

Review Article

The Progress of TiO₂ Nanocrystals Doped with Rare Earth Ions

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In the past decades, TiO₂ nanocrystals (NCs) have been widely studied in the fields of photoelectric devices, optical communication, and environment for their stability in aqueous solution, being nontoxic, cheapness, and so on. Among the three crystalline phases of TiO₂, anatase TiO₂ NCs are the best crystallized phase of solar energy conversion. However, the disadvantages of high band gap energy (3.2 eV) and the long lifetime of photogenerated electrons and holes limit its photocatalytic activity severely. Therefore, TiO₂ NCs doped with metal ions is available way to inhibit the transformation from anatase to rutile. Besides, these metal ions will concentrate on the surface of TiO₂ NCs. All above can enhance the photoactivity of TiO₂ NCs. In this paper, we mainly outlined the different characterization brought about in the aspect of nanooptics and photocatalytics due to metal ions added in. Also, the paper mainly concentrated on the progress of TiO₂ NCs doped with rare earth (RE) ions.

1. Introduction

As one of the most popular semiconductors, TiO₂ has attracted lots of interest for its high photodegradation efficiency, high photocatalytic activity, high stability, and other advantages [1–4]. Just for these reasons, it has been used to purify polluted water and air, to solve the environmental problems, to be host in the field of solar cell and other relative areas [5, 6]. It is well known that reduction of particle size of crystalline system can result in remarkable modification of their physical and chemical properties which are different from those of micro-sized materials, as called bulk, because of surface effect and quantum confinement effect of nanometer materials. Thus TiO₂ NCs have been one of the research central issues. But TiO₂ NCs have the limits of wide band and the trend to transform to rutile from anatase, which has a negative effect to the photocatalytic activity. Some researchers have reported that they could improve the absorption and photocatalytic activity via dye-sensitizing, surface deposition with metal or doping with metal, nonmetal, or their oxides [7–11]. And many nonmetal ions have been successfully doped, such as S, C, F, N, and B [8, 12–16]. Although doping such additives could change the band gap, they will get the oxidative capacity down. Thus,

it cannot degrade the adsorption on the surface of nano-TiO₂ absolutely. In addition, the structure stability is not that well. Also, doping metal ions to nano-TiO₂ has also been studied extensively, such as Pt and W [17–20]. Particularly, many studies have been focused on doping RE ions into TiO₂ NCs to improve this situation [21–27]. Because of the perfect ability of titanium oxide to form complexes with the f-orbital from RE, it will adsorb foreign ions around the surface, then enhancing the photocatalytic activity or other optoelectronic characteristics [27, 28]. Among all the RE elements, the Eu/Er ions are considered as the best choice for its excellent physical and chemical performance. The RE ions will form complexation with RE–O–Ti bond on the inner-sphere surface. On the one hand, this bond will inhibit the transformation from anatase to rutile, and on the other hand, the formed complexation will strengthen the ability to adsorb foreign ions [27]. In addition, the absorption of TiO₂ NCs doped with RE ions may be adjusted from UV to visible light region because the RE ions have large amounts of energy levels. So it is very necessary for researchers to explore the theory and the experimental results on such field. And now it has been widely known that the photocatalytic reactivity of titanium dioxide depends on microstructure, particle size, preparative route, foreign ions, and so forth [29–31].

In this paper, we introduced the recent development of nanocrystalline TiO₂ doped with RE ions or other additives.

2. The Approaches to Fabricate TiO₂ NCs

The synthesis technique can affect nanocrystalline TiO₂ on the structure, purity, morphology, and other qualities. The soft chemical method, such as sol-gel, hydrothermal method, has many advantages, such as easy, cheaper, preparation processes being controlled and has been applied to prepare TiO₂ NCs extensively. The comparison among these methods was listed in Table 1.

