A facile one-pot synthesis of N-La codoped TiO$_2$ porous materials with bio-
hierarchical architectures and enhanced photocatalytic activity

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Abstract: Bio-hierarchical TiO$_2$-based porous structures (denoted as morph-TiO$_2$) with N and La co-doping (denoted as N-La-morph-TiO$_2$) are successfully synthesized via a facile one-pot reaction by using butterfly wings as bio-template and surfactant as co-template. Due to the novel dual-template strategy, the well-aligned 3D bio-
hierarchical porous structures in combination with N-La codoping not only modify the band structure of TiO$_2$ to make it more responsive to visible light, but also increase the surface area and lead TiO$_2$ to have enhanced photocatalytic activity for methyl orange (MO) degradation under UV and/or visible light illumination as compared with P25 TiO$_2$ and pristine TiO$_2$. The optimized N-La-morph-TiO$_2$ nanostructures present a narrow pore size distribution with an average pore diameter of 8.7 nm and a high specific surface area (196 m$^2$ g$^{-1}$), which is nearly four times that of P25 TiO$_2$. The enhanced photocatalytic activity is attributed to the combination of the doped inorganic elements, the fine hierarchical and well-aligned porous nanostructures as analyzed by SEM, TEM, XPS, BET, UV-vis absorption and photodegradation tests. The promotional mechanisms and principles reported in this work are believed to have great significance in heterogeneous photocatalysis.

Keywords: Nanostructures; Inorganic compound; Sol-gel growth; Microstructure.
1. Introduction

The environmental pollution has become a main threat to human lives. Organic pollutants from pharmaceutical wastewater and textile industry represent serious problems, particularly in the developing countries [1]. At present, the traditional treatment technologies are still limited in eliminating organic pollutants via bio-treatment and physico-chemical methods because of the complex biological process or the non-renewable adsorption materials [2,3]. The semiconductor photocatalysis, which have potential advantages of low-cost, environmental friendly and superior ability in purifying water by decomposing organic compounds into CO₂ and H₂O at ambient conditions, has played a major role in eliminating toxic and recalcitrant organic compounds in waste water and drinking water [3-5]. Therefore, this advanced oxidation technique is expected to be both supplementary and complementary to the conventional approaches for the destruction or transformation of hazardous and complex chemical wastes [6]. So the development of semiconductor photocatalysts has been the focus of considerable attention and has made a great progress over the past decade. Despite this, further optimization and innovation are still in great demands [7].

Due to its non-toxicity, low cost, high stability and excellent oxidation capability, titanium dioxide (TiO₂) has long been regarded as one of the most promising photocatalysts and commonly applied to the area of environmental pollution control [8]. Photocatalytic processes involving TiO₂-based semiconductor particles have hence been proved to be advantageous in the photodegradation of organic pollutants [9]. However, with the wide band gap (3.2 eV), TiO₂ is only sensitive to the UV light which only accounts for a little portion (3~5%) of solar light in comparison to the visible region (~45%) [10]. Moreover, the rapid electron-hole recombination often leads to low quantum efficiency and weak photosensitivity [11]. It has attracted great attention in the past decades to fabricate those well designed TiO₂-based materials that can work in the visible-light region and have the improved separation efficiency of electrons and holes, leading to the higher photo-efficiency and photocatalytic activity [12,13]. A lot of efforts have been devoted to modify TiO₂ to visible light active photocatalysts, such as elements doping [14-18], dye-sensitization [19], junction’s formation with noble metal [20-22], and coupling with other narrow band gap semiconductors [12,23,24]. One of the efficient and economical approaches is to dope elements into TiO₂ to improve the photocatalytic performance [25]. For
example, when nitrogen (N) and lanthanum (La) elements are doped simultaneously into TiO$_2$, the introduced impurity energy levels could broaden the visible-light response of TiO$_2$ and favor the separation of electron-hole pairs, resulting in highly enhanced activity for organic pollutant degradation [26].

Templates are commonly employed to induce ordered nanostructures for desired properties [27]. Recently, various bio-materials sourced from different parts of insects or plants are studied as templates to fabricate biomorphic-inorganic nano- or micro-structures that express the properties of the subtle hierarchical structures of biological frameworks [28]. Butterfly wings, as is well known, have many unique and complex microstructures that can be used as bio-templates to fabricate inorganic materials [29,30]. What is more, because of the inherent photonic crystal structure, the quasi-butterfly wings’ structure is a better candidate of templates to enhance TiO$_2$ photocatalysis through intensifying light harvesting [31-33].

