

Recent progress on mixed-anion type visible-light induced photocatalysts

ZHAO ZhiHuan^{1,2*}, FAN JiMin¹, CHANG HongHong¹, ASAKURA Yusuke² & YIN Shu^{2*}

¹ College of Chemistry and Chemical Engineering, Taiyuan University of Technology, Taiyuan 030024, China;

² Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, 2-1-1, Katahira, Aoba-ku, Sendai 980-8577, Japan

Received December 30, 2016; accepted February 28, 2017; published online May 12, 2017

Environmentally friendly soft chemical processes, including solvothermal/hydrothermal process and mechanochemical process, for the synthesis of mixed anion type visible-light induced photocatalysts are introduced in this review paper. Titania and strontium titanate based anion doped photocatalysts can be effectively prepared at such low-temperature as below 200 °C. Especially, the mechanochemical process is a useful method for the synthesis of various mixed ions doping functional materials at low temperatures. The mixed anion type photocatalytic compounds consisted of N/O, N/F/O, S/O, N/C/O, show excellent visible light absorption ability and photocatalytic activities, indicating the potential applications in environmental purifications. Full-spectra active long wavelength light induced photocatalyst, full-time active photocatalyst system and infrared radiation (IR) shielding multifunctional photocatalysts will be introduced also.

solvothermal, hydrothermal, mechanochemical, mixed-anion, visible light induced photocatalyst

Citation: Zhao Z H, Fan J M, Chang H H, et al. Recent progress on mixed-anion type visible-light induced photocatalysts. *Sci China Tech Sci*, 2017, 60: 1447–1457, doi: 10.1007/s11431-016-9022-9

1 Introduction

In recent years, semiconductor photocatalysts for treatment of waste gas and waste water have attracted widespread attentions [1–7]. Titanium oxide photocatalyst is regarded as one of the most effective photocatalysts because of its excellent stability, non-toxic, inexpensive, high activity. Besides titanium oxide, some oxides such as zinc oxide, tungsten oxide, and ABO₃ type perovskite compounds are well studied. However, due to their relatively large band gap, titanium oxide can only use 5% of ultraviolet rays contained in sunlight. So it is necessary to develop other catalysts which could utilize visible light. Although tungsten oxide can absorb visible light, its stability is not enough due to the photolysis

of itself during light irradiation. Until now, some excellent works on graphitic carbon nitride, surface modified titania and plasmonic metal-TiO₂ composites based photocatalysts have been reviewed [8–12]. In the past decades, various kinds of cation doping have been tried and carried out to realize the visible light induced photocatalysis. However, their activities were still not satisfied enough. Under the circumstances, mixed anion type photocatalysts became to be a better choice. The first principle calculation on electronic state density of titanium was carried out by considering various anion elements (such as N and S) doping in oxygen site of titanium oxide, the results implied that the band gap values might be effectively narrowed by introducing a series of anion elements [13,14]. It is predicted that mixed anion doped titanium oxide exhibits enhanced visible light responsiveness and possess excellent visible light induced photocatalytic activities. Since then, various mixed anion type visible light type photocatalysts,

*Corresponding authors (email: zhaozhihuan@tyut.edu.cn; shuyin@tagen.tohoku.ac.jp)

such as B and Zr titania [15], sulfur-doped g-C₃N₄ [16], (Fe, N) co-doped TiO₂ [17], AgX/g-C₃N₄ (X=Cland Br) [18], and N-doped TiO₂ nanocrystals with exposed {001} facets [19], have been developed by using a variety of techniques. In inorganic functional materials research, mixed anions plays important roles. Even though the anion elements are closed together in the periodic table, properties such as electronegativity are greatly different. The mixed anion compound, in which multiple anions such as oxygen, sulfur, carbon, nitrogen, and hydrogen are included in the same compound, possesses unique coordination structure and shows the possibility for the innovative functions.

In this review, the recent progress on mixed anion type photocatalysts, including the soft chemical synthesis, applications on novel photocatalysis system etc. will be introduced in details. The composites combined the high-sensitive anion doped photocatalysts with up-conversion or long after-glow phosphors showed excellent deNO_x photocatalytic activity under UV/visible/near infra-red (NIR) light irradiation, or even after turning off light irradiation. Significant contributions are expected for the development and applications by using mixed anion type photocatalytic materials synthesized by environmental friendly soft chemical processes.

2 Synthesis of mixed anion type photocatalysts

2.1 Traditional synthesis process

Since 2001 the anion doped titania photocatalyst was reported, many researches were focusing on the synthesis, characterization and improvement of the mixed anion type photocatalysts. It was known that nitrogen-doped titanium oxide with high visible-light photocatalytic activities could be prepared by sputtering a TiO₂ target in an N₂ (40%)/Ar gas mixture followed by annealing in N₂ gas at 550 °C or by treating anatase TiO₂ powder in an NH₃ (67%)/Ar atmosphere at 600 °C [13]. Irie et al. [20] prepared the synthesis of TiO_{2-x}N_x with different nitrogen concentrations in an NH₃ atmosphere at 550–600 °C. They also prepared C-doped TiO₂ by oxidative annealing of TiC in air/O₂ at 600 °C for 5 h [21]. Khan et al. [22] synthesized chemically modified TiO_{2-x}C_x by flame pyrolysis of Ti metal sheet at 850 °C in a natural gas flame with a controlled amount of oxygen. Umabayashi et al. [23] prepared S-doped titania by oxidative annealing of TiS₂ in air at 500–600 °C. Anpo [24] reported that various ions might be doped in the lattice effectively by an ion injection method.

2.2 Soft chemical synthesis of mixed anion photocatalysts

Soft chemical synthesis means the material synthesis under moderate or soft conditions. As a presentative concept, “soft

solution processing” was suggested by Yoshimura [25], in which advanced ceramics materials might be preferably fabricated in solutions directly into desired composition, structure, shape, size, location, orientation, etc., in a closed system at low temperatures. Soft chemical synthesis not only consists of soft solution process, but also consists of some other low temperature processes such as mechanochemical treatment [7]. It is well known that photocatalytic activity is strongly related with physical properties such as crystal phase, particle size, specific surface area (SSA), crystallinity, and morphology. The above mentioned traditional methods are high-temperature processes, using expensive precursors or preparation instruments. In order to depress the environmental load and synthesis the well-crystallized fine photocatalytic products, some environmental friendly green processes for the synthesis of mixed anion type photocatalysts were carried out.

2.2.1 Hydrothermal & solvothermal synthesis

Hydrothermal and solvothermal synthesis have become a promising method for functional material synthesis because of the possibility of producing nano-size crystals with soft agglomeration, and controlling the phase composition or morphology by optimizing reaction conditions [6,26]. The hydrothermal/solvothermal process can be operated under moderated reaction conditions, is an environmental friendly green process. By controlling the parameters of the hydrothermal or solvothermal reaction, it is possible to produce anhydrous crystalline powders with controlled particle size, controlled stoichiometry, or controlled particle morphologies. The nitrogen doped titania with anatase, brookite and rutile single phase was successfully and selectively prepared by a homogeneous precipitation—hydrothermal/solvothermal process at 190 °C, without any post-solvothermal calcination treatment (Figure 1) [27,28]. The chemical bonding between titanium and nitrogen could be confirmed by the X-ray photoelectron spectroscopy (XPS) analysis. All the as-prepared nitrogen doped titania showed two apparent light absorption bands, one in UV light rang is related to the original bandgap of titania, and another excellent absorption around 700–800 nm is related to nitrogen doping. All the samples showed excellent visible light induced deNO_x activity.