2.1. Hydrothermal Method. The hydrothermal growth of TiO₂ nanowires with using TiO₂ powder in a 5–10 M alkali solution has been extensively applied [33, 34]. However, these films fabricated by this method are very thin, and the processing temperature is too high to be large-scale applications. Still, there are two major controversies about the chemical structure and formation mechanism in the hydrothermal process of TiO₂ NCs doped with RE ions [32]. These chemical structures and their lattice parameters are shown in Table 2. The chemical composition of Na_xH_{2-x}Ti₃O₇ and Na_xH_{2-x}Ti₂O₄(OH) groups are more acceptable. The replacement of Na⁺ by H⁺ during acid washing and the existence of [TiO₆] play a very important role in forming the TiO₂ nanotubes. And rutile is thought to have a better ability to rearrange than anatase phase. The TiO₂ NCs doped with RE ions are usually formed during the sol-gel process [35–38]. After annealing at a relatively high temperature, the RE ions are absorbed on the surface of NCs or enter into the vacancies of lattice just for the theory of solid reaction. Doping of RE ions will inhibit the transformation from anatase to rutile, then it maybe have a high affect on the TiO₂ nanotube growing as thin-and-long state. It is important and interesting that Tong et al. reported that the TiO₂ NCs-doped Ce⁴⁺ ions by hydrothermal method could effectively improve the photocatalytic activity of TiO₂ NCs under both UV light irradiation and visible light irradiation due to the important role 4f electron configuration of Ce⁴⁺ ions played in interfacial charge transfer and elimination of electron-hole recombination [39]. Yan et al. thought that the expansion of the lattice that probably results from the formation of RE–O–Ti bonds [35]. Also they found that the percentage of anatase phase in RE-doped TiO₂ decreasing in the order of Nd³⁺ > Pr³⁺ > Y³⁺ > La³⁺, as is shown in Table 3, but the degree of red shift increases in the order of La³⁺ < Pr³⁺ < Nd³⁺ < Y³⁺-doped samples, in contrast with the ion radii of RE. We can conclude, the doping of RE ion will cause the energy transfer with TiO₂ conduction or valence band, which will lead red shift due to the transition of the electrons situated in the inner 4f orbital to the 5d orbital (4f-5d transition) or to other 4s orbital (f-f transition) [40]. The applied temperature, treatment time, the type of alkali solution, and the Ti precursor during the hydrothermal treatment [32] are considered as the predominant factors affecting the fabrication of TiO₂ doped with RE. So the study on how the RE ions affect the formation of TiO₂ associating

with these factors above is very necessary to put the TiO₂ NCs into actual application.

2.2. Sol-Gel Synthesis. Sol-gel approach is one of the most practical manners to prepare inorganic materials for its simpleness and low cost. And we can acquire nanoparticles with dimensions ranging from 5 to 100 nm. The material obtained by this method shows many desirable properties such as high surface area, high homogeneity [41–43]. But because the precursor has a so high reactivity that it is hard to control the structure development during the hydrolysis and condensation, which makes it difficult to fabricate monolithic TiO₂ NCs [44–48]. Chen et al. have reported C-, N-modified porous monolithic TiO₂ NCs through sol-gel technique with average particle size of 7.8 nm [48]. And the reaction rate of decolorization of methyl orange is 0.0026 min⁻¹, which proves that the ratio of the precursors plays an important role in the structure and photo activity. Moreover, Zeng et al. had prepared Eu:TiO₂ with a strong photoluminescence emission with the average particle size of 13 nm [49]. As for the RE ions, it is often doped into the solution of precursor in the form of nitrate or chloride. After several hours of stirring, we can obtain transparent sol with RE. Then the sample must be annealing at a certain temperature for a certain period to ensure Ln(III)-TiO₂ NCs obtained. Stengl et al. studied the affects of RE (La, Ce, Pr, Nd, Sm, Eu, Dy, Gd) on the physical and chemical properties of titania NCs by sol-gel method [50], as is shown in Figure 1. They found that best photocatalytic properties in visible light were the TiO₂ NCs doped with Nd³⁺ ions ($k = 0.0272 \text{ min}^{-1}$ for UV and 0.0143 min^{-1} for visible light). Xu et al. also got the similar result that Gd³⁺-doped TiO₂ showing the highest reaction activity among all concerned RE-doped samples (Sm³⁺-, Ce³⁺-, Er³⁺-, Pr³⁺-, La³⁺-, and Nd³⁺-doped TiO₂ NCs catalyst) because of its specific characteristics [23], which was similar with the result from the study of El-Bahy et al., who also thought that Gd³⁺-doped TiO₂ NCs are more effective than La³⁺, Nd³⁺, Sm³⁺, Eu³⁺, and Yb³⁺ just because Gd³⁺/TiO₂ NCs have the lowest band gap and particle size, and also the highest surface area and pore volume [51]. At the meantime, the conclusion that the synthesized Eu/TiO₂ catalyst exhibits strong red emissions under excitation wavelength at 394 and 464 nm from the comparison Eu/TiO₂ and Gd/TiO₂ by Zhou et al. [52]. As can be concluded that, the relationship between RE and luminescent properties or catalytic efficiency needs further research in the field of TiO₂ NCS synthesized by sol-gel technique.

