Hierarchical rattle-like N-doped anatase TiO₂ superstructure: one-pot synthesis, morphological evolution and superior visible light photocatalytic activity†

Guoliang Li,* Gang Li, Jie Li and Guibin Jiang

Morphology control and impurity doping have been considered as two potent strategies for improving the photocatalytic activity of TiO₂ photocatalysts. Here, a one-pot solvothermal method was developed for the preparation of N doped rattle-like TiO₂ with spherical mesoporous cores and hierarchical shells composed of ultrathin nanosheets to simultaneously realize those two strategies. This method involves the formation of nascent nanoparticles in a sonication treatment before the solvothermal reaction, and the morphology evolution from condensed spheres to core@shell structures, and eventually to a core@void@shell architecture, switched by the crystalline nature of the products during the solvothermal reaction. The as-prepared sample features a high surface area (258.5 m² g⁻¹), abundant porous texture and a unique rattle-like structure, which allows for multiple reflections of incoming light and thus optimizes light absorption ability. The concomitant N doping helps to extend the light absorption edge to the visible light region, optimizing the utilization of solar energy. As expected, when used as a photocatalyst for degradation of Rhodamine B and formic acid under visible light irradiation, the as-prepared N doped rattle-like TiO₂ exhibited superior visible light photocatalytic activity thanks to its unique structure and specific N doping.

1. Introduction

It has been widely recognized that the properties and performances of nanomaterials are strongly related to their morphologies, sizes, and structures.¹ Recent progress in nanostructure fabrication has made it possible to controllably synthesize inorganic colloidal particles with complex morphologies, compositions, and even internal textures. In particular, inorganic nanomaterials with 3D hierarchical structures have received rapidly increasing attention, since they exhibit great potential in various fields of application, e.g. adsorption, separation, photocatalysis, biology, electronics, sensors, dye-sensitized solar cells, and lithium ion storage.² Among the reported 3D inorganic nanomaterials, the kind of so-called core-shell structures, which are usually produced by coating or encapsulating a core particle within a shell to endow them with diverse functions including magnetic, optical, catalytic, and biological features, have been extensively exploited owing to their unique properties and versatile applications.³

Rattle-like structures (also called “yolk–shell” structures), special core@shell structures featuring a unique core@void@shell configuration, have attracted increasing interest in both theoretical and technical studies because of their advanced characteristics, finding great potential applications that could not be achieved by traditional core@shell structures.⁴ These advantages can be detailed in the following aspects: 1) diverse functions of the different parts. The discrete core and shell can play different roles in certain reaction systems. For example, when used as catalysts, the discrete core with a high specific surface area takes the catalytic role, while the outer shell, with a porous texture, takes the role of preventing aggregation of the catalytic cores.⁵ 2) Facile modification. Rattle-like particles can be controllably made of different materials, e.g. metal or metal oxide cores with nonmetal (silica, carbon, polymer, etc.) shells. Such cores can be designed as either a reactive participator (e.g. gold, silver, palladium particles for catalysis), or as a functioning element (e.g. Fe₃O₄ and γ-Fe₂O₃ magnetic particles) for convenient control of the reaction process. The shell usually has the advantages of facile grafting or modification endowing them with improved application efficiency.⁶ 3) The high surface area and porous structure helps to accelerate the mass transfer process.
transfer of reactants and products, and thus improves their application efficiency. Traditional core@shell particles are commonly composed of nanoparticles with a condense texture, leading to a limited surface area, while rattle-like materials usually possess a much higher surface area for their pore-abundant shell and extra void contribution. Typically, templating strategies are adopted to synthesize rattle-like particles. A core@template@shell structure was firstly fabricated, followed by selective removal of sacrificial template materials by either calcination (for carbon, polymer, or other pyrolysis-susceptive templates) or chemical etching (extreme acidic or alkaline etching for metal or nonmetal templates) treatment to form the void. This strategy is considered reliable and highly efficient, whereas tedious multiple coating steps and the inevitable waste of sacrificial template materials are two major obstacles in terms of reproducibility and actual scale-up for industrial application. Recently, a more facile strategy was developed for the fabrication of rattle-like structures, which transforms a solid metal coating into metal oxide or sulfide hollow shells through a chemical process analogous to the classic Kirkendall effect. However, this method also needs pre-preparation of a core@shell compound. Li et al. made great progress in synthesizing a hollow TiO2 sphere through a one-pot solvothermal method, during which the yolk@shell structure was an intermediate product. The precise control of the formation process was necessary, or else the yolk@shell structure would vanish and just result in hollow sphere structures. Additionally, the products of such methods usually exhibit poor crystallinity, so complementary calcination treatment is desired to make it mature. Therefore, it is still a great challenge to develop novel strategies of simplicity and reproducibility for synthesizing rattle-like materials.

