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N and Ti³⁺ co-doped 3D anatase TiO₂ superstructures composed of ultrathin nanosheets with enhanced visible light photocatalytic activity†

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Structure-maneuvering and impurity element-doping are considered two of the most effective ways to enhance the photocatalytic activity of TiO₂ catalysts. A facile solvothermal strategy was developed to simultaneously realize these two superiorities. The experimental results reveal that the as-prepared TiO₂ exhibits a three-dimensional mesoporous hierarchical superstructure self-assembled by ultrathin nanosheets, which endows the product with a high surface area (~240 m² g⁻¹) and abundant mesopores resulting in high adsorption capacity for pollutant molecules and high absorption ability for incoming light. N doping and concomitant Ti³⁺ incorporation systematically account for reduction of the bandgap and thus realize vis-photocatalytic activity. As expected, the as-prepared TiO₂ catalyst exhibits good photocatalytic activity under visible light irradiation.

Introduction

With the increasing interest in the field of clean energy and the urgent desire for environmentally friendly techniques, efficient application of solar energy has become a hot spot in green chemistry, electrical energy and many other fields of great potential prospects.¹ Photocatalysts, to which researchers have paid great attention, can absorb radiated light, convert solar energy into electrical or chemical energy and thus have been effectively applied in many fields, *e.g.* photodegradation of organic pollutants, solar water-splitting, dye-sensitized solar cells, and photoreduction of CO₂.² Furthermore, all of these applications feature low cost, high efficiency and convenient application processes.

Since Fujishima and Honda achieved hydrogen production from water-splitting with TiO₂ in 1972,³ it has been considered to be one of the most useful semiconducting metal oxides for applications ranging from sensors to photonic crystals, energy storage, and photocatalysis.⁴ However, TiO₂ suffers from low solar light absorption due to its large bandgap (~3.2 eV) and relatively fast electron-hole recombination (ns–μs domain),⁵ which limits its photocatalytic activity efficiency. Therefore, how to improve the photocatalytic activity has long been a subject of great importance and potential. It is generally agreed that the photocatalytic performance of TiO₂ can be improved by

several strategies involving: (1) structure maneuvering, (2) impurity element doping, and (3) forming a semiconductor heterojunction. The structure-maneuvering strategy achieves the improvement of photocatalytic activity through optimization of the useful structural properties of the TiO₂ photocatalyst, *e.g.* large surface area and abundant pores, well-facilitating adsorption capacity and the superior light harvesting ability derived from multi-reflection of the incoming light.⁶ In contrast, the latter two strategies realize the improvement by changing the electric and chemical nature of the TiO₂ catalyst. The impurity doping strategy improves the photocatalytic activity by either introducing sub-bandgap states or reducing the bandgap width to extend the light absorption onset of TiO₂.^{4b} Forming a semiconductor heterojunction by coupling with a secondary substance (noble metals, other semiconductors and so on) can improve photocatalytic efficiencies by enhancing the utilization of sunlight or improving the separation/transportation of electron-hole pairs.^{4c} Then, what if these two strategies were simultaneously realised by using an integrated catalyst. Therefore, designing materials of 3D hierarchical structures combined with impurity doping has become a hotspot in expectation of realizing synergistic application efficiency.⁷

Among the numerous metal (Au, Ag, Fe, Zn, Co, *etc.*)⁸ or nonmetal ion (F, C, S, N, *etc.*)⁹ doping, N and Ti³⁺ doping have been employed and considered to be two of the most effective ways to improve the photocatalytic activity under visible light illumination. N doped TiO₂ realises the improvement due to narrowing of the bandgap through localized N 2p states above the valence band (VB) maximum and thus expands the light response range to the visible light region.¹⁰ Ti³⁺ self-modified TiO₂ achieves the same purpose due to incorporation of Ti³⁺