Here we report a simple one-pot synthesis that integrates good crystallinity, N-La co-doping, nanoparticles and bio-hetero-structures by directly using butterfly wings as bio-templates and cetyltrimethyl ammonium bromide (CTAB) as co-templates into a hierarchical 3D porous N-La-morph-TiO$_2$ photocatalyst. The N-La codoped TiO$_2$ nanoparticles were self-assembled to the butterfly wings and exactly duplicated the morphology of original butterfly wings, indicating the well-aligned 3D hierarchical porous structure. The photocatalytic activities of as-prepared 3D hierarchical ordered porous samples have been investigated under UV-visible and visible-light irradiation ($\lambda > 420$ nm) by using MO as the illustrating example, and the optimal sample showed a degradation rate constant of as high as 0.00612 min$^{-1}$ in visible range. With its high degradation efficiency, good stability, and broad active light wavelength, the N-La-morph-TiO$_2$ represents a low-cost, effective, environmental friendly and recyclable photocatalyst, which will have wide applications in photodegradation of various organic pollutants.

2. Experimental

2.1 Materials

Titanium (IV) isopropoxide, 97%, was obtained from Aldrich Chemical Co., Inc. All of the other reagents (analytical grade purity), such as Lanthanum nitrate ($\text{La(NO}_3\text{)}_3$), Titanium tetrachloride (TiCl$_4$), and Cetyltrimethyl ammonium bromide (CTAB), were purchased from Sinopharm Chemical Reagent Co., Ltd. and
used without further purification. The *Papilio maackii* Menetrie butterfly wings chosen as bio-templates were supplied by Beijing Jiaying Art Insect Kingdom Co., Ltd. Butterfly wings were cut into 20 mm × 20 mm pieces and cleaned by alcohol for several times, then dipped in 6 wt % HCl solutions for 3 h and then in 10 wt % NaOH solution at 45 °C for another 3 h. At last, the pieces were washed to neutral by water and air-dried [31].

2.2 Synthesis of the series morph-TiO$_2$ materials

In a typical synthesis procedure as described in a previous paper [32], 1 g CTAB, 0.039 g La(NO$_3$)$_3$ and 0.048 g (NH$_2$)$_2$CO were dissolved in 20 mL absolute ethanol with vigorous stirring for 2 h in room temperature at first. Then 0.44 mL TiCl$_4$ and 2.1 mL (CH$_3$CH$_3$CHO)$_4$Ti were added under the sufficient agitation condition. After the reaction mixture was further stirred for another 3 h, the as-prepared butterfly wings pieces were carefully dipped into the mixture followed by aging for two days in room temperature. Then the mixture was dried at 60 °C for 8 h followed by calcinations at 380 °C in air for 5 h to remove the organic templates, and finally N-La-morph-TiO$_2$ was obtained. In contrast experiments, the samples of different elements doped and templates used were synthesized under identical conditions, marked as N-La-morph-TiO$_2$, La-morph-TiO$_2$, N-morph-TiO$_2$, morph-TiO$_2$, N-La-TiO$_2$ and non-CTAB-TiO$_2$. Their composition details are shown in Table 1. As control sample, pristine TiO$_2$ was also prepared without N, La-codoping and butterfly wings as bio-template under the same conditions.