Since the pioneer demonstration of its hydrogen production ability under UV irradiation by Honda and Fujishima, TiO2 has been and remains one of the most frequently and intensively studied semiconductor materials due to its high stability, low toxicity, and abundance. Over the past few decades, great effort has been devoted to developing strategies to improve the catalytic activity of TiO2-based photocatalysts. In essence, they all realize improvement through two ways: improving the light-harvesting ability, or extending the light absorption edge to the visible light region. It has been proven that a high surface area and a hierarchical structure are two important factors affecting the light harvesting ability. Impurity doping and semiconductor-conjunction could reduce the bandgap of TiO2, resulting in vis-photocatalytic activity. Therefore, fabricating TiO2 catalysts simultaneously realizing improved light-harvesting ability and extended light absorption ability has become a hotspot in the catalysis field. In terms of light-harvesting ability, the structural advantages of rattle-like materials (e.g. higher surface area, porous structure and unique hollow voids between the core and shell) can be expected to be of great benefit for improving the light-harvesting ability of TiO2. However, according to the above introduction, the facile preparation of such a TiO2 catalyst remains a great challenge. In terms of extending the light absorption ability, special equipment and/or rigorous experimental conditions are usually needed. Taking N-doped TiO2, one of the most effective strategies for improving the visible light response, for example, incorporating N atoms into substitutional sites in the crystal structure of TiO2 by calcination in an ammonia atmosphere, chemical vapor deposition, or by a wet chemical route in ammonia aqueous solutions followed by calcination are commonly adopted strategies, which still have obstacles for scale-up preparation. Therefore, more simple and convenient methods are still desirable.

Although it is theoretically ideal and achievable to realize improved photocatalytic activity by fabricating TiO2 with a rattle-like structure and concomitant N doping, there has been little report on fulfilling this goal. In the present study, we present a one-step solvothermal method for preparing N doped rattle-like TiO2 superstructures (NDRTs) with spherical porous cores and hierarchical shells composed of ultrathin nanosheets (NSs). Compared to traditional strategies, it is free of sacrificial templates and complicated coating procedures. By the way, N was simultaneously introduced into the TiO2 crystals without extra treatment. A mechanism analogous to the Kirkendall effect involving the nucleation of nascent nanoparticles, aggregation, redissolution, and regrowth driven by compulsion of crystal ripening was suggested for the formation process of the N doped rattle-like TiO2. This process features high reproducibility and scale-up application, which derives from being free of heterogeneous coating steps and special experimental conditions. Moreover, superior photocatalytic activity under visible light irradiation, deriving from the ingenerate N-doping was also investigated.

2. Experimental

2.1. Chemicals

All chemicals were used as received. Titanium(IV) isopropoxide (TIP, >97%), isopropanol (>99.9%), ethanol (>99%) and diethylenetriamine (DETA, 99%) were purchased from Sigma-Aldrich. The water used in all experiments was produced in a Millipore Milli-Q system with a resistivity higher than 18.2 MΩ cm−1.

2.2. Synthesis of the samples

NDRTs were synthesized through a solvothermal method developed from a previous report. Typically, 0.032 mL DETA and 0.1 mL H2O were injected into 50 mL isopropanol under magnetic agitation, respectively. After agitation for 5 min, the solution container was put into an ultrasonic bath. Then, 1.5 mL TIP was added dropwise into the above mixture solution under ultrasonication. After the transparent solution turned into a white turbid liquid, it was transferred into a 100 mL Teflon lined stainless steel autoclave. The autoclave was then heated to 200 °C with an increase rate of 3 K min−1 and held for 24 h. After being cooled to room temperature, the products of the solvothermal reaction were centrifuged, and
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. The samples were named after the corresponding solvothermal reaction time as NDRT\textsubscript{t}. For example, NDRT\textsubscript{24} is the product after solvothermal treatment for 24 h.