It is accepted when N³⁻ is substituted for O²⁻, the anion defect which causes recombination of electron/hole pairs is generated due to the charge compensation. Since fluorine and nitrogen co-doping potentiates the substitution of nitrogen without generation of any defect, photocatalytic activity under UV and visible light irradiation could be greatly improved. Figure 2 shows the effect of mixed anions co-doping on the enhancement of doping amount together with the photocatalytic CO₂ generation capacity via the decomposition of aldehyde [29]. The nitrogen contents in the nitrogen and fluorine co-doped titania powders were about three times higher than those of the nitrogen doped ones, indicating that the

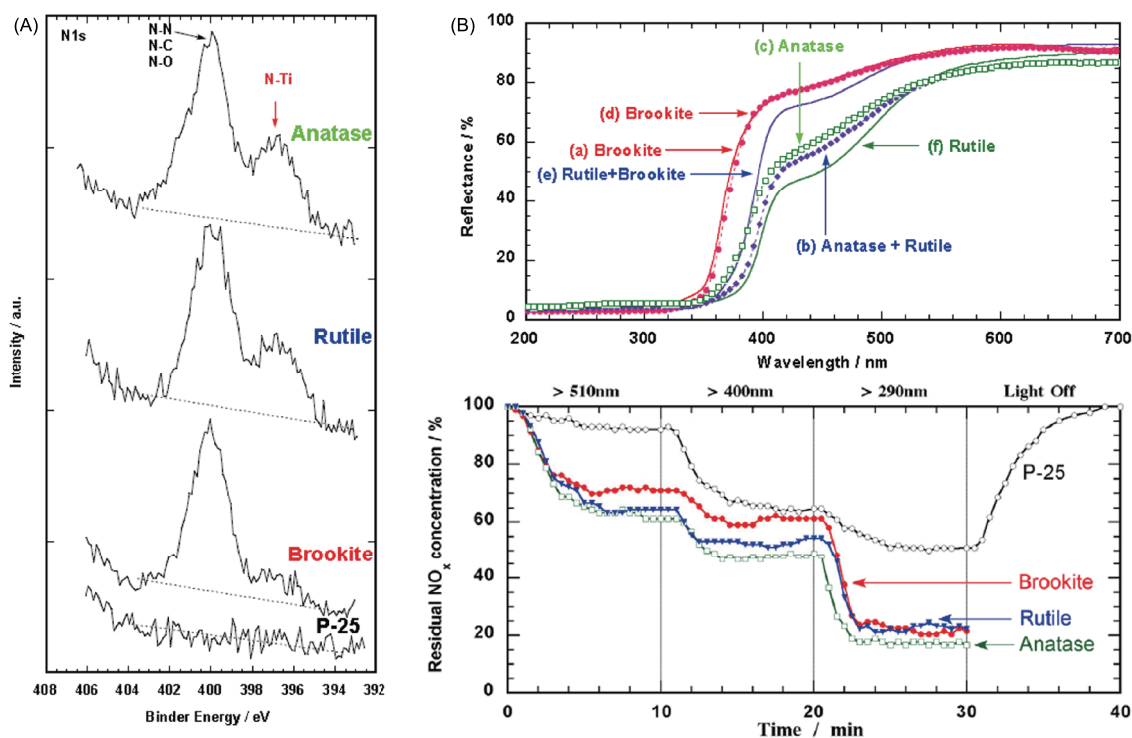


Figure 1 (Color online) XPS spectra (A), diffraction reflectance spectra (DRS) (B) and photocatalytic deNO_x activity of anatase, rutile and brookite phase TiO_{2-x}N_y powders prepared by solvothermal reaction at 190 °C for 2 h in TiCl₃-HMT system. Reproduced from ref. [27] with permission from The Royal Society of Chemistry.

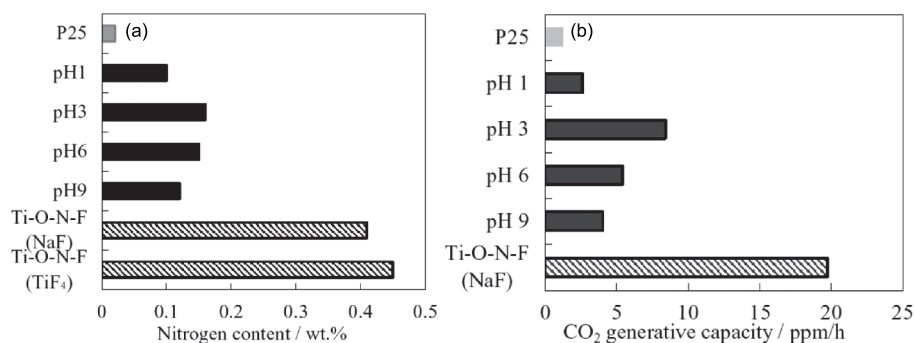


Figure 2 Mixed anions co-doping effect on the enhancement of doping amount (a) and photocatalytic CO₂ generation capacity via the decomposition of aldehyde (b). Reproduced from ref. [29] with permission from Transactions-Materials Research Society of Japan.

nitrogen and fluorine co-doping is very effective to increase the amount of nitrogen doping. It is also notable that the photocatalytic ability of the nitrogen and fluorine co-doped titania powder was more higher than that of the nitrogen doped samples.

It may be due to the decrease in anion defects by the nitrogen and fluorine co-doping. Besides nitrogen doped titania, many kinds of anion doped/co-doped visible light induced photocatalysts, such as carbon doped titania [30], Fe-N codoped TiO₂ [7,31], and Nd-C codoped TiO₂ [32], were successfully synthesized by the solvothermal process. Not only anion doped titania based materials, but also anion doped SrTiO₃ also showed excellent visible light induced photocat-

alytic activity [33–35]. In the case of nitrogen doped SrTiO₃, with the increment of hexamethylenetetramine (HMT) additive amount, the increment of photocatalytic activity might be observed, which might be related to the formation of finer particles under high pH conditions (Figure 3).

2.2.2 Mechanochemical doping

Usually, the mechanical stressing induces the formation of fresh oxygen-rich surface, results in the electron transfer from O²⁻ ion on oxide surface to other organic substance, and as a result, leads to the destruction of weak bonding in organic substance and the formation of new bonding between oxide and nonmetallic element [36,37]. It was discovered that

mechanochemical technology might be an effective method for doping anions such as nitrogen and fluorine in the lattice of various photocatalysts around room temperature [38–43]. The fresh active surfaces could be exposed by the milling treatment.

Carbon-doping [38,39], carbon/nitrogen co-doping [39], and sulfur doping [40] were also successfully and easily prepared by grinding TiO_2 with adamantane, HMT or sulfur. Especially in the case of sulfur doping, usually it is partic-

ularly difficult to be realized by normal method because of its large ionic size of sulfur element and very easy to be oxidized. The C/N co-doped titania possessed the highest photocatalytic de NO_x activity (Figure 4). Also it was found that all the anion doped titania possessed two bandgaps, which were related to the original bandgap of titania and that by anion doping. The chemical bond of Ti–N and Ti–C were actually produced by the mechanochemical treatment at room temperature. The de NO_x activity increased with the

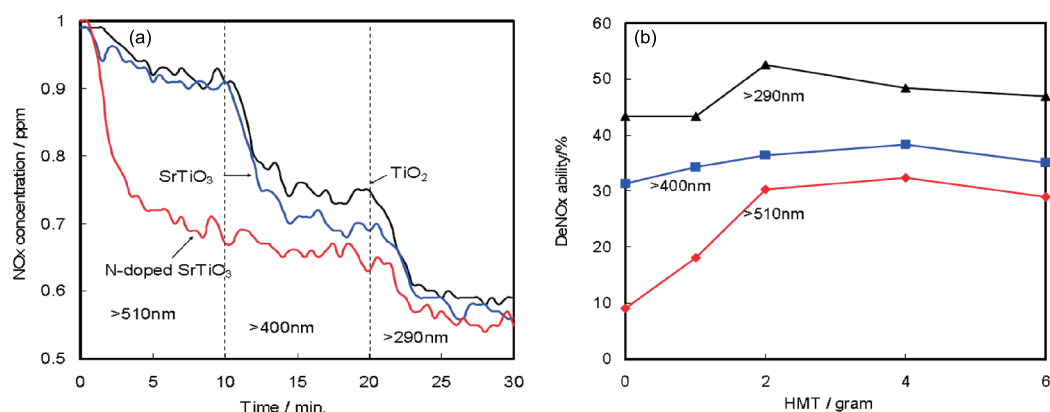


Figure 3 (Color online) (a) Photocatalytic activities of SrTiO_3 and N-doped SrTiO_3 (with 4 g of HMT) for the photocatalytic de NO_x under irradiation of various wavelength lights together with those of commercial TiO_2 ; (b) photocatalytic activities of N-doped SrTiO_3 prepared with variation of HMT content for the oxidative destruction of NO_x . Reproduced from ref. [34] with permission from Elsevier.