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states which results in an isolated band in its forbidden gap and thus realize a greater response to visible light radiation.¹¹ However, there still remain obstacles to be overcome not only in preparation techniques for scale-up fabrication but also in functional mechanisms for deeply understanding the application process. In respect of preparation techniques, a commonly adopted strategy for N doping is introducing N atoms into substitutional sites in the crystal structure of TiO₂ by calcination in an ammonia atmosphere or by a wet chemical route which needs to undergo high temperature treatment.^{10b,12} However, incorporating Ti³⁺ ions is usually achieved by reduction of Ti⁴⁺ to Ti³⁺ under harsh reducing conditions such as high temperature in reducing gas (H₂ or CO) using expensive special equipment, *e.g.* hydrogen plasma treatment,¹³ Ar⁺ ion bombardment,¹⁴ and thermal treatment under vacuum¹⁵ or a reducing atmosphere.¹⁶ Additionally, oxygen vacancies (Ti³⁺) are usually not stable even in air and could be easily oxidized to Ti⁴⁺ within a short period. Hence, it remains a great challenge to develop facile synthetic routes for preparing N doped TiO₂ and Ti³⁺ doped TiO₂, respectively. Not to mention fabricating a TiO₂ catalyst simultaneously co-doped with N and Ti³⁺ impurities and exploiting its properties, since it seems they could not be realised simultaneously by presently existing methods. In respect of functional mechanisms, Asahi and co-workers deem that the doped N narrows the bandgap of TiO₂ and thus makes it active in the visible light region.^{9a} However, Ihara *et al.* believe it is the oxygen vacancies that account for the visible light activity, N only enhanced the stabilization of the oxygen vacancies.¹⁷ Therefore, it is still an open question how N and oxygen vacancies function in improving the vis-photocatalytic activity.

Herein, we present a facile one-pot synthetic method for synthesizing a novel 3D hierarchical TiO₂ photocatalyst simultaneously co-doped with N and Ti³⁺ species (hierarchical co-doped TiO₂, HCDT), thus simultaneously realising structure-manoeuvring and impurity-doping. The feasibility of the vis-photocatalytic activity of the as-prepared sample was experimentally proved, and a possible photodegradation mechanism was also proposed. To the best of our knowledge, this is the first report on this kind of TiO₂. The as-prepared TiO₂ photocatalyst can efficiently overcome the drawbacks mentioned above to some extent. The 3D hierarchical structure composed of ultrathin nanosheets could not only supply a high surface area for adsorbing as much pollutant molecules as possible and a framework with abundant pores for accelerating the mass transfer rate in the photodegradation system, but also achieve higher light harvesting ability through multi-reflection of the incoming light. The concomitant doping of N and Ti³⁺ results in improved vis-photocatalytic activity due to the reduced bandgap. Both N and Ti³⁺ doping function systematically and synergistically to reduce the bandgap of the as-prepared HCDT to a lower level and thus result in higher photocatalytic activity under visible light illumination. We believe the preparation method introduced in this work provides a green, effective way for the rational design of 3D hierarchical anatase TiO₂ superstructures with both non-metal doping and self-component doping. The proposed photocatalytic mechanism provides a

new perspective for designing novel photocatalysts of higher activity.

Experimental

Materials and preparation

Materials. Titanium(IV) isopropoxide (TIP, >97%), isopropanol (>99.9%), ethanol (>99%) and diethylenetriamine (DETA, 99%) were used as purchased from Sigma-Aldrich. Ultrapure deionized water (>18 MΩ cm⁻¹) from a Millipore Milli-Q system was used throughout the experiments.

Preparation. In a typical experimental procedure, 0.03 mL DETA and 0.1 mL H₂O were injected into 50 mL isopropanol under magnetic agitation. After agitating for 5 min, the solution was put into an ultrasonic bath and 1 mL TIP was added dropwise into the solution mixture under ultrasonication. 10 min later, the solution mixture was transferred into a 100 mL Teflon pot and sealed tightly in a stainless steel bomb. The sealed bomb was then heated to 200 °C at an increasing rate of 2 K min⁻¹ and held for 20 h. After cooling to room temperature, the products of the solvothermal reaction were washed with absolute ethanol and distilled water three times, respectively. The precipitates were then collected and vacuum dried at 80 °C overnight and kept in a desiccator for further use.