2.3. Characterization

The morphology of the products was determined using a field-emission electron microscope (SU8000, Hitachi, Japan) equipped with an energy dispersive X-ray spectrum (EDX). The samples were free of gold-sputtering. Higher resolution transmission electron microscopy (HRTEM) was obtained with a JEM-2100 transmission electron microscope (JEOL, Japan) operated at an accelerating voltage of 200 kV. The X-ray diffraction (XRD) patterns were obtained with a PANalytical X Pert Pro X-ray diffractometer (PANalytical, The Netherlands) equipped with Al K\textalpha\textalpha radiation (40 kV, 200 mA). Raman spectra were obtained on a Renishaw Invia Raman microscope. The X-ray photochemical spectra (XPS) were obtained on a Thermo SCIENTIFIC ESCALAB 250 equipped with Al-K\textalpha radiation. Nitrogen adsorption–desorption isotherms were measured with a Micromeritics ASAP2000 V3.01 analyser. The Brunauer-Emmet-Teller (BET) specific areas were calculated using the BET equation. The pore size distribution was calculated using the Barrett-Joyner-Halenda (BJH) equation. Thermogravimetric/differential thermal analysis (TG/DSC) was carried out on a Netzsch STA449 instrument from room temperature to 800 °C with a heating rate of 5 K min\textsuperscript{-1} under air flow. UV-vis diffuse reflectance spectra (DRS) were examined on a Hitachi U4100 spectrometer. Photo-electrochemical (PEC) measurements were performed in a conventional three-electrode system connected to a computer-controlled potentiostat (Gamry, Reference 600), which contained a photoanode, a coiled Pt wire, and an Ag/AgCl/KCl (sat) electrode as working, counter, and reference electrodes, respectively; an aqueous solution of 0.1 M KOH was used as the electrolyte.

2.4. Photocatalytic activity

The visible light photocatalytic activity of the product was examined by the 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 beside the reactor as a light source with a glass optical filter inserted to cut off the short wavelength components (λ < 420 nm). 0.02 g NDRTs was added into 50 mL Rh. B solution (5 mg L\textsuperscript{-1}) in the reactor and magnetically stirred in the dark at a speed of 800 rpm for 1 h to ensure adsorption equilibrium and eliminate the diffusion effects. The mixture was then irradiated by visible light (λ > 420 nm). Samples were taken at certain intervals, filtered through a 0.2 micrometre glass fibre membrane and detected by a UV-vis spectroscope (Hitachi U4100, Japan). The vis-photocatalytic activity of a commercial anatase TiO\textsubscript{2} was also carried out for comparison, abiding by the same protocol as the NDRTs. The pseudo-first-order reaction rate equation was used to evaluate the degradation kinetics. The equation was defined as ln(C/C\textsubscript{0}) = kt, where C and C\textsubscript{0} refer to the concentration of Rhodamine B (Rh. B) at the irradiation time t and 0 min, and k and t stand for the reaction rate constant and photodegradation time, respectively. Taking into consideration that the photo-degradation of organic dyes is believed to be significantly influenced by various factors, such as the dye sensitization of catalyst particles, a colourless probe pollutant also should be tested to exclude other influencing factors. Because its mineralization occurs without any intermediate during the photo-degradation process (yielding CO\textsubscript{2} and H\textsubscript{2}O\textsubscript{2}), formic acid was chosen as the colourless probe pollutant to further examine the photocatalytic activity of the product. The experimental process was the same as that for the degradation of Rh. B. The concentrations of the pipetted samples were determined through an Agilent 1200 LC system consisting of a quaternary bump and a UV/vis detector set at 210 nm.

3. Results and discussion

XRD and Raman analysis performed at room temperature were carried out to identify the crystal structure of the as-prepared NDRT\textsubscript{24}. From the XRD pattern shown in Fig. 1a, it can be observed that diffraction peaks at around 2θ values of 25.27°, 37.86°, 47.94°, 53.95°, 54.96°, 62.65°, 75.02° and 82.58° can be assigned to the planes of (101), (004), (200), (105), (210), (204), (116) and (224), respectively.