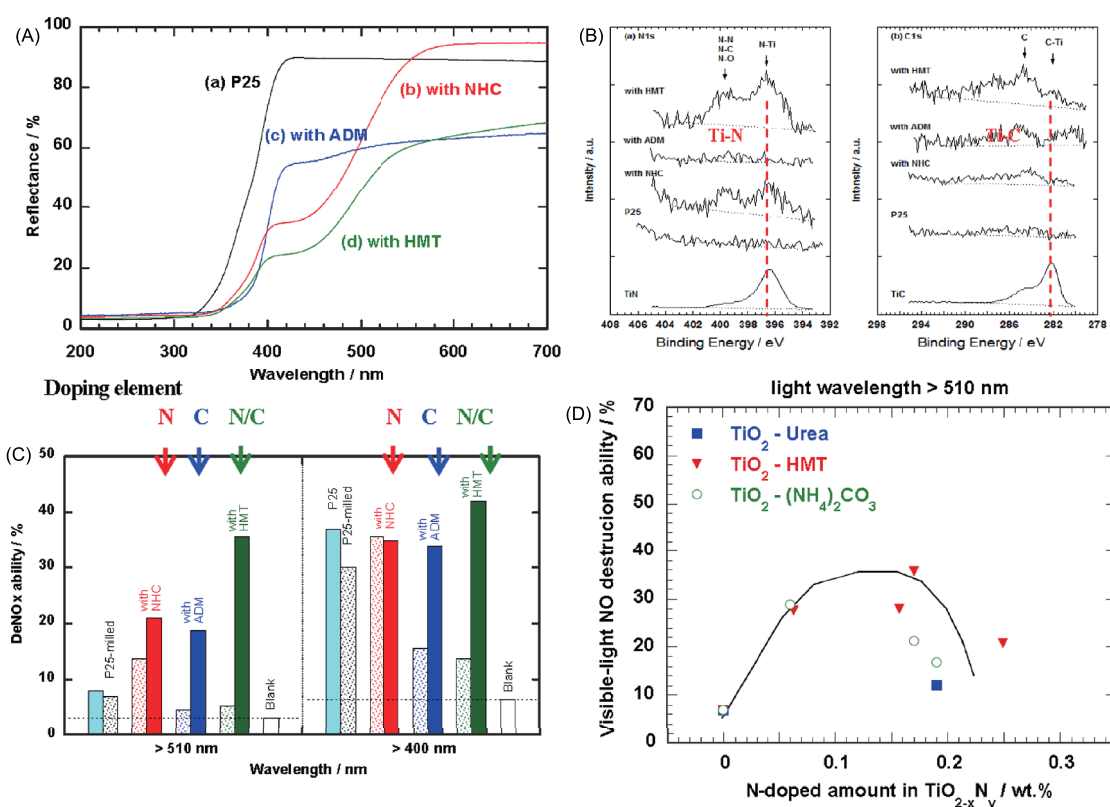


Figure 4 (Color online) DRS (A), XPS (B), de NO_x ability (C) and nitrogen doped amount (D) of the mixed anion type titania photocatalysts prepared by mechanochemical doping process using urea/ammonia carbonate (NHC), adamantane (ADM) and hexamethylenetetramine (HMT) as reaction reagents. For comparison, some results of P25 before and after ball-milling are also plotted. Reproduced from ref. [43] with permission from Elsevier.

increment of nitrogen doped amount, while decreased in the case of exceed doping.

2.2.3 Summary for the synthesis methods

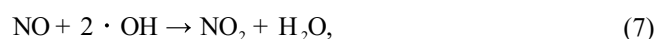
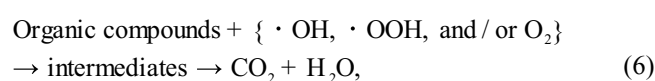
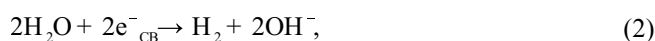
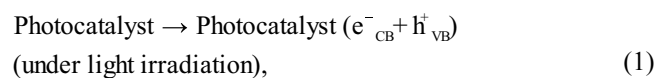
As mentioned above, difference synthesis method possesses related advantages and disadvantages. Table 1 summarized the advantages and disadvantages of different synthesis methods. Compare with other synthesis method, the hydrothermal and solvothermal method prefer to obtain the mixed anion doped or co-doped photocatalytic materials with many advantages, such as the possibilities for morphological & composition control with high surface area & reactivity, high homogeneity and high purity with soft agglomeration, especially no additional calcination step and milling step are required. The soft chemical method might be the best choice for the synthesis of functional photocatalysts with low environmental loading.

3 Development and applications of high sensitive mixed anion type photocatalysts

3.1 Photocatalysis principle and reaction mechanism

It is accepted that photocatalyst particles absorb light energy greater than its band gap to generate electron/hole pairs (eq. (1)) [6,7]. In the absence of oxygen, the electrons in the conduction band generated by the light irradiation would reduce water to produce hydrogen gas by the eq. (2). On the other hand, in the presence of oxygen, the electrons are photoinduced to the conduction band (e^-_{CB}), and the holes in the valence band (h^+_{VB}) are subsequently trapped by H_2O to yield H^+ and $\cdot OH$ radicals (eq. (3)). The photoinduced electrons are immediately trapped by the molecular oxygen to form $\cdot O_2^-$ (eq. (4)), which can then generate active $\cdot OOH$ radicals (eq. (5)) [44,45]. Environmental organic pollutants in the solution react with these reactive oxygen radicals

and/or molecular oxygen, to produce intermediates or complete decomposition products of CO_2 and H_2O (eq. (6)). While in the case of $deNO_x$ photocatalysis, the reaction relates to oxidation through active oxygen species, such as $\cdot OH$ or $\cdot O_2^-$ as shown in the eqs. (7) and (8) [24,32]. The mixed anion doping might lead to the narrow of bandgap, and result to the improvement of visible light absorption and visible light induced photocatalysis effects [13,14].



3.2 Weak LED light induced photocatalytic activity

Hydrothermal and solvothermal synthesized photocatalyst particles possessed high crystallinity, small particle size, high specific surface area, and showed excellent weak light induced photocatalytic activity. Figure 5 shows the irradiation time dependence of the concentration of NO_x in the presence of samples irradiated by various monochromatic light-emitting diode (LED) lamps [32]. In the case of photocatalytic characterization, usually strong light sources were utilized. It was reported that even with the use of very weak

Table 1 Advantages and disadvantages of various synthesis methods for the mixed anion photocatalysts

Synthesis method	Disadvantages	Advantages	Ref.
Sputtering	Moderate cost; Limited treatment capacity	Simple operation	[13,14]
High temperature treatment in gas atmosphere	High temperature; Agglomeration	Simple operation; Low cost	[13]
Partial oxidation	High cost; Low surface area; Large particle size	Precise composition control	[20,21,23]
Ion injection	High cost; Limited treatment capacity	Universal doping method	[24]
Mechanochemical	Contamination; Agglomeration; Surface vacancy	Universal doping method; Low cost; Low temperature treatment; co-doping	[38–42]
O_2 plasma treatment	Limited treatment capacity	Low temperature treatment; Strong mechanical strength of thin films	[43]
Hydrothermal & solvothermal	Moderate treatment pressure; Moderate cost	Morphological & composition control; Homogeneity; High purity, co-doping; Soft agglomeration; No calcination step; No milling step; High surface area & reactivity	[27,28,31–33,35]