Characterization

The morphology of the products was obtained on a field-emission electron microscope (SU8020, Hitachi, Japan) with an accelerating voltage of 3 kV. The samples were free of gold-sputtering. Higher resolution transmission electron microscopy (HRTEM) was performed on a transmission electron microscope (JEOL, JEM-2100, Japan) operated at 200 kV. The X-ray diffraction (XRD) patterns were recorded on a PANalytical X'Pert Pro X-ray diffractometer (PANalytical, The Netherlands) equipped with Al Kα radiation (40 kV, 200 mA). Nitrogen adsorption-desorption isotherms were measured with a Micromeritics ASAP2000 V3.01 analyser. The Brunauer-Emmett-Teller (BET) specific area was calculated using the BET equation. The pore size distribution was obtained using the Barrett-Joyner-Halenda (BJH) equation. The X-ray photochemical spectra (XPS) were obtained on a Thermo SCIENTIFIC ESCALAB 250 equipped with Al-Kα radiation. The electron paramagnetic resonance (EPR) spectra were obtained using a JES-FA200 X-band spectrometer. The UV-vis diffuse reflectance spectra (DSR) were examined on a Hitachi U4100 spectrometer.

Photocatalytic activity

The visible light photocatalytic activity of the product was first examined by degradation of azo-dye Rhodamine B (Rh.B) at room temperature in a custom made 100 mL quartzose reactor. A Xe lamp as a sunlight simulator was placed 10 cm beside the reactor as the light source with a glass optical filter inserted to cut off the short wavelength components ($\lambda < 400$). 0.01 g as-prepared HCDT was added into 50 mL Rh.B solution (3 mg L⁻¹) in the reactor and magnetically stirred in the dark at a speed of 800 rpm for 1 h to ensure the adsorption equilibrium and

eliminate the diffusion effects. Then, the solution mixture was irradiated under visible light ($\lambda > 400$) to determine its vis-photocatalytic activity. The samples were taken at an interval of 20 min, filtered through 0.2 μm cellulose acetate membranes and detected by using a UV-vis spectroscope (Hitachi U4100, Japan). The vis-photocatalytic activity of DeGussa P25 was obtained according to the same protocol as for HCDT. Considering that degradation of organic dyes is believed to be significantly influenced by various factors such as the dye sensitization of catalyst particles,¹⁸ formic acid was chosen as another model pollutant molecule due to the fact that its degradation occurs without any intermediate species. The degradation procedure is the same as that for degradation of Rh.B, the initial concentration of formic acid was 5 mg L^{-1} . The concentrations of the formic acid after adsorption and photo-degradation were determined using an Agilent 1200 LC system consisting of a quaternary pump and a UV/vis detector set at 210 nm. In order to investigate the stability of the as-prepared HCDT, cycling degradation of formic acid was carried out abiding by the same procedure as described above. After every cycle of degradation treatment (1 h for adsorption and 3 h for vis-photodegradation), the solution mixture was centrifuged at a speed of 10 000 rpm. The supernatant was sampled to determine the residue concentration of the formic acid, the precipitate was used for the following cycle of degradation treatment after being washed with deionized water 3 times.

Results and discussion

The morphological and structural features of the as-prepared HCDT were examined by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). As shown in Fig. 1a, it is obvious that the spherical 3D superstructures are quite uniform, with an average size of ~ 600 nm (Fig. 1a). From the FESEM image (Fig. 1b), it can be seen that the product appears as a 3D hierarchical superstructure constructed by nanosheet (NS) constituents that are clearly visible and shown to adopt random orientations. Also evidenced from Fig. 1b is that the NSs appear quite thin at the nanometer level. The TEM image (Fig. 1c–f) further proved the structure and constituent details of the products. Consistent with the SEM results, the TEM image in Fig. 1c shows very thin NSs with about 100 nm in length and 40 to 80 nm in width. The higher magnification TEM image in Fig. 1d indicates that the NSs have turned-up edges. As seen in Fig. 1e, the high resolution TEM image of the turned-up edges of the NSs from the marked area (red frame) in Fig. 1d shows the lattice fringes with a spacing of 0.35 nm, corresponding to the $d(101)$ of the anatase phase, which indicates that the NSs grew along the $[101]$ direction. Based on the information obtained from TEM (Fig. 1d–e), the immediate thickness of the constituent NSs was estimated to be 0.4–0.5 nm approximating to the height of one layer of the $[\text{TiO}_6]$ octahedron (0.38 nm), which suggests that the obtained TiO_2 NSs are single layered. High-resolution TEM analysis was also employed to determine the crystal facets of the as-prepared sample. Fig. 1f exhibits the lattice fringes of a part of a single NS (green frame in Fig. 1d). It shows well resolved lattice fringes with a spacing