Fig. 1 XRD pattern (a) and Raman spectrum (b) of the as-prepared rat-tle-type TiO\textsubscript{2} (NDRT\textsubscript{24}).
(105), (211), (204), (215) and (224) of pure anatase TiO₂, respectively, matching well with the reported crystal structure of the anatase TiO₂ phase (space group: I₄₁/amd; tetragonal symmetry, a₀ = 3.7919 Å and c₀ = 9.4973 Å, JCPDS file no. 72-7059). The intense and narrow diffraction peaks are indicative of the high crystallinity of the product. Further analysis of the crystal structure from the Raman spectra (Fig. 1b) shows 5 active modes at 151, 399, 513, 521, and 641 cm⁻¹, which are assigned to the Eg, Bₑ₈, A₁g, B₂g, and E₉ modes of the anatase phase, respectively. Moreover, compared to that of the bulk anatase, appreciable shifts and broadening of the Raman bands for the as-prepared sample can be observed,¹⁹ which implies the presence of size effects due to optical phonon confinement that relaxes the k = 0 selection rule in Raman scattering of nanostructured materials.²⁰

Fig. 2 shows SEM and TEM images of the as-prepared rat-tle-like TiO₂ sample (NDRT₂₄). It can be clearly observed from Fig. 2a that the sample appears in spherical morphology with a well-defined core@void@shell structure. The high-resolution SEM image (Fig. 2b) further proves that the rattle structure contains an inner core composed of nanoparticles and an outer shell constructed by numerous self-attached ultrathin nanosheets (NSs) with bottom edges pointing toward the center core. The cross-linked slightly-curled NSs result in the highly open and stable structure. The strong contrast in the TEM observations (Fig. 2c) clearly demonstrates that the sample possesses a unique rattle-like structure, in which a dark sphere is encapsulated in the surrounded separated gray shell, with a more light void space located between them. Also evidenced from Fig. 2c is that the shell is composed of self-assembled NSs, which is in good accordance with the SEM results. The thickness of the outer shell is estimated to be ~200 nm. The high resolution TEM image (Fig. 2d) clearly shows that the self-assembled NSs are extremely thin. The enlarged image of the red framed area in Fig. 2d is shown as Fig. 2e, which shows lattice fringes with a d-spacing of ~0.35 nm, corresponding to d(101) of the anatase phase. Fig. 2f shows the high resolution TEM image of the green framed selected area in Fig. 2d, which clearly exhibits that the NSs appear in lamellar structures with the number of each NS varying in the range of 1-5. As observed from the upper yellow ellipse area in Fig. 2f, the thickness of a single turned-up edge of a NS was about 0.4 nm, which is very close to the height of one layer of the [TiO₆] octahedron (0.38 nm). Thus, it can be estimated that the thickness of the NSs varies in the range of 0.4 to 2 nm. Fig. 2g is the electron diffraction pattern by focusing the electron beam on the sample in Fig. 2e, which can be assigned to the diffraction pattern of polycrystalline anatase TiO₂, further determining the crystalline nature of the as-prepared sample.

Scanning electron microscopy performed at high voltage (15 kV) of the free standing rattle-like sample, combined with
EDX elemental mapping and energy dispersive X-ray spectroscopy (EDS) analysis, was carried out to identify the elemental composition and distribution status. The integrated EDS (Fig. 3a) confirms that the sample mainly contains Ti, O, as well as N elements. SEM performed at high voltage (Fig. 3b) clearly reveals the rattle-like core@void@shell structure with a concrete core and loose hierarchical shell. From the elemental mapping (Fig. 3c and d), it can be observed that the distribution of Ti and O appears to be quite unique, with a large number of mapping dots concentrated at the inner core position, with sparse elemental dots scattered around the shell, and with much fewer residing between them representing the void part. This result is in good agreement with the TEM and SEM analysis. Also, the existence of N verifies that our method not only successfully synthesized a unique yolk shell structure, but also simultaneously incorporated TiO₂ with N, which has been proven to have the ability of narrowing the bandgap and thus extending light absorption to the visible light region.16 Therefore, it is a reasonable deduction that the as-prepared samples would function actively under visible light illumination to degrade organic pollutants.