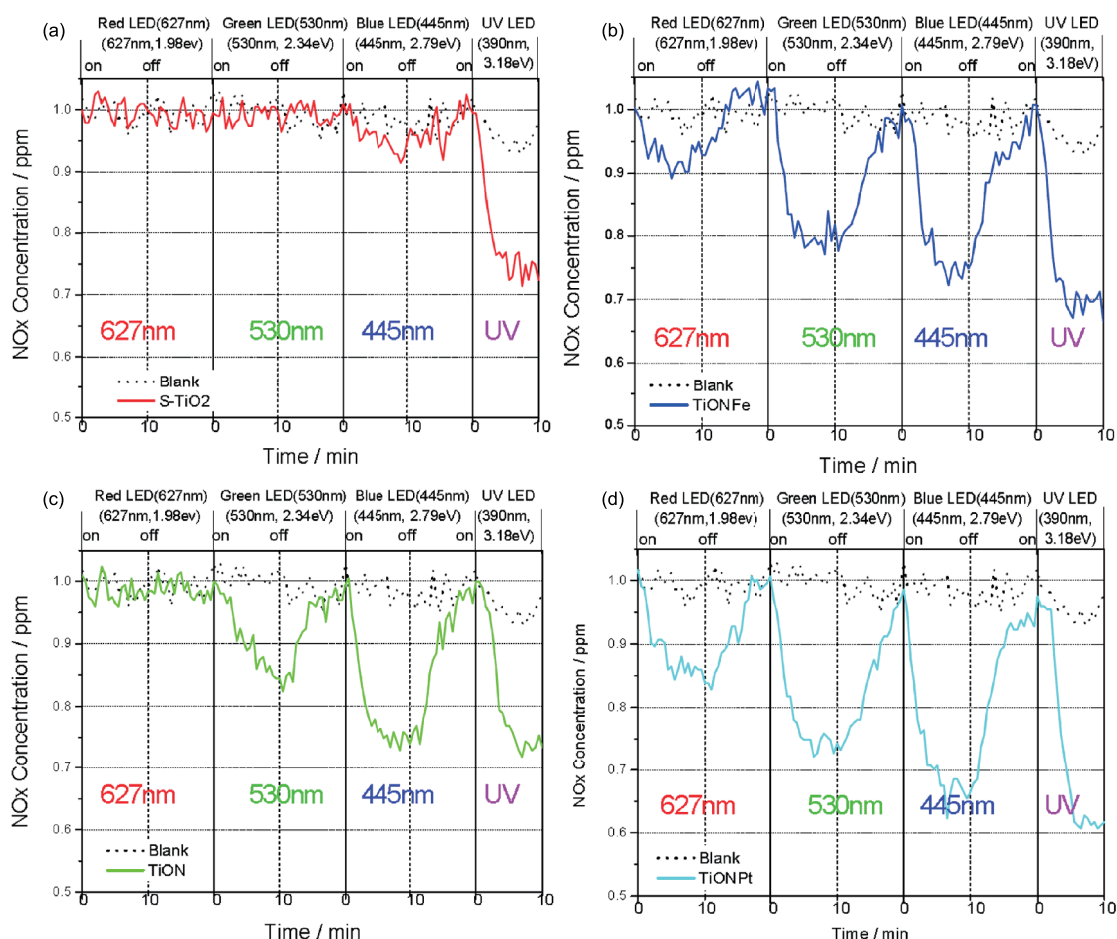


Figure 5 (Color online) Weak LED visible light irradiation, time dependence of NO_x concentration as a function of sample type. (a) S- TiO_2 ; (b) TiON; (c) TiONFe; (d) TiONPt. 1 ppm NO gas was pumped continuously through the reactor (373 cm^3). Irradiation was carried out using various LED light sources with a light intensity of 2 mW for 10 min; the light was then turned off to allow the concentration to return to 1 ppm. Reproduced from ref. [32] with permission from Elsevier.

monochromatic LED lamps (2.5 W), high deNO_x photocatalytic activity could be realized. Different samples showed quite different light wavelength dependencies. Normal non-doping titania S- TiO_2 displayed excellent UV light induced activity and very weak photocatalytic activity under blue light irradiation, while nitrogen doped titania TiON showed excellent UV light and visible light induced photocatalytic activity under both blue light (445 nm) and green light (530 nm) irradiation. It is notable that the Fe- and Pt-loaded nitrogen titania samples TiONFe and TiONPt showed excellent deNO_x abilities even under red light (627 nm) irradiation. The Pt-loaded sample showed the highest deNO_x abilities in all light wavelength ranges. The LED light irradiation system is suitable for the mechanism research, because LED light could provide single-color light with monodispersed wavelength irradiation without obvious heat irradiation.

3.3 Full-time active photocatalytic system

Photocatalyst usually does not work without light irradiation in night. In order to effectively utilize the night time for

atmosphere purification, a full-time active photocatalytic system was developed [46–51]. The coupling of photocatalysts with a proper long afterglow phosphor such as $\text{CaAl}_2\text{O}_4:(\text{Eu},\text{Nd})$ was expected to prolong the photocatalytic activity even after turning off the light by using the fluorescence as the light source [46–51]. Usually the nano-size photocatalyst is suitable for loading on the surface of large geometric dimension long afterglow materials, because the large surface area of nano-size photocatalyst on the surface is required for the photocatalysis, while the long afterglow materials can provide enough intensity of emission luminescence for the photocatalytic reactions even if coated by the photocatalyst nanoparticles.

Figure 6(a) shows the schematic illustration of the concept of the multifunctional persistent full-time reactive photocatalytic system. This photocatalytic system not only worked under light irradiation, but also in night without light irradiation. Although normal titania absorbed only UV light of the wavelength less than 400 nm, anion-doped titania showed absorption of visible light up to 700 nm, showing a nice overlap

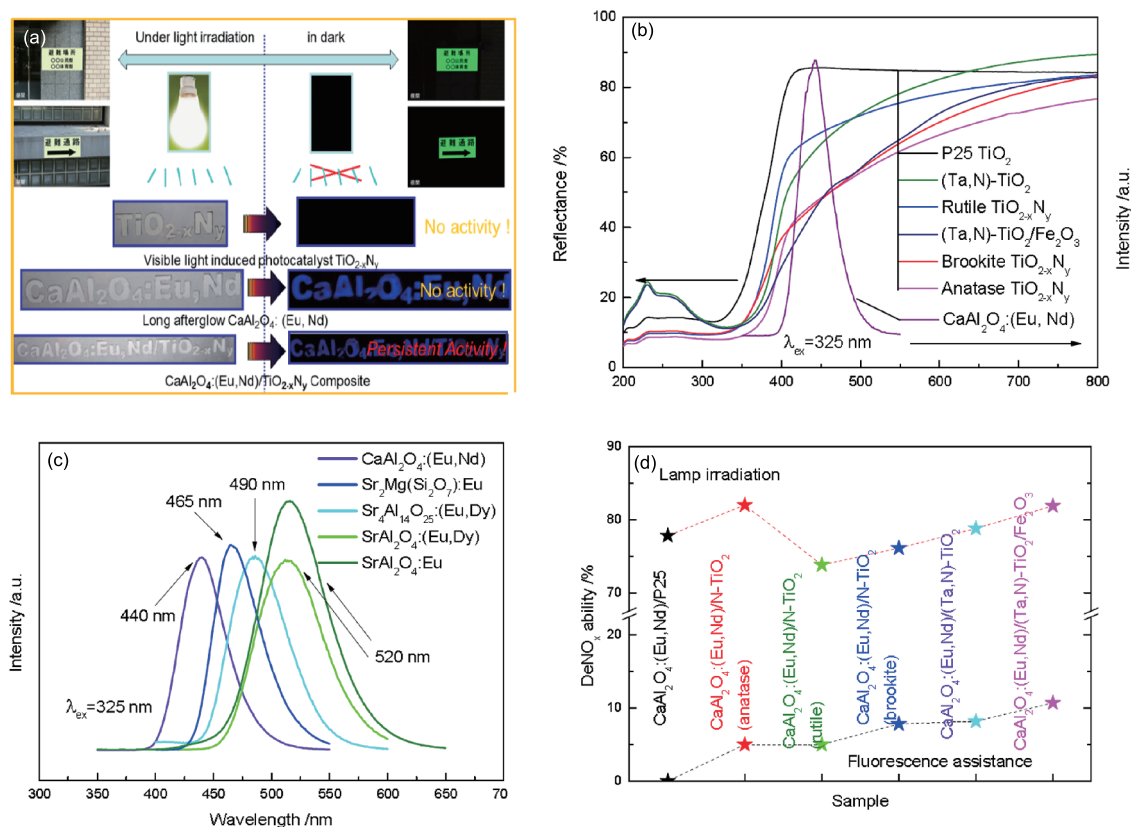


Figure 6 (Color online) (a) Schematic illustration of full-time reactive photocatalytic system; (b) overlap of the emission spectra of long afterglow phosphor $\text{CaAl}_2\text{O}_4:(\text{Eu}, \text{Nd})$ and diffuse reflectance spectra of various mixed anion type $\text{TiO}_{2-x}\text{N}_y$ -based composites; (c) emission spectra of various long-afterglow phosphors; (d) NO_x degradation ability of various titania based visible light induced composite type photocatalysts under light irradiation followed by fluorescence assisted catalytic activity in dark. Reproduced from refs. [7,49,50] with permission from Ceramic Society of Japan, Elsevier, and American Chemical Society, respectively.