Fig. 1 SEM (a and b), TEM (c and d) and high-resolution TEM (e and f) images of the as-prepared HCDT. Note: (e and f) exhibit the enlarged SEM images of the corresponding marked areas (red frame and green frame) in (d), respectively.

of 0.35 nm, which is attributed to the spacing of the (101) planes of anatase TiO_2 , indicating good crystallinity of the NSs.

The X-ray diffraction (XRD) pattern and Raman spectrum were obtained to determine the crystallinity of the HCDT. Fig. 2a shows the XRD pattern of the as-prepared HCDT, which demonstrates strong and clear diffraction peaks matching exactly with the tetragonal anatase phase (space group: $I4_1/amd$; tetragonal symmetry, $a_0 = 3.7770$ Å and $c_0 = 9.5010$ Å, JCPDS file no. 89-4921), indicating a phase-pure material. The diffraction peaks with 2θ values of 25.35, 37.01, 37.85, 48.14, 53.97, 55.19, 62.81, 68.88, 70.46, 75.21, and 82.87 correspond to the (101), (103), (004), (200), (105), (211), (204), (116), (220), (215), and (224) crystal faces of anatase TiO_2 , respectively. To further confirm the crystalline structure of the as-prepared sample, Raman spectroscopic analysis was performed (Fig. 2b). The result is in good agreement with the XRD analysis. It can be observed that peaks centered at 146 cm^{-1} (Eg, very strong), 198 cm^{-1} (Eg, weak), 398 cm^{-1} (B1g, medium), 519 cm^{-1} (A1g, medium), and 640 cm^{-1} (Eg, medium) are present, which can be attributed to the characteristic vibrations of the anatase lattice.¹⁹

In order to investigate the detailed elemental composition and distribution of the as-prepared HCDT, energy dispersive X-ray (EDX) analysis was carried out. The energy dispersive spectrometry (EDS) analysis of the sample (Fig. 3a) exhibits strong Ti and O signals, as well as relevantly weak signals of the N element indicating that the as-prepared HCDT mainly contains Ti, O, and N. From the elemental mapping, it can be observed

Fig. 2 XRD pattern (a) and Raman spectra (b) of the as-prepared HCDT.

that the Ti, O and N are well defined with sharp contrast. The profile of N is close to those of Ti and O, indicating that N is distributed uniformly throughout the whole sample. The above analysis verified that our method is effective in introducing the N element into TiO_2 .

The surface chemical composition and states of the as-prepared TiO_2 superstructures were analyzed by X-ray photoelectron spectroscopy (XPS). As shown in Fig. 4a, the characteristic peaks of titanium, oxygen, carbon, as well as nitrogen can be seriously observed in the survey spectrum of the sample, further revealing the presence of N. The binding energy of Ti 2p, O 1s, N 1s, and C 1s is 458.5, 531, 400, and 284 eV, respectively, which are in good agreement with the reported data of other studies.²⁰ The C 1s peak at 284 eV is attributed to the residual carbon of the product and the adventitious hydrocarbon from the XPS instrument itself. The atomic concentration of N in the sample was determined to be about 1.85% according to the integral area of the peaks.