2.3 Characterization

X-ray diffraction (XRD) patterns were collected in θ-θ mode by an XD-3 X-ray diffract meter (Cu $K_a$ radiation, $λ$=1.5406 Å). The field emission scanning electron micrographs (FE-SEM) were obtained with a Hitachi s-4800 microscope by an accelerating voltage of 5 kV. The morphologies of samples were observed via transmission electron microscopy (TEM), and the images were obtained on a JEOL JEM-2100 electron microscope operating at 200 kV. Energy dispersive X-ray analysis (EDS) was used to confirm elemental components of the samples. The N$_2$ sorption measurement was performed using specific surface and pore size analyzer (JW-BK112, Beijing JWGB Sci. & Tech. Co., Ltd.,) and the samples were vacuum-degassed for 3 h at 300 °C to reduce the moisture before measurement. The specific surface area and pore size distribution were calculated with the Brunauer-Emmett-Teller (BET) and the Barrett-Joyner-Halenda (BJH) methods.
respectively. The UV-vis diffuse reflectance spectra of the solid powder materials were measured on a Perkin Elmer Lambda 950 UV-vis spectrophotometer (USA), equipped with an integrating sphere attachment. The photocatalytic tests were conducted by photochemical reaction cell from Yan Zheng Shanghai Experimental Instrument Co., Ltd. The X-ray photoelectron spectroscopy (XPS) measurements were done on an ESCALAB 250 Xi XPS instrument with Mg Kα source. Total organic carbon (TOC) analyzer (TOC-VCPH) was conducted to study the mineralization of MO.

2.4 Photocatalytic tests

Catalytic MO degradation was used to evaluate the photocatalytic performance of the as-synthesized samples. The quartz photochemical reactor was adopted in photocatalytic tests, containing 10 mg of catalysts, 50 mL of 5 mg/L MO or 10 mg/L phenol aqueous solution and a 300 W Xe lamp light source (a optical filter,). The cooling water circulator was installed to keep the reaction temperature constant. The pH of the aqueous solution was about 7.0. The suspension was stirred vigorously in the dark for 30 min to achieve adsorption-desorption equilibrium between the catalysts and the MO/phenol. After adsorption equilibrium, the concentration of suspensions was taken as the initial concentration and the Xe lamp was turned on to initiate the photocatalytic reaction. At regular interval, about 5 mL of the suspensions was taken and centrifuged at 10,000 rpm to obtain the supernatant solution. The absorbance of supernatant solution was analyzed by a UV-vis spectrophotometer (JASCO V-550, Japan) at its characteristic wavelength to determine the degradation yield. The rate of photocatalytic MO/phenol degradations was obtained by recording the changes in the absorbance of the reaction solution. The relationship between degradation percentages ($w\%$) and the light absorbance of MO/phenol is shown as.

$$ w\% = \frac{A_0 - A_t}{A_0} \times 100\% \quad (1) $$

Where $A_0$ is the initial absorbance of MO/phenol, $A_t$ is the absorbance of MO/phenol at different time.

3. Results and discussion

3.1 Nanocrystal structure, size and morphology Characterization
Fig. 1 shows the X-ray diffraction (XRD) patterns of morph-TiO\textsubscript{2}, N-morph-TiO\textsubscript{2}, La-morph-TiO\textsubscript{2}, and N-La-morph-TiO\textsubscript{2}. All the XRD data of the as-synthesized samples can be easily found to match well with the standard anatase TiO\textsubscript{2} pattern, with six main characteristic diffraction peaks located at 2θ values of 25.4°, 37.9°, 48.1°, 53.9°, 55.1° and 62.8° corresponding to (101), (004), (200), (105), (211), and (204) lattice planes of the anatase phase, respectively. No diffraction peaks could be attributed to the ion dopants, indicating no discrete impurity-phases formation in the doping process or cannot be detected due to its amorphous or microcrystalline nature [14]. The broad diffraction peaks can be attributed to the small grain size of TiO\textsubscript{2} nanoparticles. The crystal size calculated by the Scherrer formula (peak 101) using the diffraction peaks’ full width at half maximum (FWHM) values is about 8 nm [34]. The XRD results in Fig. S1 show that the templates don’t influence crystal phases of TiO\textsubscript{2} samples during preparation.

The morphology and microstructure of the samples were then examined by scanning electron microscopy (SEM). Fig. 2a and 2b show the fine structures of the original butterfly wings, while the porous architecture is composed of parallel ridges and longitudinal irregular frame. From Fig. 2c and 2d, it can be seen that N-La-morph-TiO\textsubscript{2} replica keep the original morphology of butterfly wings well, showing highly ordered hierarchical nanostructures and evenly distributed nanochannels with a diameter from 80 to 200 nm that can facilitate the adsorption and transfer of reactants or products. Meanwhile in Fig. 2c-d, it also can be found that the shrinkage of the overall size of the wings has happened during calcination. Fig. 2e and 2f reveal that the bio-hierarchical structure is composed of numerous aggregated TiO\textsubscript{2} nanoparticles (~8 nm) in the presence of the surfactant (CTAB) as co-templates. Pristine TiO\textsubscript{2} sample is agglomerated by small nanoparticles without bio-hierarchical structure as shown in Fig. S2.