between the diffuse reflectance spectra of mixed anion type photocatalysts and the emission spectrum of long afterglow phosphor $\text{CaAl}_2\text{O}_4:(\text{Eu}, \text{Nd})$ (Figure 6(b)). Besides $\text{CaAl}_2\text{O}_4:(\text{Eu}, \text{Nd})$ (emission peak at 440 nm), various kinds of long afterglow material such as $\text{Sr}_2\text{Mg}(\text{Si}_2\text{O}_7):\text{Eu}$ (peak: 465 nm), $\text{Sr}_4\text{Al}_{14}\text{O}_{25}:(\text{Eu}, \text{Dy})$ (peak: 490 nm), and $\text{SrAl}_2\text{O}_4:(\text{Eu}, \text{Dy})$ (peak: 520 nm) could also be utilized in the proposed system (Figure 6(c)). Not only NO_x and VOC (such as CH_3CHO), but also some dyes in solution (such as MO and RhB dyes solutions), the persistent photocatalytic purification effect with light irradiation was confirmed [51–53].

3.4 Infra-red light induced full spectrum active photocatalytic system

In order to improve the solar light utilize effectively, another composite type photocatalyst system was suggested [54,55]. The combination of weak visible light induced carbon doped titania (C- TiO_2) photocatalyst with up-conversion phosphor ($(\text{Yb}, \text{Er})\text{-NaYF}_4$) might be the more promising way to effectively use the UV, visible, and near infra-red (NIR) lights for photocatalytic applications. The Yb and Er co-doped NaYF_4 designated as possessed two main emission peaks at

about 545 and 655 nm under the irradiation of 980 nm. For pure C- TiO_2 , although excellent deNO_x activity could be observed under various visible LED light irradiation until 627 nm, no NIR light induced activity could be observed, because C- TiO_2 could not be excited by 980 nm NIR light directly. There was no deNO_x activity for $(\text{Yb}, \text{Er})\text{-NaYF}_4$ alone under irradiation of various wavelength of light, because $(\text{Yb}, \text{Er})\text{-NaYF}_4$ was not a photocatalyst. However, when C- TiO_2 was combined with $(\text{Yb}, \text{Er})\text{-NaYF}_4$ up-conversion phosphor, NO_x gas was continuously destructed even when the NIR diode laser was used as the irradiation light source. This NIR light induced activity was owing to the synergetic effect of C- TiO_2 photocatalyst and $(\text{Yb}, \text{Er})\text{-NaYF}_4$ up-conversion phosphor (Figure 7).

3.5 Infra-red light shielding multifunctional photocatalyst system

In order to improve the functionality of photocatalyst materials, multifunctionality development is also a research hotspot. Some multifunctionality such as photocatalytic activity together with magnetic property has been developed because it is useful for the recovering of photocatalyst particles [56]. Also it was suggested to combine the NIR shielding effect

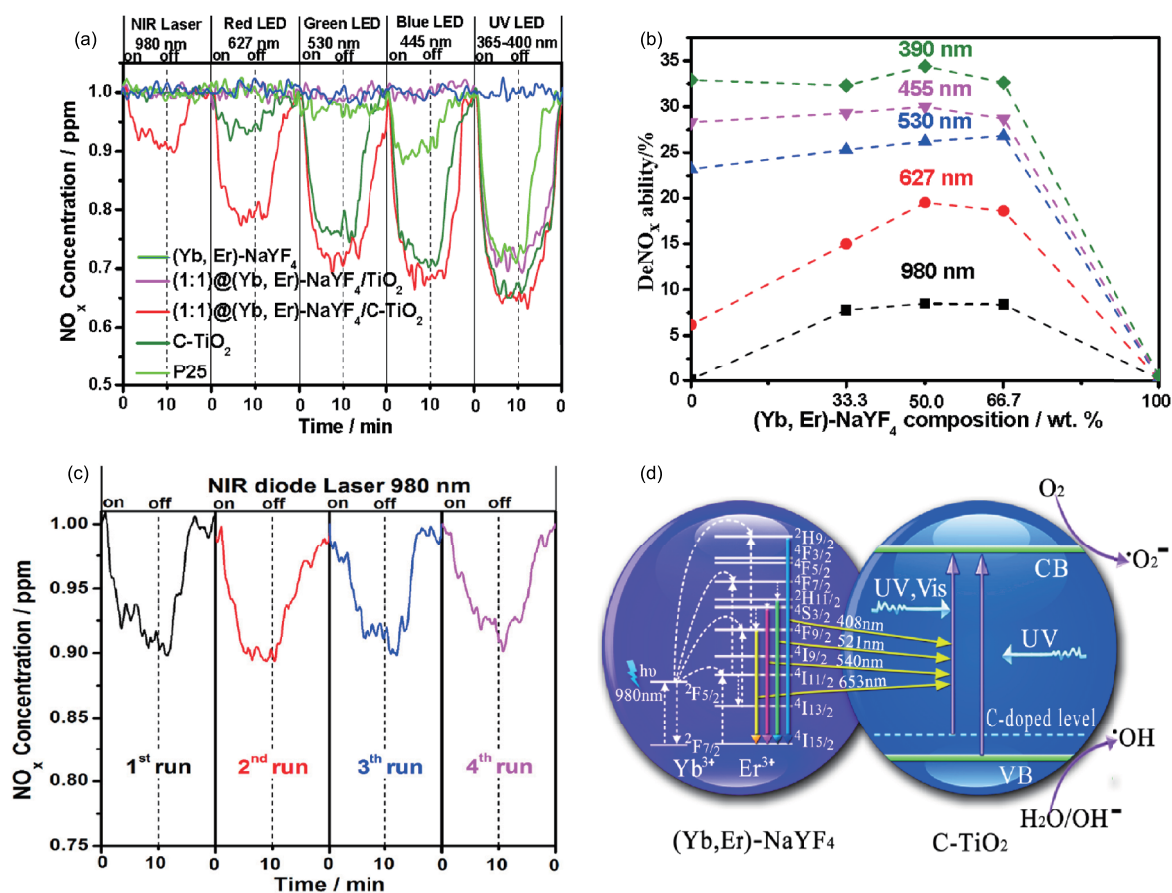


Figure 7 (Color online) (a), (b) Photocatalytic deNO_x activities under irradiation of visible light LED and NIR laser light; (c) the multi-cycles of deNO_x ability of (1:1)@(Yb,Er)-NaYF₄/C-TiO₂ under the irradiation of 980 nm light; (d) schematic illustration of the photoluminescence and photocatalytic mechanism. Reproduced from ref. [54] with permission from the Nature Publishing Group.

with the photocatalytic performance together in one technique. M_xWO₃ has been researched as an excellent infrared radiation (IR) shielding material [57–60]. Since the energy saving and environmental cleanup can be achieved by this proposal simultaneously, it would have a brilliant prospect in our daily life. Until now, some related materials such as W-C co-opted TiO₂ [61], Cs_xWO₃/ZnO nanocomposite [62,63], and K_xWO₃/F-TiO₂ nanocomposite [64] have been successfully synthesized (Figure 8). FT-KWO nanocomposite film with an appropriate mass ratio of F-TiO₂ to K_xWO₃, exhibiting a great synergistic effect on blocking NIR and UV light as well as transmitting most of visible light [64].