To further identify the chemical composition and states of the surface elements in the as-prepared rattle-like TiO₂, XPS analysis was performed (Fig. 4). It can be observed from the survey spectrum (Fig. 4a) that characteristic peaks are centered at 458.5, 531, 399.4, and 284 eV, corresponding to the binding energies of Ti 2p, O 1s, N 1s, and C 1s, respectively, which is in good agreement with other reported anatase TiO₂ with N, which has been proven to have the ability of narrowing the bandgap and thus extending light absorption to the visible light region.16 Therefore, it is a reasonable deduction that the as-prepared samples would function actively under visible light illumination to degrade organic pollutants.

In order to penetrate into the formation mechanism of the unique structure, we carried out time-dependent experiments exhibiting the morphology evolution process. Fig. 5 shows the SEM, TEM and XRD patterns of the products formed at different solvothermal reaction times. What is needed to be emphasized is that the primary ultrasonication treatment is essentially important. It was reported that sono-cation could result in an acoustic cavitation effect, namely the formation, growth, and implosive collapse of bubbles in a liquid, which produces unusual chemical and physical environments. Localized “hot spots” with transient temperatures of about 5000 K and pressures of about 1000 atm can be generated upon collapse of the bubbles.27 Such an instantaneous
extreme condition will lead to accelerated hydrolysis of the Ti precursor, and thus the formation of nanoparticles before the solvothermal reaction in this work. This can be evidenced by SEM analysis of the primary product of the sonication treatment. As shown in Fig. S1, small nanoparticles formed upon ultrasonication, with some growing a little bigger. Thereafter, under solvothermal conditions, those nascent nanoparticles acted as growing seeds for the following growth and evolution. With the prolonging of the solvothermal reaction time, these primary nanoparticles grew to larger and well-defined spherical structures and eventually evolved into the unique hierarchical rattle-like architecture. As shown in Fig. 5a1 and b1, after 6 h solvothermal reaction, well-defined spheres of about 1.5 μm were formed, which were composed of fine nanoparticles (Fig. S2a†). The XRD pattern (Fig. 5c1) shows several weak characteristic peaks of crystal TiO₂, demonstrating the very poor crystallinity of the sample, with the majority of the component remaining amorphous. Upon increasing the solvothermal treatment time to 12 h, the spheres grew and evolved to a kind of core@shell structure with an average diameter of 1.6 μm (Fig. 5a2–b2). The shell was composed of loosely compacted anomalous plate-like units (inset in Fig. 5a2), while the core was composed of nanoparticles, which appear larger than that of the last stage (Fig. S2b1†). An intuitive observation from the HRSEM image (Fig. S2b2†) is that the core@shell structure is abundant in pores, which can be further evidenced by BET and BJH analysis. The crystal nature of the product (Fig. 5c2) at this stage became more mature with more distinct characteristic peaks appearing. By further prolonging the reaction to 24 h, voids appeared between the core and shell, forming the core@void@shell rattle-like structure (Fig. 5a3–b3). The diameters expectedly became greater, to reach an average value of 1.8 μm. It was noteworthy that the plate-like units at the last stage evolved to thin nanosheets, which cross-linked forming hierarchical shells (inset in Fig. 5a3). The nanoparticle components of the core also grew larger accordingly (Fig. S2c†). As a result, a much higher surface area and pore volume were expected. As for the crystallinity, it can be observed from Fig. 5c3 that samples at this stage possess high crystallinity with an almost complete crystal pattern of the anatase phase. The increased maturity of the crystalline nature of the NDRTs prepared for different solvothermal reaction times can be further supported by TG analysis (Fig. S3†). The TGA curves reveal that the overall weight loss of the NDRTs decreased with increasing solvothermal reaction time, which indicates that the samples became less hydrated and the organic content also decreased with increasing solvothermal reaction time.