The high resolution XPS spectra of Ti 2p (Fig. 4b) were obtained to investigate the presence and chemical states of Ti^{3+} ions in the sample. It can be seen that the Ti 2p spectra exhibit a slight deformation in the relevantly lower side of binding energy, indicating that the chemical states of Ti atoms in the sample are different from that in the raw TiO_2 samples.²¹ Two peaks at the binding energies of 458.33 eV and 464.35 eV, which

Fig. 3 EDS spectrum (a), selected SEM image, and the corresponding EDX mapping images of titanium, oxygen, and nitrogen elements.

can be ascribed to the Ti 2p_{3/2} and Ti 2p_{1/2}, can be observed in the high resolution Ti 2p spectrum of the sample. Especially, the Ti 2p_{3/2} peak was well fitted by the two peaks of Ti^{4+} (458.52 eV) and Ti^{3+} (457.91 eV), which clearly demonstrates the existence of Ti^{3+} ions. The molar ratio of $\text{Ti}^{3+}/(\text{Ti}^{3+} + \text{Ti}^{4+})$ calculated from the XPS peak areas of Ti^{3+} and Ti^{4+} is about 12.5%. Since

Fig. 4 The survey XPS spectra of the as-prepared HCDT (a), and deconvolution of Ti 2p (b), N 1s (c), and O 1s peaks.

Ti^{3+} is more hydrophilic than Ti^{4+} , O_2 and H_2O molecules are more easily adsorbed on the surface of TiO_2 , thus facilitating the formation of surface OH groups.²² Fig. 4c shows the high resolution XPS spectra of the N 1s region. The peak centered at around 400.2 eV is related to the oxidized nitrogen such as Ti–O–N or Ti–N–O bonding, indicating that the N element in the sample appears as anionic N^- in the interstitial nitrogen.^{20,23} The O 1s XPS spectra are shown in Fig. 4d; two deconvolution peaks centered at 529.7 eV and 531.48 eV can be ascribed to Ti–O–Ti and surface OH species, respectively, which indicate that the as-prepared sample has many more OH species on the surface.

To further identify the presence of Ti^{3+} ions, low temperature electron paramagnetic resonance (EPR) was performed. Fig. 5 shows the low temperature EPR result of the as-prepared HCDT sample. It can be observed that two peaks appear at $g = 1.993$ and 2.002, which can be attributed to the presence of Ti^{3+} and oxygen vacancies, respectively. This result is in good accordance with the previous report that oxygen vacancy has a g -value of 2.004 and paramagnetic Ti^{3+} at 1.94–1.99.²⁴ Also, it is known that the surface Ti^{3+} is prone to be oxidized by oxygen and is not stable under illumination in air or water, and the EPR signal of the surface Ti^{3+} was reported to reside at $g = 2.02$ corresponding to O^{2-} .²⁵ So the absence of such a peak in the figure indicates that Ti^{3+} mainly exists in the bulk of the HCDT sample, which reinforces its high stability in air or water.

In general, because the photocatalysis of TiO_2 is a surface-based process, it is a necessity to investigate the surface condition and textural state of the prepared sample. Thus N_2 adsorption–desorption isotherms were obtained to determine the specific surface area, pore volume, and pore size distribution of the sample. Fig. 6 shows the N_2 adsorption–desorption isotherms and the pore size distribution of the as-prepared HCDT. It gives a typical type IV curve with an H3 hysteresis loop according to the IUPAC classification, indicating a slit-type mesoporous structure fabricated by sheet-like particles.²⁶ The relatively narrow pore size distribution calculated using the

Fig. 6 N_2 adsorption–desorption isotherm and pore size distribution curves (inset picture) of the as-prepared HCDT.

Barrett–Joyner–Halenda (BJH) method from the two branches of the isotherm indicates that most of the pores fall in the range of 2.1–4.9 nm. These types of pores were derived from the removal of organic moieties in the samples by calcination treatment. It can be also noticed there are other types of pores around ~12 nm, which could be the distance between the nanosheet subunits. Such an abundant porous structure gives rise to a very high specific surface area of up to $244.7 \text{ m}^2 \text{ g}^{-1}$, as calculated by the Brunauer–Emmett–Teller (BET) method. This result is much higher than other reported 3D hierarchical superstructures, most of which fall below $100 \text{ m}^2 \text{ g}^{-1}$.²⁷ Such a high specific surface area and abundant pores can facilitate photocatalysis in three aspects: (1) adsorb as much pollutant molecules as possible; (2) accelerate mass transfer in the reaction system; and (3) make more surface reactive sites accessible for incoming light and therefore generate more reactive species for degradation of pollutants.