The inner structures of N-La-morph-TiO\textsubscript{2} samples were further investigated by transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) measurements, as shown in Fig. 3. It can be seen from Fig. 3a and 3b that the microstructures of the as-synthesized samples are assembled by these aggregated TiO\textsubscript{2} nanoparticles with an average crystallite size of about 8 nm, which agrees well with SEM and the results calculated by Scherrer formula [24]. The spacing between lattices calculated from Figure 3c is 0.348 nm, which agrees with the lattice spacing of (101) of anatase TiO\textsubscript{2}. Energy-dispersive X-ray
spectroscopy (EDS) analysis (Fig. 3d) confirmed that the N-La-morph-TiO₂ sample is composed of Ti, La, O, and N.

3.2 XPS analysis and BET surface area

XPS analysis was further performed to obtain the atomic doping amount and chemical nature of as-synthesized N-La-morph-TiO₂ samples (Fig. 4). Pure pristine TiO₂ sample was conducted as a reference. The surveys spectra (Fig. 4a) demonstrate that the N-La-morph-TiO₂ sample contain La, N, Ti, O elements, confirming the successful doping of La and N. In Fig. 4 b-e, the high-resolution XPS scans over La 3d, N 1s, Ti 2p, and O 1s peak regions are presented. Two peaks around 458.5 and 465.1 eV were observed, which are assigned to the binding energy values for Ti 2p3/2 and Ti 2p1/2, respectively, indicating the characteristic value of Ti⁴⁺ in TiO₂. This is consistent with the XRD results. Compared with TiO₂, there is a negative shift of Ti 2p peaks for the N-La-morph-TiO₂ (458.2 and 464.5 eV). This negative shift is a consequence of the electronegativity effect due to the electronic interactions between Ti and N atoms as supported by the peak of O-Ti-N. As shown in Fig.4d, the binding energy peaks for N 1s were confirmed at 399.5 eV and 400.6 eV, respectively. The peak at 399.5 eV is ascribed to the N species located in the interstitial site in TiO₂ lattice, while another peak at 400.6 eV is attributed to substituted N in O-Ti-N, indicating that two forms of N such as interstitial N and substituted N coexisted in the N-La-morph-TiO₂ sample [35].

The two peaks at ca. 530.5 and 532.1 eV can be attributed to the bulk oxygen in the TiO₂ lattice (Ti–O) and surface hydroxyl oxygen in the form of M–OH, respectively. The surface hydroxyl groups of TiO₂ play an important role in enhancing photocatalytic activity, which are transformed into reactive hydroxyl radicals by trapping photogenerated holes. The peaks at ca. 835.1 and 851.3 eV in the samples could be ascribed to the main peaks of La 3d5/2 and La 3d3/2, respectively, and the peaks at 838.2 and 855.5 eV are the shake-up satellite peaks of La 3d5/2 and La 3d3/2, demonstrating that La element existed as forms of La³⁺[14]. The concentrations of La and N in N-La-morph-TiO₂ sample derived from XPS analysis were 1.90% and 0.91% (At.%), respectively.

The N₂ adsorption/desorption isotherm curves and pore size distributions of all TiO₂ samples are shown in Fig. S3. As shown in Fig. S3, all the samples have the isotherms of typical type IV curve with H1-type hysteresis loop [36]. The hysteresis loop at a lower relative pressure (0.65 < P/P₀ < 0.9) range is demonstrated the existence
of pores, and at the high relative pressure range \((0.9 < P/P_0 < 1)\) is associated with the empty spaces between nanoparticles [37], which proves that the hierarchical ordered porous structure exists in each as-prepared samples. The mean pore size distributions determined by the BJH method are shown in Fig. S3. It is clear that each sample has a narrow single-peak distribution. In addition, the BET specific surface area, the pore size distributions, and pore volumes derived from the nitrogen sorption/desorption isotherms are listed in Table 2. The BET specific surface area of morph-TiO\(_2\), N-morph-TiO\(_2\), La-morph-TiO\(_2\), N-La-TiO\(_2\), and N-La-morph-TiO\(_2\) nanostructure are calculated to be 206, 210, 185, 83, and 196 m\(^2\) g\(^{-1}\), respectively. There is little difference between doped samples and undoped sample about the specific surface area, indicating that the samples have a comparable surface area. It can be found that the surface area significantly increase compared with commercial P25 TiO\(_2\) and is nearly four times as larger than of P25 (50 m\(^2\) g\(^{-1}\)) [38].