Based on the above results, we propose here a para-Kirkendall effect mechanism, which can be schematically illustrated as Scheme 1. Firstly, driven by minimization of the surface energy, primary fine nanoparticles formed at the ultrasonication stage tended to aggregate together forming larger well-defined spheres during the early stages of the solvothermal reaction. As the solvothermal reaction proceeded, hydrolysable moieties in those amorphous spheres reacted with water in the precursor solvent, leading to dissolution and regrowth at the surface of the spheres. As a model for nanoparticle aggregation proposed by Nomura et al. says: when a significant number of “ordered” attachments have taken place, the “released” ions may be numerous enough to induce a second nucleation process. So, the metastable crystalline phase of the condensed spheres switched on the dissolution and regrowth of the surface component, forming core@shell structures of a more crystalline shell and relatively poor crystal core. Anomalous plate-like units were firstly induced, forming a loosely composed shell with abundant pores, which made it possible for water molecules to enter into the inner part of the spheres, thus realizing the further hydrolyzation of the nanoparticles, leading to the formation of semicrystalline phases. When the reaction time was increased further to 24 h, nanoparticles of the core with relatively poor crystallinity continuously underwent a systematic evolution process of redissolution, renucleation, reattachment and regrowth. The dissolution occurred on the core area leading to shrinkage of the core. Accompanying renucleation and reattachment happened on the shell area leading to outward growth of the shell components, and thus voids appeared between those two parts, forming the unique core@void@shell structure. Additionally, with ripening of the crystals to form a fully crystal phase, the evolution process was eventually switched off without evolving to hollow spheres.

Considering that the product has an open structure (as proved by SEM and TEM analysis) and that photocatalysis is a surface-based process, it is necessary to investigate the surface conditions of the as-prepared products. Thus, N₂ adsorption–desorption isotherms of the samples prepared for different solvothermal reaction times were examined. As shown in Fig. 6a, N₂ adsorption–desorption isotherms of all three samples display typical type IV curves according to the IUPAC nomenclature with a distinct hysteresis loop observed in the range of 0.45–1.0 P/P₀, indicating characteristics of a mesoporous structure. The BET surface areas were estimated to be 159.6, 213.0, and 238.5 m² g⁻¹ for NDRT₆, NDRT₁₂, and NDRT₂₄, respectively. The detailed pore size distributions, calculated based on the nonlocal density functional theory (NLDFT), are shown in Fig. 6b, indicating that these three samples possess different porous structures. For TRHT₆, a relatively narrow pore size distribution falling in the range of
2.8–4.2 nm was observed (Fig. 6b1). NDRT12 mainly possesses pores with diameters between 2.9 and 6.0 nm (Fig. 6b2), which are bigger than those of NDRT6. But in general, the pore distribution patterns for both of them appear in a narrow range, because their pores arose from the interparticle and intraparticle voids. As for NDRT24, a completely different porous pattern with a broader distribution range was observed (Fig. 6b3), which can be ascribed to the unique core@void@shell structure. Those pores around 3.76 nm can be ascribed to interparticle pores of the core section. Other pores in the range of 6 to 25 nm arose from the distance between the NSs composing the hierarchical shell. By the way, based on the above results, it can be concluded that with the prolonging of the solvothermal reaction, bigger pores were obtained. This is due to the fact that the nanoparticles which composed the spheres grew larger, accordingly. This result corresponds to the above SEM and TEM analysis. Such an open structure, with a higher surface area and broad pore distribution is of great benefit for usage as a photocatalyst in the following aspects: 1) the high surface area means that as much pollutant molecules can be adsorbed as possible; 2) the open structure means more incoming light can be absorbed through multiple reflection between the core and shell and among the cross-linked NSs; and 3) the porous texture makes the mass transfer rate accelerated, resulting in a higher degradation rate.