In order to determine the responses of the as-prepared HCDT to light irradiation, UV/vis diffuse reflectance spectra (UV-vis DRS) were obtained. Fig. 7 shows the UV-vis DRS of the as-prepared HCDT sample and Degussa P25 TiO_2 . Compared to P25 TiO_2 , the prepared sample exhibits an apparent absorption in the visible light region between 400 and 600 nm, which can be ascribed to mixing of the N 2p and O 2p states on the top of the valence band, thus forming a new mid-gap state leading to visible light responses. As expected, DETA performed as a good nitrogen source for N doping, and the light yellow product may have visible-light photocatalytic activity. There might exist another reason for the increased response to the visible light illumination, which lies in Ti^{3+} self-doping. The introduced Ti^{3+} ions can form a new sublevel state below the conduction band and thus generate more electrons and holes,²⁸ which combined with the mid-gap state induced by N doping, synergistically reduce the bandgap to a lower level and thus further improve the active response to visible light radiation. What is more, it is reported that N-doped anatase TiO_2 contains thermally stable single N atom impurities either as charged diamagnetic N^-

Fig. 5 Low temperature EPR result of the as-prepared HCDT and P25.

Fig. 7 The UV-vis diffuse reflectance spectrum of the as-prepared HCDT and the Degussa P25. The inset picture shows the estimated bandgap of the HCDT using Tauc's plot.

centers or as neutral paramagnetic $N^{\bullet}$ centers. Both of the N centers give rise to localized states in the bandgap of the oxide, thus accounting for the related reduction of absorption band edge, whereas, the N -induced defect states for the diamagnetic charged species N^{-} are slightly higher in energy than the corresponding singly occupied levels for the paramagnetic neutral species ($N^{\bullet}$). Upon reduction, oxygen vacancies form and transfer electrons from Ti^{3+} ions to the $N^{\bullet}$ with the formation of Ti^{4+} and N^{-} , thus realising further improvement of vis-photocatalytic activity.²⁹ In contrast, N also has the ability to stabilize oxygen vacancies. The electron transference circulates systematically as illustrated by eqn (1), which ensures long-term function of the vis-photocatalysis. The possible photocatalytic mechanism of the prepared co-doped sample was proposed as illustrated in Scheme 1.

Scheme 1 Proposed photocatalytic mechanism of the as-prepared HCDT.

The optical band gap (E_g) of the synthesized sample can be estimated based on the Tauc method (the following expression):³⁰

$$(\alpha h\nu)^{1/n} = B(h\nu - E_{bg}) \quad (2)$$

where α is the absorption coefficient, $h\nu$ is the incident photon energy, E_{bg} is the band gap energy, and B is a constant related to the effective masses of charge carriers associated with valance and conduction bands. The value of n depends on the type of interband transition: $n = 2$ for a direct transition, while $n = 1/2$ for an indirect transition. The adsorption coefficient is plotted against $(h\nu - E_{bg})$.³¹ As shown in the inset picture in Fig. 7, two absorption thresholds located at *ca.* 2.98 eV and 2.81 eV can be distinguished, both of which are lower than the typical E_{bg} of traditional anatase TiO_2 (~ 3.2 eV). The decrease of the E_{bg} by about 0.22 eV to 2.98 eV is related to the onset of the absorption at short wavelengths near the UV region, whereas the other decrease by about 0.4 eV to 2.81 eV corresponds to absorption in the visible spectral region.

