule exhibit a fringe spacing of ~ 0.33 nm which corresponds to a d-spacing of {110} crystal planes of rutile phase. This indicates that nanospicules have an inherent growth along (001) direction. Noting that the (001) has the highest energy [33], HRTEM results supports the assertion that the growth takes place along (001) direction. Such high energy facets, if completely exposed, are therefore a suitable candidate for photocatalytic applications.

Photocatalytic activity of synthesized nanospicules was investigated by the photocatalytic degradation of methylene blue in an aqueous solution under sunlight. The change in the blue colour of the aqueous solution for N-doped sample was, remarkably, observable by the naked eye during exposure to sunlight, as shown in Figure 4I.

Figure 4II shows the variations of the UV–V is absorption spectra of MB after 60 min exposure to sunlight for un-doped and N-doped TiO₂ nanospicules. A sharp absorption band at about 665 nm was observed in the spectrum before exposure to sunlight, whereas the absorbance of the band decreased nearly to zero after 60 min exposure for N-doped sample.

As it is clear from Figure 4I, un-doped TiO₂ has small photocatalytic activities under sunlight. In contrast, the intense photocatalytic activity of N-doped TiO₂ sample is clear. This is mainly due to the doping of nitrogen and also high surface area of N-TiO₂ nanospicules. Furthermore, Figure 4III shows N-doped TiO₂ powders with a new absorption band (or two step absorption edges) in the visible range that might be the reason for the great improvement in MB degradation of the N-doped TiO₂. The new spectral band in the range of 397 λ <math>< 550</math>, is related to the excitation of electrons from local states in the band-gap to unoccupied states, not to a band-to-band transition [35,36]. Consequently, doped catalysts will be activated by absorbing sunlight and the resulting electron-hole pairs (h^+e^-) are used in the photocatalytic reactions directly. Therefore, we believe that the new spectral absorption band has the ability to degrade organic substance in the photocatalytic reactions under sunlight. The UV-Vis spectra were processed in order to obtain the energy band gap E_g . The band gap E_g was calculated using the Tauc's Equation (1):

$$\alpha = \frac{k(h\nu - E_g)^n}{h\nu} \quad (1)$$

where, α is the absorption coefficient (cm^{-1}), $h\nu$ is the photon energy (eV), k is a constant, and the value of n can be 0.5 or 2 depending on whether it is direct or

indirect transitions. The optical band gap was estimated by extrapolating the straight line portion of the $(\alpha h\nu)^{1/2}$ vs. $h\nu$ plot. The band gap of the un-doped sample, calculated based on the absorption spectra, was 3.34 eV. This value is higher than the bulk rutile which can be attributed to the nanocrystalline nature of the powder. However, the band gap of N-doped sample decreased to 2.59 eV. This result indicates that the band gap narrowing occurs upon the N-doping of TiO₂ which is responsible for the visible-light responding of N-TiO₂, which is shown in Figure 4I.

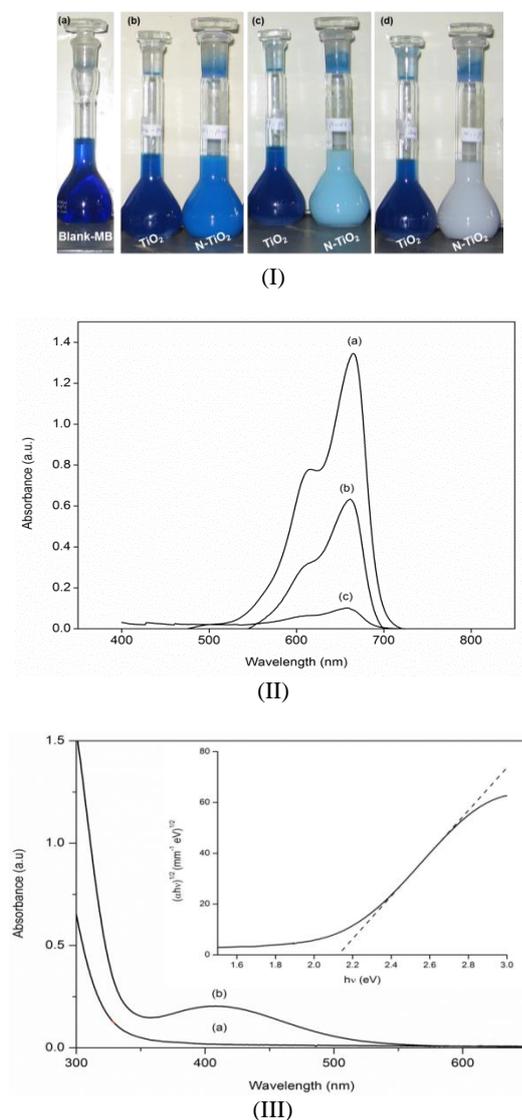


Figure 4. (I): The photodegradation of (a) Blank-MB (b) before exposure (c) after 30 min and (d) after 1hr under sunlight, (II): Variations of the UV-Vis absorption spectra of (a) Blank MB, (b) MB after 1hr exposure to sunlight for un-doped and (c) N-doped TiO₂ nanoparticles and (III): UV-vis absorption spectra of (a) un-doped and (b) N-doped TiO₂ nanoparticles dispersion in water.

4. CONCLUSION

Highly visible light N-doped urchin-like rutile TiO₂ nanostructure was prepared at room temperature by a simple method (sol-gel technique). The N-doped TiO₂ sample exhibited a high BET surface area and a new absorption band in the visible region. In addition, N-doped TiO₂ showed higher photocatalytic activity than pure TiO₂ under sunlight that can be attributed to the smaller band gap and higher surface area. The morphology of rutile nitrogen-doped titania was urchin like specular such as the un-doped one. The achievement of this study will lead to the production of environment friendly photocatalysts, specifically those that are activated in sunlight, surpassing the efficiency of existing catalysts.

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PAPER INFO

چکیده

Paper history:

Received 26 September 2015

Received in revised form 07 October 2015

Accepted 16 October 2015

Keywords:

Rutile TiO₂

Nanostructure

Nitrogen- doped

Room Temperature

Photocatalytic Activity

نانوساختار دی اکسید تیتانیوم آلاینده شده با نیتروژن با ساختار جوجه تیغی شکل در دمای اتاق بدون هیچگونه عملیات حرارتی سنتز شده است. این نانوساختار از طریق آمیناسیون مستقیم تترابوتیل اورتو تیتانات تهیه شده که با پراش اشعه ایکس (XRD)، میکروسکوپ الکترونی روبشی (SEM)، میکروسکوپ الکترونی عبوری (TEM)، طیفسنجی رامان و BET (جهت اندازه گیری سطح ویژه) تعیین مشخصات گردید. فعالیت فوتوکاتالیستی محصول نیز از طریق تجزیه متیلن بلو زیر نور خورشید ارزیابی شد. این بررسی‌ها نشان داد که اکسید تیتانیوم بدست آمده دارای ساختار کریستالی روتایل بوده که به شکل جوجه تیغی رشد کرده اند و تشکیل نانوساختارها در سطح سبب افزایش سطح ویژه در نمونه شده است. خاصیت فوتوکالیستی بسیار خوبی در زیر نور خورشید از خود نشان می‌دهد که این به دلیل مساحت سطح ویژه بالا ($148 \text{ m}^2 \text{ g}^{-1}$) و باند جذبی جدیدی است که در محدوده نور مرئی به دلیل وجود نیتروژن ایجاد شده است.

doi: 10.5829/idosi.ije.2015.28.10a.01