As shown by the working model, obviously, this smart window plays different roles in various conditions. In summer days, the FT-KWO film side towards the outside; with the irradiation of the solar light, the smart window can not only block most of the NIR lights for heat preservation and keep cool indoor, but also isolate harmful UV light and transmit Vis light. In winter days, this window should be rotated 180° to make the FT-KWO film side towards the inside. In this case, the smart window not only reduces heat loss from inside to outside, but also blocks UV light and transmits Vis light ef-

fectively. At the same time the high hydrophilic capacity can control the production of water vapour on the window and enhance the visibility available [64].

3.6 Mixed anion type photocatalysts for photocatalytic hydrogen evaluation

As mentioned above, recently the mixed anion type photocatalysts have attracted great attention. Various novel anion type photocatalysts have been successfully synthesized, and reported as high active hydrogen evaluation photocatalysts. Domen *et al.* reported that TaON, LaMg_xTa_{1-x}O_{1+3x}N_{2-3x} (x≥1/3) [65], and MgTa₂O_{6-x}N_y/TaON Z-scheme photocatalyst [66] showed excellent hydrogen evolution ability based on water splitting. Wang *et al.* [67] reported the synthesis and effects of N, S, C, and P monodoping and N–N, C–S, P–P, and N–P cooping on the NaTaO₃ photocatalyst, and indicated that N and S can shift the valence band edge upward without losing the ability to split water into H₂ and O₂.

Kato *et al.* [68] successfully synthesized the solid solutions between LaTaON₂ and SrTiO₃. The photocatalytic activities of LaTaON₂-SrTiO₃ for H₂ and O₂ evolution under visible light could be successfully realized by

bandgap turning using different fraction of perovskite SrTiO₃ (Figure 9). It was found that the valence band maxima (VBM) shifted to positive sides as the fraction of SrTiO₃ increased, resulting in the appearance of activity for O₂ evolution. The bare La_{0.5}Sr_{0.5}Ta_{0.5}Ti_{0.5}O₂N exhibited

the activity for O₂ evolution 9 times higher than LaTaON₂ modified with a CoO_x cocatalyst. It has been found that the driving force for water oxidation of La_{0.5}Sr_{0.5}Ta_{0.5}Ti_{0.5}O₂N was 0.8 V, and was larger than those in other perovskite-type oxynitrides [68].

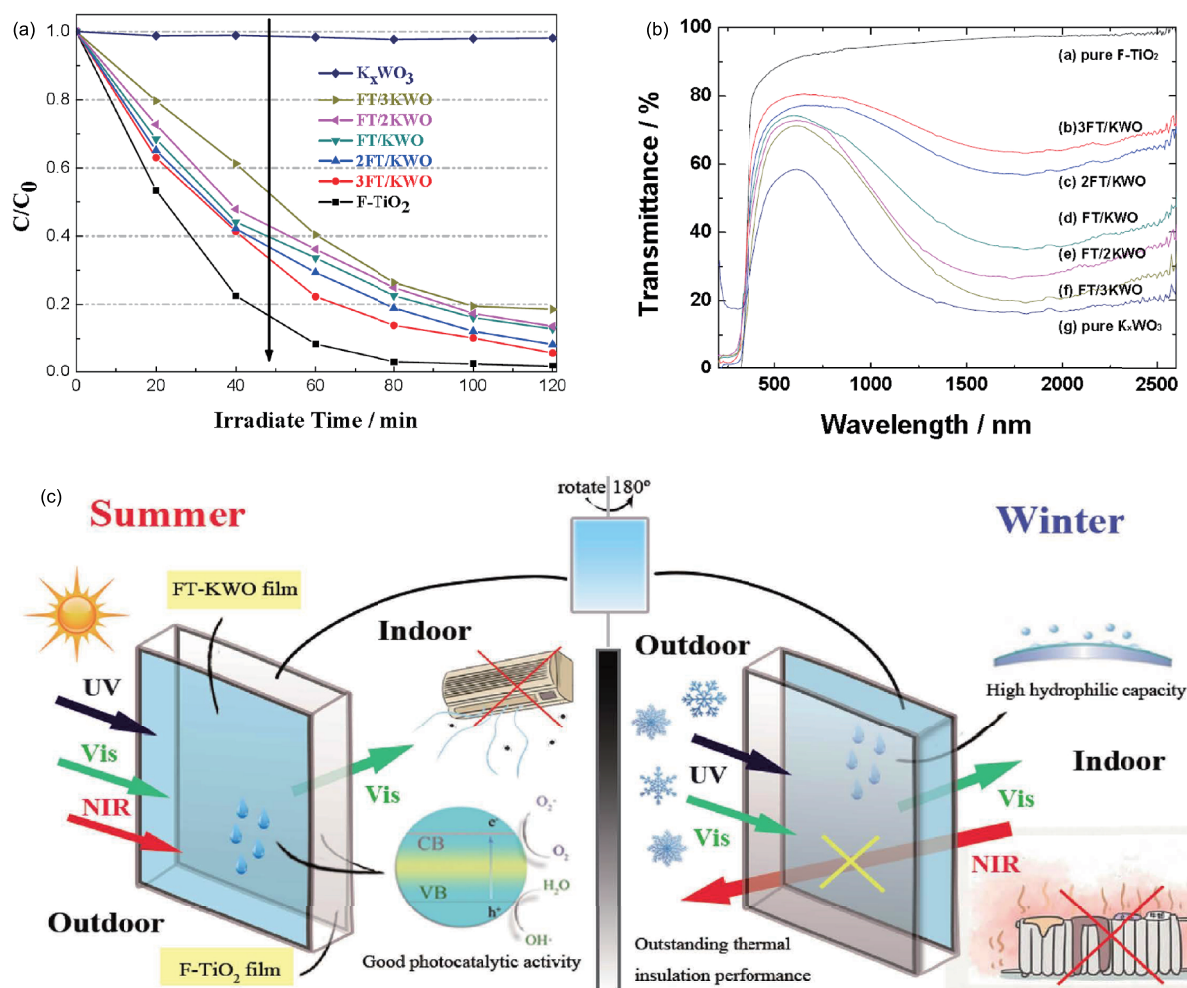


Figure 8 (Color online) (a) Time dependence of MO concentration, (b) transmittance spectra, and (c) working image of smart window using FT-KWO/F-TiO₂ composite coating. Reproduced from ref. [60] with permission from the Nature Publishing Group.

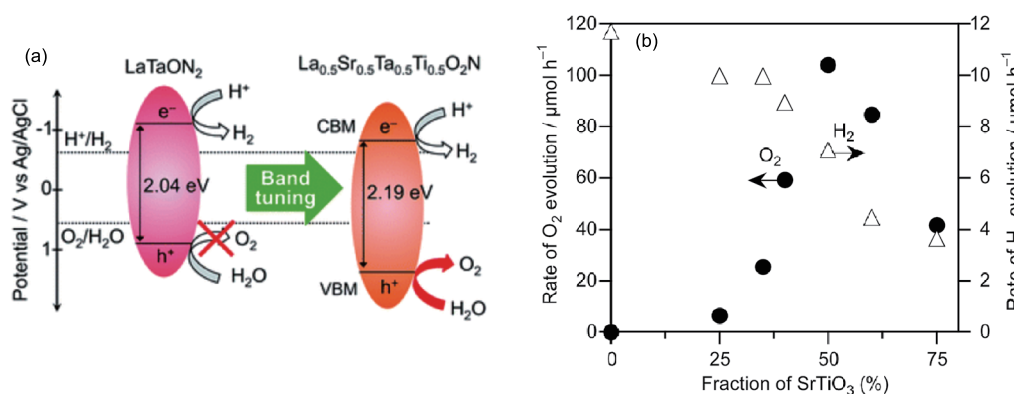


Figure 9 (Color online) Bandgap turning (a) and photocatalytic activities (b) of LaTaON₂-SrTiO₃ for H₂ and O₂ evolution under visible light ($\lambda > 420$ nm). Reproduced from ref. [68] with permission from The Royal Society of Chemistry.