### 3.3 UV–Vis spectra

The UV-vis absorption spectra of morph-TiO\(_2\), N-morph-TiO\(_2\), La-morph-TiO\(_2\), N-La-TiO\(_2\), and N-La-morph-TiO\(_2\) were characterized to testify the visible-light-harvesting ability (Fig. 5). It could be seen that all samples extend their absorption edge into the visible-light range [29]. What is more, the N-La-morph-TiO\(_2\) nanostructure shows the maximum red shift among four samples and the strongest absorption both in the UV and visible light range, indicating the much higher utilization of visible light than the single-doped and non-doped samples. The optical band gap \(E_g\) was calculated from the following equation (2)

\[
(\alpha h\nu)^{1/2} = A(h\nu - E_g) \quad (2)
\]

Where \(E_g\) is the band gap energy, \(A\) is a constant, \(\alpha\) is the absorption coefficient, and \(h\nu\) is the photon energy. \(E_g\) was obtained from the intercept of the tangent drawn to the cure according to the plot of \(\alpha h\nu^{1/2}\) versus \(h\nu\). The results are listed in Table 2. It can be found that a decrease order of morph-TiO\(_2\) (3.13ev) > N-morph-TiO\(_2\) (3.11ev) > La-morph-TiO\(_2\) (3.07ev) > N-La-TiO\(_2\) (2.99ev) > N-La-morph-TiO\(_2\) (2.92ev) in terms of Values of \(E_g\).

### 3.4 Photocatalytic properties

The observed photocatalytic activity of the N-La-morph-TiO\(_2\) is consistent with the optical absorption characteristics. The photocatalytic activities of TiO\(_2\)-based catalysts, including direct photolysis of MO, P25,
morp-TiO₂, N-morp-TiO₂, La-morp-TiO₂, and N-La-morp-TiO₂ were evaluated by photodegradation of MO in solution under UV-visible and visible-light irradiation. The MO degradation percentages over the catalysts under UV-visible-light irradiation were plotted in Fig. 6a, which reach about 5%, 17%, 21%, 26%, 66% and 100% for direct photolysis, P25, morph-TiO₂, N-morp-TiO₂, La-morp-TiO₂ and N-La-morp-TiO₂, respectively. Furthermore, mineralization of MO was investigated through TOC measurement. As shown in Fig. 6b, the as-fabricated N-La-morp-TiO₂ possessed the highest mineralization rate than that of others, in which 73.5% of MO could be degraded to CO₂ and H₂O molecules.

While in the case of visible-light irradiation as shown in Fig. 7a, P25 lost its catalytic activity heavily so that only about 5% of MO was degraded after 6 h illumination. However, morph-TiO₂, N-morp-TiO₂, La-morp-TiO₂ and N-La-morp-TiO₂ still remains about 10.9%, 17.9%, 38.1% and 89.9%, respectively. The photodegradation rates of MO over different samples are also characterized by corresponding first-order kinetics (k). The corresponding kinetic constant (k) and regression coefficients were calculated using the equation: 

\[ \ln \frac{C_0}{C_t} = kt \]  

with \( C \) and \( C_0 \) being the reaction concentration and the initial concentration of MO, respectively. The results were given in Fig. 7b. The linear relationship \( R^2>0.95 \) suggests that the reaction obeys a first-order equation. Fig. 7b shows that the degradation rate constants of morph-TiO₂, N-morp-TiO₂, La-morp-TiO₂ and N-La-morp-TiO₂ samples by visible-light irradiation. Significantly, the N-La-morp-TiO₂ samples exhibit the highest photocatalytic activity among all these synthesized samples.

Phenol was also used to evaluate the visible-light photocatalytic activity performance. N-La-morp-TiO₂ sample still exhibited the highest visible-light degradation efficiency than that of other samples, in which 92.5% of phenol could be degraded in 2.5 h (Fig. 8).