Because the electronic band structure is deemed to be an important factor that affects the photocatalytic activity of TiO₂, we have performed UV-visible diffuse-reflectance spectra, in combination with valence band XPS (VB-XPS) spectra, to deduce the electronic band gap alignment of the as-prepared NDRT₂⁴ sample. As shown in Fig. 7a1, the UV-vis absorption spectrum shows the enhanced absorption of the NDRT₂⁴ sample in the whole visible region and an obvious red shift of the absorption edge can be observed in comparison with commercial anatase TiO₂ nanoparticles (Fig. 7b1). This result indicates the occurrence of the narrowing of the band gap of nanocrystalline TiO₂ with the introduction of alien ions, which should be attributed to chemical bonding between the nanocrystalline TiO₂ and the impurity dopant, e.g. Ti–O–N and Ti–N–O bonds shown in the XPS results (Fig. 4). As a result, a more efficient utilization of the solar spectrum could be achieved. It is known that anatase TiO₂ is an indirect semiconductor, whose band gap can be estimated by extrapolating the linear portion of the modified Kubelka-Munk function (detailed in ESI†) versus the energy of light. As shown in the inset picture in Fig. 7a1, the derived band gap of NDRT₂⁴ is estimated to be 3.05 eV, which shows a slight red shift compared to the bulk bandgap of 3.21 eV of the commercial anatase TiO₂ used as a comparison (inset picture in Fig. 7b1). On the other hand, the valence band maxima can be estimated by linear extrapolation of the curves in VB-XPS to the baseline. As shown in Fig. 7a2, the VB maximum edge of NDRT₂⁴ occurs at 1.88 eV below the Fermi level. Compared with that of the comparison anatase TiO₂ (1.98, Fig. 7b2), the conduction-band minimum of NDRT₂⁴ is decreased by 0.06 eV. Also, from the viewpoint of the photoelectrochemical (PEC) activity under visible light illumination, the as-prepared NDRT₂⁴ shows overwhelming superiority over the comparison anatase TiO₂ (Fig. S4†). Thus, based on the above results, the as-prepared NDRT₂⁴ is expected to have improved photoresponse in the visible light region.

In order to justify the abovementioned deduction that the as-prepared NDRT₂⁴ has vis-photo-catalytic activity, we carried out photo-degradation experiments using Rh. B and formic acid as probe organic pollutants, and a commercial anatase TiO₂ was used to compare the photocatalytic efficiency. As shown in Fig. 8a, the removal of Rh. B from aqueous solution appears as a time-dependent process. The as-prepared NDRT₂⁴ performed better than that of the comparison catalyst in both of the two continuous sections, adsorption in the dark and photo-degradation under visible light radiation. Before visible light illumination, 30.9% of the pollutant was
removed by NDRT$_{24}$ through surface adsorption effects, which is over two times higher than that of the comparison catalyst (14.7%). This result corresponds to the higher surface area and abundant pores of the prepared NDRT$_{24}$, which is of great importance, as discussed above. Upon visible light illumination, a degradation efficiency of 90% was obtained after 3 h of photocatalytic treatment, while only 42.8% was achieved by the comparison catalyst. To further elucidate the better vis-photic activity of the NDRT$_{24}$ over the comparison catalyst, reaction kinetics for degradation of Rh. B was investigated using a pseudo-first-order reaction equation $\ln(C/C_0) = kt$. As shown in Fig. 8b, the plots for both of the samples abide by a linear pattern, indicating that they fit well with pseudo-first-order reaction kinetics. The degradation rate of NDRT$_{24}$ is 0.00879 min$^{-1}$, which is much faster than that of the comparison catalyst (0.00283 min$^{-1}$). Compared to other reported work, the decolorization efficiency of the as-prepared NDRT$_{24}$ appeared faster under similar experimental conditions (load of catalyst, concentration of organic dyes and illumination parameters). As for the photo-degradation of formic acid, the same degradation pattern as the Rh. B was observed (Fig. S5†). Compared to the adsorption efficiency of the comparison catalyst (10.3%), the prepared NDRT$_{24}$ adsorbed more formic acid (20.2%) after 1 h adsorption treatment. Furthermore, the NDRT$_{24}$ exhibited a much higher degradation efficiency (61.3%) than that of the comparison anatase TiO$_2$ (15.5%) under visible light irradiation for 3 h. In general, the as-prepared NDRT$_{24}$ is a more ideal photocatalyst for the degradation of organic pollutants under visible light illumination. This conclusion is in good agreement with the beneficial characteristics of the unique structure, which can be detailed in the following aspects: 1) the higher surface area makes more pollutant molecules able to be adsorbed on the reactive surface sites of the catalyst; 2) the abundant porous structure supplies communicable channels for pollutant molecules and the degradation products travelling in the reaction system and thus accelerates the mass transfer rate; 3) the hierarchical and the unique core@void@shell structure allows for multiple reflections of the incoming light, leading to higher absorption of the irradiated light and high accessibility of the reactive components of the catalyst; 4) the introduction of N ions into the crystal structure helps to narrow the bandgap of the catalyst, thus extending the light absorption to the visible light region.