4 Remarks

In this review, the synthesis, characterization, and novel applications of various kinds of mixed anion type photocatalysts were introduced. Because of the large electronegativity of anions, the doping of anions in the oxygen site of semiconductors would result to big changes in electronic structure, crystalline phase, and other physical-chemical properties, compare with those of cation doping. This is the reason that anion doping or mixed-anion doping prefers to produce some novel functionality, in some cases even fantastic photocatalytic activity for energy and environmental applications. The mixed anion type photocatalysts are expected to be a future trend in photocatalytic researches. The environmentally friendly green processes, including hydrothermal/solvothermal process and mechanochemical doping process are effective for the synthesis of photocatalysts with high crystallinity and small particle size. The concept design of full-time active and full-spectra active photocatalytic system greatly contribute to the improvement of solar light utilization efficiency. Some novel functionality and new applications are expected to be developed. The design of novel photocatalysts has great potential in environmental applications.

This work was partly supported by the Japan Society for the Promotion of Science (JSPS) KAKENHI (Grant No. JP16H06439), the Dynamic Alliance for Open Innovation Bridging Human, Environment and Materials, the Cooperative Research Program of "Network Joint Research Center for Materials and Devices", TAGEN project 2016-2017, and partly by the Natural Science Funds of Shanxi Province (Grant No. 2016011079), and the Open Funds of the State Key Laboratory of Rare Earth Resource Utilization (RERU2017008).

- Fujishima A, Honda K. Electrochemical photolysis of water at a semiconductor electrode. *Nature*, 1972, 238: 37–38
- Kubacka A, Fernández-García M, Colón G. Advanced nanoarchitectures for solar photocatalytic applications. *Chem Rev*, 2012, 112: 1555–1614
- Barbé C J, Arendse F, Comte P, et al. Nanocrystalline titanium oxide electrodes for photovoltaic applications. *J Am Ceramic Soc*, 2005, 80: 3157–3171
- Altun I, Sökmen M. Preparation of TiO₂-polystyrene photocatalyst from waste material and its usability for removal of various pollutants. *Appl Catal B-Environ*, 2014, 144: 694–701
- Mills A, Le Hunte S. An overview of semiconductor photocatalysis. *J Photochem Photobiol A-Chem*, 1997, 108: 1–35
- Sato T, Zhang P, Yin S. High performance visible light responsive photocatalysts for environmental cleanup via solution processing. *Prog Cryst Growth Ch*, 2012, 58: 92–105
- Yin S. Creation of advanced optical responsive functionality of ceramics by green processes. *J Ceram Soc Jpn*, 2015, 123: 823–834
- Ong W J, Tan L L, Ng Y H, et al. Graphitic carbon nitride (g-C₃N₄)-based photocatalysts for artificial photosynthesis and environmental remediation: Are we a step closer to achieving sustainability? *Chem Rev*, 2016, 116: 7159–7329
- Low J, Cheng B, Yu J. Surface modification and enhanced photocatalytic CO₂ reduction performance of TiO₂: A review. *Appl Surface Sci*, 2017, 392: 658–686
- Ni Z, Sun Y, Zhang Y, et al. Fabrication, modification and application of (BiO)₂CO₃-based photocatalysts: A review. *Appl Surface Sci*, 2016, 365: 314–335
- Gomathi Devi L, Kavitha R. A review on plasmonic metal TiO₂ composite for generation, trapping, storing and dynamic vectorial transfer of photogenerated electrons across the Schottky junction in a photocatalytic system. *Appl Surface Sci*, 2016, 360: 601–622
- Li X, Yu J, Wageh S, et al. Graphene in photocatalysis: A review. *Small*, 2016, 12: 6640–6696
- Asahi R, Morikawa T, Ohwaki T, et al. Visible-light photocatalysis in nitrogen-doped titanium oxides. *Science*, 2001, 293: 269–271
- Morikawa T, Asahi R, Ohwaki T, Aoki K, Taga Y. Band gap narrowing of titanium dioxide by nitrogen doping. *Jpn J Appl Phys*, 2001, 40: L561–L563
- Fu C, Gong Y, Wu Y, et al. Photocatalytic enhancement of TiO₂ by B and Zr co-doping and modulation of microstructure. *Appl Surface Sci*, 2016, 379: 83–90
- Wang K, Li Q, Liu B, et al. Sulfur-doped g-C₃N₄ with enhanced photocatalytic CO₂-reduction performance. *Appl Catal B-Environ*, 2015, 176-177: 44–52
- Liu W X, Liu Q, Li X F, et al. Photocatalytic degradation of coking wastewater by nanocrystalline (Fe, N) co-doped TiO₂ powders. *Sci China Tech Sci*, 2010, 53: 1477–1482
- Ong W J, Putri L K, Tan L L, et al. Heterostructured AgX/g-C₃N₄ (X=Cl and Br) nanocomposites via a sonication-assisted deposition-precipitation approach: Emerging role of halide ions in the synergistic photocatalytic reduction of carbon dioxide. *Appl Catal B-Environ*, 2016, 180: 530–543
- Li D, Chen F, Jiang D, et al. Enhanced photocatalytic activity of N-doped TiO₂ nanocrystals with exposed {001} facets. *Appl Surface Sci*, 2016, 390: 689–695
- Irie H, Watanabe Y, Hashimoto K. Nitrogen-concentration dependence on photocatalytic activity of TiO_{2-x}N_x powders. *J Phys Chem B*, 2003, 107: 5483–5486
- Irie H, Watanabe Y, Hashimoto K. Carbon-doped anatase TiO₂ powders as a visible-light sensitive photocatalyst. *Chem Lett*, 2003, 32: 772–773
- Khan S U M, Al-Shahry M, Ingler W B. Efficient photochemical water splitting by a chemically modified n-TiO₂. *Science*, 2002, 297: 2243–2245
- Umebayashi T, Yamaki T, Itoh H, et al. Band gap narrowing of titanium dioxide by sulfur doping. *Appl Phys Lett*, 2002, 81: 454–456
- Anpo M. Recent Developments on Visible Light Response Type Photocatalysts. Tokyo: NTS, 2002. 9
- Yoshimura M. Soft solution processing: Concept and realization of direct fabrication of shaped ceramics (nano-crystals, whiskers, films, and/or patterns) in solutions without post-firing. *J Mater Sci*, 2006, 41: 1299–1306
- Byrappa K, Yoshimura M. Handbook of Hydrothermal Technology. New York: Noyes Publications, 2001
- Yin S, Aita Y, Komatsu M, et al. Synthesis of excellent visible-light induced TiO_{2-x}N_y photocatalyst by homogeneous precipitation—solvothermal process. *J Mater Chem*, 2005, 15: 674–682
- Yin S, Aita Y, Komatsu M, et al. Visible-light-induced photocatalytic activity of TiO_{2-x}N_y prepared by solvothermal process in urea-alcohol system. *J Eur Ceramic Soc*, 2006, 26: 2735–2742
- Komatsu M, Aita Y, Yin S, et al. Solvothermal synthesis of visible-light reactive titania nanocrystals. *Trans Mater Res Soc Jpn*, 2004, 29: 2297–2300
- Wu X, Yin S, Dong Q, et al. Synthesis of high visible light active carbon doped TiO₂ photocatalyst by a facile calcination assisted solvothermal method. *Appl Catal B-Environ*, 2013, 142-143: 450–457
- Wu X, Yin S, Dong Q, et al. Photocatalytic properties of Nd and C codoped TiO₂ with the whole range of visible light absorption. *J Phys Chem C*, 2013, 117: 8345–8352
- Yin S, Liu B, Zhang P, et al. Photocatalytic oxidation of NO_x under