The photocatalytic activity of the prepared sample was examined by using decomposition of an azo-dye Rhodamine B (Rh.B) and formic acid in aqueous solution as a function of irradiation time under visible light ($\lambda > 400$ nm) illumination. A well-known highly efficient commercial titania photocatalyst, Degussa P25, was used for comparison. As shown in Fig. 8a, it is clear that the concentration decrease of Rh.B in the dark reveals that the HCDT possesses stronger adsorption capacity (32.4% of the total amount) than that of P25, which is due to the privilege of hierarchical porous structure and large surface area of the as-prepared HCDT. Under visible light irradiation, the target pollutant was almost completely decomposed in 160 min. In contrast, under the same experimental conditions, P25 not only possesses lower adsorption capacity (13.7%), but also exhibited much weaker vis-photocatalytic activity (28.3%) than HCDT. As shown in Fig. 8b, the same degradation pattern was also observed for formic acid. After adsorption for 1 h and the following illumination treatment under visible light for 3 h, very little formic acid (<11%) was removed by P25, including adsorption removal of 5.6%. In contrast, the prepared HCDT exhibited an improved adsorption ability (12.6%) and a more significant degradation efficiency under visible light irradiation (>51%). Fig. S1† shows the cycling degradation efficiency of the

Fig. 8 Degradation of Rh.B (a) and formic acid (b) ($(C_0 - C)/C_0$ vs. radiation time) under visible light illumination ($\lambda > 400$) catalyzed by as-prepared HCDT and Degussa P25 nanoparticles.

as-prepared HCDT, it can be observed that after 5 cycles of treatment, the serviceability of the washed HCDT remained satisfactory. The degradation efficiency was 94.3% of the first cycle. This result demonstrates that the as-prepared HCDT showed stable vis-photocatalytic activity during the cycling processes. The EPR analysis (Fig. S2†) also reveals that the self-doped Ti^{3+} and oxygen vacancies remain stable after 5 cycles of the photodegradation process. Based on the above experimental results, it is clear that the as-prepared HCDT possesses high visible light photocatalytic activity, which echoes the result of UV-vis DRS that the as-prepared HCDT exhibits a strong response under visible light illumination. Also, the unique NS constructed hierarchical structures realize multiple reflections of the incoming light, which can maximize light harvesting ability, and therefore improve the photocatalytic responses (production of photogenerated electrons and the holes) functioning in the photocatalytic reactions. In general, there exist four reasons for the superior vis-photocatalytic activity of the as-prepared HCDT according to the above-mentioned discussions: (1) incorporation of N extends the absorption edge to the visible light region, and thus endows the HCDT with vis-photocatalytic activity; (2) concomitant Ti^{3+} helps to reduce N^+ to diamagnetic charged N^- which is slightly higher in energy, thus realising improvement of vis-photocatalytic activity; (3) the unique 3D hierarchical structure constructed by ultrathin NSs provides multiple reflections of the incoming light, which maximize light harvesting ability and thus increase the photo-responses of producing more photogenerated electrons and the holes accounting for the photodegradation reaction; (4) the high surface area and abundant pore networks enable the HCDT to adsorb more pollutant molecules participating in the photo-reactions on the surface of the catalyst and to accelerate the mass exchange rate through porous texture.

Conclusions

In summary, a facile one-pot approach for synthesizing 3D hierarchical anatase TiO_2 superstructures constructed by ultrathin nanosheets (0.4–0.5 nm thickness) has been developed. What is more interesting is that the as-prepared TiO_2 was simultaneously doped with N and Ti^{3+} , both of which contribute to improving the photocatalytic activity of TiO_2 under visible light illumination. The unique 3D hierarchical mesoporous superstructure endows the samples with a high specific surface area of $\sim 240 \text{ m}^2 \text{ g}^{-1}$. Inspired by the unique structure and the inherent electronic properties of the narrowed bandgap, we evaluated its photocatalytic activity under visible light illumination by photocatalytic degradation of two model organic pollutants (Rh.B and formic acid). The results show that the as-prepared N and Ti^{3+} co-doped 3D hierarchical anatase TiO_2 catalyst manifests an excellent vis-photocatalytic activity, which was derived from its superior light harvesting ability, narrowed bandgap from the co-doping strategy, and advanced adsorption capacity and accelerated mass transfer rate. Besides its superior vis-photocatalytic activity, it is reasonable to anticipate that the as-prepared anatase TiO_2 with unique structural and compositional properties will realize multiple and prospective

applications in lithium ion battery electrodes, dye-sensitized solar cells, energy storage, and many other relevant fields.

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