4. Conclusions

In summary, a facile one-pot approach has been developed to synthesize a novel rattle-like hierarchical TiO$_2$ superstructure, during which N ions were concomitantly doped into the crystal structures. The pre-treatment under ultrasonication and the following solvothermal reaction function systematically to realize the morphology evolution from amorphous nanoparticles to the core@void@shell structure. The cavitation effect in the sonication treatment helps to form nascent nanoparticles, which function as growing seeds in the evolution process. A para-Kirkendall effect switched by the crystalline nature was proposed, taking charge of the following morphology evolution from condensed spheres composed of nanoparticles to rattle-like structures constructed from a inner sphere and a hierarchical shell composed of ultrathin nanosheets. The as-prepared rattle-like hierarchical superstructure features a high surface area, abundant porous structure, and narrowed bandgap, thus exhibiting superior photocatalytic activity over the commercial pure anatase TiO$_2$ under visible light illumination. Owing to its unique characteristics, we believe this N doped rattle like TiO$_2$ has great potential in solar cells, energy storage, sensors, and many other fields. More importantly, the “crystalline switched para-Kirkendall effect” strategy proposed here should be a heuristic method for controlling the crystallinity and morphology of core@shell catalysts for the improvement of catalytic activity.

Acknowledgements

Financial support of this work was jointly provided by the National Natural Science Foundation of China (21207148), the National Basic Research Program of the PR (2011CB936001), and the National Key Technology R&D Program (2012BAC07B02).

Notes and references

1 (a) Z. Liu, Y. G. Andreev, A. R. Armstrong, S. Bruttì, Y. Ren and P. G. Bruce, Prog. Nat. Sci., 2013, 23, 235; (b) Y.–F. Li and Z.–P. Liu, J. Am. Chem. Soc., 2011, 133, 15743.
2 (a) G. Li, Q. Chen and J. Lan, ACS Appl. Mater. Interfaces, 2014, 6, 22561; (b) G. Li, J. Liu, J. Lan, G. Li, Q. Chen and G. Jiang, CrystEngComm, 2014, 16, 10547; (c) C. Zhang, Z. Chen, Z. Guo and X. W. Lou, Energy Environ. Sci., 2013, 6, 974; (d) L. Zhang, H. B. Wu, Y. Yan, X. Wang and X. W. Lou, Energy Environ. Sci., 2014, 7, 3302; (e) S. J. Ding, D. Y. Zhang, J. S. Chen and X. W. Lou, Nanoscale, 2012, 4, 95; (f) W. Yang, J. Li, Y. Wang, F. Zhu, W. Shi, F. Wan and D. Xu, Chem. Commun., 2011, 47, 1809.
3 (a) Q. Zhang, I. Lee, J. B. Joo, F. Zaera and Y. D. Yin, Acc. Chem. Res., 2013, 46, 1816; (b) J. S. Chen, Y. L. Tan, C. M. Li, Y. L. Cheah, D. Luan, S. Madhavi, F. Y. C. Boey, L. A. Archer and X. W. Lou, J. Am. Chem. Soc., 2010, 132, 6124; (c) M. Ye, Q. Zhang, Y. Hu, J. Ge, Z. Lu, L. He, Z. Chen and Y. Yin, Chem. – Eur. J., 2010, 16, 6243; (d) R. G. Chaudhuri and S. Paria, Chem. Rev., 2012, 112, 2373; (e) R. A. Perez and H. W.
9 | Catal. Sci. Technol., 2016, 6, 3108–3116
This journal is © The Royal Society of Chemistry 2016

Published on 26 November 2015. Downloaded by RESEARCH CENTRE FOR ECO-ENVIRONMENTAL SCIENCES, CAS on 20/03/2017 06:55:54.