The influence of templates on the photocatalytic activity was investigated and plotted in Fig. S4. The MO removal percentages can reach only about 5.6% for pristine TiO₂, 24.0% for non-CTAB-TiO₂ and 39.1% for N-La-TiO₂, which suggests both of surfactant template and bio-template are crucial in the formation of hierarchical ordered porous structure, provided larger light harvesting surface, and enhanced photocatalytic activity.

Further studies show that the photocatalytic activity of the N, La co-doped TiO₂ varies with the N and La mole ratio, as depicted in Fig. S5 and Fig. S6. It can be seen that the photocatalytic degradation rate first increases
with the increase of the dopant concentration of N and reaches a maximum value at 0.085 wt \%, and then decrease with the continuous increase of the dopant concentration of N (Fig. S5). So the optimum additions of (NH\textsubscript{2})\textsubscript{2}CO in this research is 0.048 g. In the same way, the optimum additions of La(NO\textsubscript{3})\textsubscript{3} in this research is 0.039 g.

3.5 Photocatalytic mechanism

On the basis of experimental results and analysis, a probable visible-light photocatalytic mechanism for the photodegradation of MO by the N-La-morph-TiO\textsubscript{2} photocatalyst is proposed by the schematic diagram of the band structure as shown in Fig. 9. At first, La\textsuperscript{3+} ions could be uniformly absorbed on the TiO\textsubscript{2} particle surface in the form of Ti-O-La, leading to higher density of oxygen vacancies, anomalously high dielectric constant, and greater space-charge region [14,39]. In addition, the nitrogen-doped TiO\textsubscript{2} has great help for enhancing visible-light activity by mixing substitutional N 2\textit{p} states and O 2\textit{p} [15], which could be attributed to the new impurity energy level [40]. When TiO\textsubscript{2} were modified with La and N, it allows additional electronic transitions at lower energy. These additional transitions produce band tails that corresponds to the photoactivity shift to visible region that can be detected as broad shoulders which extends to wavelength longer than 400 nm. Secondly, La\textsuperscript{3+} acts as charge carrier trapping centers due to the existence of 4\textit{f} orbit. The trapped electrons can easily be transferred to O\textsubscript{2} adsorbed on the surface of TiO\textsubscript{2} to form superoxide anion radicals (O\textsubscript{2}\textsuperscript{•−}) and thereafter the La\textsuperscript{3+} ions could return to the original stable electronic structure. This process effectively postpones the recombination of electron-hole. The surface hydroxyl groups of TiO\textsubscript{2} are transformed into reactive hydroxyl radicals by trapping photogenerated holes according to XPS. So both La and N co-doping could be an effective way to further boost the photocatalytic activity and to reduce the recombination efficiency of photogenerated electron-hole pairs.

Thirdly, the hierarchical ordered porous structure and surface area can greatly enhance the opportunity for organic pollutant loading, adsorption, and transport [41]. These are very important factors that provide more active sites and lead to the stronger photocatalytic activity. The bio-hierarchical architectures of N-La-morph-TiO\textsubscript{2} porous materials have the high photocatalytic activity because of the high surface areas (196 m\textsuperscript{2} g\textsuperscript{−1}), which offers larger light harvesting surfaces and more active sites. The hierarchical porous structure offers an efficient transport pathway to facile dispersal of reactants and resultants, leading to easier photocatalytic reactions [42].

4. Conclusions
In summary, the bio-hierarchical architectures of N-La-doped TiO$_2$ materials with ordered microspores were successfully synthesized by an economic and practical sol-gel method with acid-base pair theory. The as-prepared N-La-morph-TiO$_2$ successfully replicated not only the outer but also the inner hierarchical porous structures of the butterfly wings, which provided larger light harvesting surfaces. Moreover, it also shows excellent photocatalytic activity under visible light illumination. The enhanced photocatalytic activity could be attributed to the 3D hierarchical well-aligned porous nanostructures, La-N co-doping and the large specific surface area. This work presents an efficient self-assembly of 3D hierarchical ordered porous structure using butterfly wings as bio-template and surfactant as co-template, which could be extended to the design of other hierarchical porous structures for the rational design and synthesis of highly effective photocatalyst by co-templates.