- visible LED light irradiation over nitrogen-doped titania particles with iron or platinum loading. *J Phys Chem C*, 2008, 112: 12425–12431
- 33 Wang J, Yin S, Zhang Q, et al. Mechanochemical synthesis of fluorine-doped SrTiO₃ and its photo-oxidation properties. *Chem Lett*, 2003, 32: 540–541
- 34 Sulaeman U, Yin S, Sato T. Solvothermal synthesis and photocatalytic properties of nitrogen-doped SrTiO₃ nanoparticles. *J Nanomaterials*, 2010, 2010: 1–6
- 35 Sulaeman U, Yin S, Sato T. Visible light photocatalytic activity induced by the carboxyl group chemically bonded on the surface of SrTiO₃. *Appl Catal B-Environ*, 2011, 102: 286–290
- 36 Ikoma T, Zhang Q, Saito F, et al. Radicals in the mechanochemical dechlorination of hazardous organochlorine compounds using CaO nanoparticles. *Bull Chem Soc Jpn*, 2001, 74: 2303–2309
- 37 Lee J, Zhang Q, Saito F. Mechanochemical synthesis of lanthanum oxyfluoride by grinding lanthanum oxide with poly(vinylidene fluoride). *Ind Eng Chem Res*, 2001, 40: 4785–4788
- 38 Yin S, Zhang Q, Saito F, et al. Preparation of visible light-activated titania photocatalyst by mechanochemical method. *Chem Lett*, 2003, 32: 358–359
- 39 Yin S, Yamaki H, Komatsu M, et al. Preparation of nitrogen-doped titania with high visible light induced photocatalytic activity by mechanochemical reaction of titania and hexamethylenetetramine. *J Mater Chem*, 2003, 13: 2996
- 40 Zhang Q, Wang J, Yin S, et al. Synthesis of a visible-light active TiO_{2-x}S_x photocatalyst by means of mechanochemical doping. *J Am Ceramic Soc*, 2004, 87: 1161–1163
- 41 Yin S, Zhang Q, Saito F, Sato T. Synthesis of titanium dioxide-based, visible-light induced photocatalysts by mechanochemical doping. In: Sopicka-Lizer M, Eds. *High Energy Ball Milling: Mechanochemical Processing of Nanopowders*. Boca Raton: CRC Press, 2010. 304–330
- 42 Kang I C, Zhang Q, Yin S, et al. Preparation of a visible sensitive carbon doped TiO₂ photo-catalyst by grinding TiO₂ with ethanol and heating treatment. *Appl Catal B-Environ*, 2008, 80: 81–87
- 43 Yin S, Ihara K, Komatsu M, et al. Low temperature synthesis of TiO_{2-x}N_y powders and films with visible light responsive photocatalytic activity. *Solid State Commun*, 2006, 137: 132–137
- 44 Pansila P, Witit-Anun N, Chaiyakun S. Influence of sputtering power on structure and photocatalyst properties of DC magnetron sputtered TiO₂ thin film. *Procedia Eng*, 2012, 32: 862–867
- 45 Yin S, Sato T. Synthesis and photocatalytic properties of fibrous titania prepared from protonic layered tetratitanate precursor in supercritical alcohols. *Ind Eng Chem Res*, 2000, 39: 4526–4530
- 46 Li H, Yin S, Wang Y, et al. Current progress on persistent fluorescence-assisted composite photocatalysts. *Funct Mater Lett*, 2013, 06: 1330005
- 47 Li H, Yin S, Sato T. Persistent deNO_x ability of CaAl₂O₄:(Eu, Nd)/TiO_{2-x}N_y luminescent photocatalyst. *Nanoscale Res Lett*, 2011, 6:5
- 48 Li H, Yin S, Sato T. Novel luminescent photocatalytic deNO_x activity of CaAl₂O₄:(Eu,Nd)/TiO_{2-x}N_y composite. *Appl Catal B-Environ*, 2011, 106: 586–591
- 49 Li H, Yin S, Wang Y, et al. Effect of phase structures of TiO_{2-x}N_y on the photocatalytic activity of CaAl₂O₄:(Eu, Nd)-coupled TiO_{2-x}N_y. *J Catal*, 2012, 286: 273–278
- 50 Li H, Yin S, Wang Y, et al. Persistent Fluorescence-assisted TiO_{2-x}N_y-based photocatalyst for gaseous acetaldehyde degradation. *Environ Sci Technol*, 2012, 46: 7741–7745
- 51 Li H, Yin S, Wang Y, et al. Green phosphorescence-assisted degradation of rhodamine B dyes by Ag₃PO₄. *J Mater Chem A*, 2013, 1: 1123–1126
- 52 Mai H X, Zhang Y W, Sun L D, et al. Highly efficient multicolor up-conversion emissions and their mechanisms of monodisperse NaYF₄:Yb,Er core and core/shell-structured nanocrystals. *J Phys Chem C*, 2007, 111: 13721–13729
- 53 Li H, Yin S, Wang Y, et al. Blue fluorescence-assisted SrTi_{1-x}CryO₃ for efficient persistent photocatalysis. *RSC Adv*, 2012, 2: 3234–3236
- 54 Wu X, Yin S, Dong Q, et al. UV, visible and near-infrared lights induced NO_x destruction activity of (Yb,Er)-NaYF₄/C-TiO₂ composite. *Sci Rep*, 2013, 3: 2918
- 55 Wu X, Yin S, Dong Q, et al. Blue/green/red colour emitting up-conversion phosphors coupled C-TiO₂ composites with UV, visible and NIR responsive photocatalytic performance. *Appl Catal B-Environ*, 2014, 156-157: 257–264
- 56 Haw C, Chiu W, Abdul Rahman S, et al. The design of new magnetic-photocatalyst nanocomposites (CoFe₂O₄-TiO₂) as smart nanomaterials for recyclable-photocatalysis applications. *New J Chem*, 2016, 40: 1124–1136
- 57 Guo C, Yin S, Zhang P, et al. Novel synthesis of homogenous Cs_xWO₃ nanorods with excellent NIR shielding properties by a water controlled-release solvothermal process. *J Mater Chem*, 2010, 20: 8227
- 58 Guo C, Yin S, Yan M, et al. Facile synthesis of homogeneous Cs_xWO₃ nanorods with excellent low-emissivity and NIR shielding property by a water controlled-release process. *J Mater Chem*, 2011, 21: 5099–5105
- 59 Guo C, Yin S, Yu H, et al. Photothermal ablation cancer therapy using homogeneous Cs_xWO₃ nanorods with broad near-infrared absorption. *Nanoscale*, 2013, 5: 6469–6478
- 60 Guo C, Yin S, Yan M, et al. Morphology-controlled synthesis of W₁₈O₄₉ nanostructures and their near-infrared absorption properties. *Inorg Chem*, 2012, 51: 4763–4771
- 61 Wu X, Yin S, Dong Q, et al. Photocatalytic performance and near infrared absorption property of tungsten and tungsten-carbon doped titania. *Mater Tech*, 2014, 29: A20–A27
- 62 Wu X, Yin S, Xue D, et al. A Cs_xWO₃/ZnO nanocomposite as a smart coating for photocatalytic environmental cleanup and heat insulation. *Nanoscale*, 2015, 7: 17048–17054
- 63 Wu X, Wang J, Zhang G, et al. Series of M_xWO₃/ZnO (M=K, Rb, NH₄) nanocomposites: Combination of energy saving and environmental decontamination functions. *Appl Catal B-Environ*, 2017, 201: 128–136
- 64 Liu T, Liu B, Wang J, et al. Smart window coating based on F-TiO₂-K_xWO₃ nanocomposites with heat shielding, ultraviolet isolating, hydrophilic and photocatalytic performance. *Sci Rep*, 2016, 6: 27373
- 65 Takata T, Pan C, Domen K. Recent progress in oxynitride photocatalysts for visible-light-driven water splitting. *Sci Tech Adv Mater*, 2015, 16: 033506
- 66 Chen S, Qi Y, Hisatomi T, et al. Efficient visible-light-driven z-scheme overall water splitting using a MgTa₂O_{6-x}N_y/TaON heterostructure photocatalyst for H₂ evolution. *Angew Chem Int Ed*, 2015, 54: 8498–8501
- 67 Wang B, Kanhere P D, Chen Z, et al. Anion-doped NaTaO₃ for visible light photocatalysis. *J Phys Chem C*, 2013, 117: 22518–22524
- 68 Kato H, Ueda K, Kobayashi M, et al. Photocatalytic water oxidation under visible light by valence band controlled oxynitride solid solutions LaTaON₂-SrTiO₃. *J Mater Chem A*, 2015, 3: 11824–11829