Acknowledgements

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:

References


Table 1 Compositions of reactants and final products

<table>
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<th>Samples</th>
<th>N source</th>
<th>La source</th>
<th>CTAB</th>
<th>Butterfly wing</th>
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<td>0.039g</td>
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<td>1g</td>
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<tr>
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<td>0</td>
<td>1g</td>
<td>0.1g</td>
</tr>
<tr>
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<td>0</td>
<td>1g</td>
<td>0.1g</td>
</tr>
<tr>
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<td>0.039g</td>
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Table 2 Physical Characteristics of samples

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<th>Av Pore size (nm)</th>
<th>pore volume (cm³/g)</th>
<th>Band gap (eV)</th>
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<td>6.49</td>
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<td>83</td>
<td>5.10</td>
<td>0.17</td>
<td>2.99</td>
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Figure captions

**Fig. 1** Standard XRD pattern of anatase TiO$_2$ (JCPDS No. 21-1272) and XRD patterns of morph-TiO$_2$ (a), N-morph-TiO$_2$ (b), La-morph-TiO$_2$ (c), N-La-morph-TiO$_2$ (d).

**Fig. 2** FE-SEM images of original butterfly (a, b), N-La-morph-TiO$_2$ (c, d), and N-La-morph-TiO$_2$ photocatalyst at high magnifications (e, f).

**Fig. 3** TEM images (a, b), HRTEM images of N-La-morph-TiO$_2$ (c) and Corresponding EDS pattern (d).

**Fig. 4** XPS (wide) spectra of TiO$_2$ and N-La-morph-TiO$_2$ (a), high resolution XPS spectra of Ti 2p of TiO$_2$ and N-La-morph-TiO$_2$ (b), High resolution XPS spectra of O 1s (c), N 1s (d), and La 3d(e) of N-La-morph-TiO$_2$.

**Fig. 5** UV-vis absorption spectra of morph-TiO$_2$, N-morph-TiO$_2$, La-morph-TiO$_2$, N-La-TiO$_2$, and N-La-morph-TiO$_2$.

**Fig. 6** Photocatalytic degradation rate (a) and TOC removal (b) of MO (5 mg·L$^{-1}$) over the different catalysts in aqueous solution under UV-visible light irritation.

**Fig. 7** Photocatalytic degradation rate (a) and apparent reaction rate constants (b) of the different catalysts in aqueous solution under visible light irritation.

**Fig. 8** Photocatalytic degradation rate of phenol on different samples under visible light irritation.

**Fig. 9** The band structure of N-La-morph-TiO$_2$ and possible photocatalytic mechanism.
Fig. 1
Fig. 2
Fig. 3

(a) Image showing a magnification of 50 nm.
(b) Image showing a magnification of 20 nm.
(c) Image showing a magnification of 5 nm with a 0.348 nm detail.
(d) EDX spectrum with peaks for Cu and Ti.

The images illustrate the nanoscale features and chemical composition of the sample.
Fig. 4
Fig. 5

- a: morph-TiO$_2$
- b: N-morph-TiO$_2$
- c: N-La-TiO$_2$
- d: La-morph-TiO$_2$
- e: N-La-morph-TiO$_2$

Absorbance (a.u.) vs. Wavelength (nm)
Fig. 6

(a) Degradation percentage (%)
- Direct Photolysis
- P25 TiO$_2$
- morph-TiO$_2$
- N-morph-TiO$_2$
- La-morph-TiO$_2$
- N-La-morph-TiO$_2$

(b) TOC removal of MO (%)
- Direct photolysis
- P25 TiO$_2$
- N-morph-TiO$_2$
- La-morph-TiO$_2$
- N-La-morph-TiO$_2$
Fig. 7

(a) Degradation percentage (%) vs. Time (min) for various TiO$_2$ samples.

(b) Rate constant ($10^{-3}$ min$^{-1}$) vs. TiO$_2$ samples with their corresponding $R^2$ values.
Fig. 8
Visible Light

Degradation

MO

La^{3+}

TiO_{2xN_x}

e^-

e^-

e^-

CB

VB

h^+
h^+
h^+

e^-

e^-

e^-

O_2

O_2^-

\cdot OH^-

\cdot OH^-

OH^-

Fig. 9