2.3. Anodic Oxidation Method. Since Grimes and coworkers first reported the fabrication of titania nanotube array via anodic oxidation of titanium foil in a fluoride-based solution in 2001 [53], the studies on precise control and extension of the nanotube morphology, length and pore size, and wall thickness [54, 55] have obtained extensive attention. As is thought that chemical dissolution and electrochemical etching process play an important role in the conformation of nanotubes. And the electrolyte used in this system is

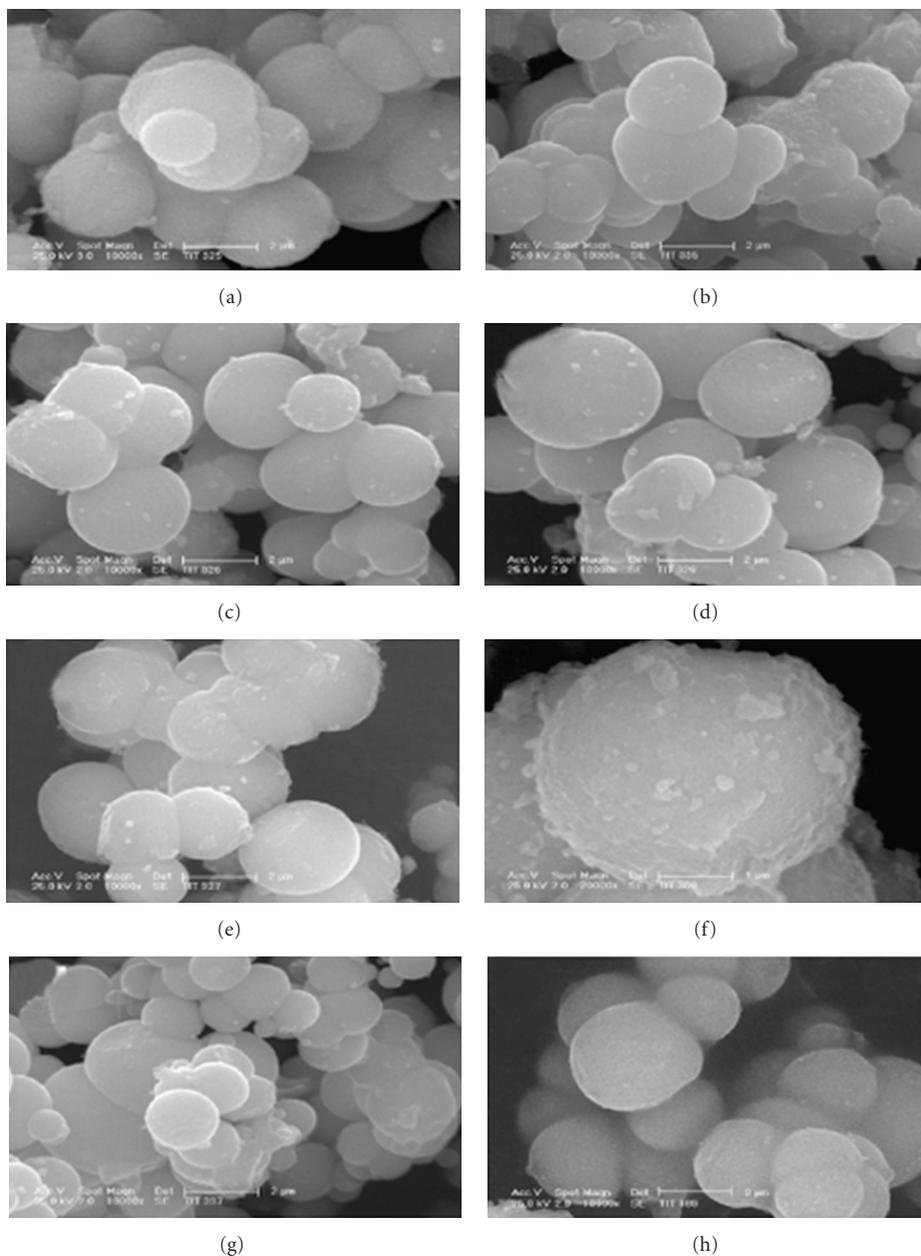


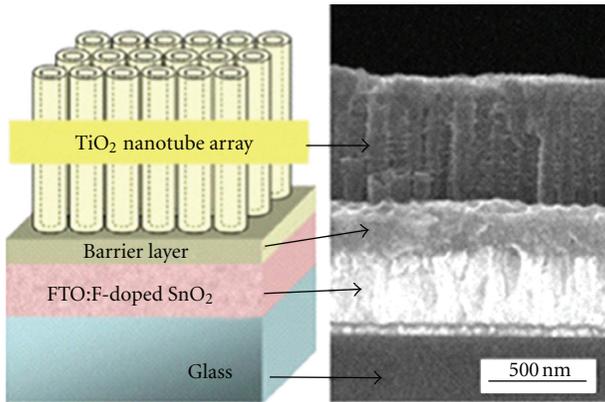
FIGURE 1: SEM images of sample denoted as (a) TiNd_1: 100 g TiOSO_4 + 3.15 g Nd, (b) TiSm_1: 100 g TiOSO_4 + 3 g $\text{Sm}(\text{NO}_3)_3$, (c) TiCe3_1: 100 g TiOSO_4 + 0.25 g $\text{Ce}_2(\text{SO}_4)_3$, (d) TiCe4_1: 100 g TiOSO_4 + 0.25 g $\text{Ce}(\text{SO}_4)_2$, (e) TiDy_1: 100 g TiOSO_4 + 3.10 g Dy_2O_3 , (f) TiEu_1: 100 g TiOSO_4 + 6.00 g Eu_2O_3 , (g) TiPr_1: 100 g TiOSO_4 + 1.50 g $\text{Pr}(\text{NO}_3)_3$, and (h) TiLa_1: 100 g TiOSO_4 + 1 g $\text{La}(\text{NO}_3)_3$. Reprinted with permission from [50].

always HF or KF, whose concentration has a strong effect on the dimensions and nanotube arrays [56]. Using the anodic potential from 10 to 20 V, self-organized TiO_2 NCs can be produced with diameters between 15 nm and 200 nm under specific electrochemical condition [57, 58]. The pH value of the electrolyte will also affect the thickness of TiO_2 nanotube layers [58, 59]. Yang et al. used anodization method then obtained TiO_2 nanotube arrays with a high surface area [60], as seen in Figure 2. It can be seen that the length and average outer diameter of this nanotube is 680 nm and

80 nm with a length-to-width aspect ratio about 8.5, which raises the conversion efficiencies to 0.31%, improving surface activities largely. RE ions are usually added into TiO_2 NCs during the preparation procedure. After heating at 400°C for a certain time for decomposing the organic compounds brought into during the preparation procedure, the samples are needed to be heated to higher temperature for the insurance of formation of RE compounds in the layers [61]. Graf et al. successfully prepared the TiO_2 doped with cerium and gadolinium ions in the anodic oxidation method, and

TABLE 1: Comparison of current methods in TNT fabrication. Reprinted with permission from [32].

Fabrication method	Advantages	Disadvantages	TNT features
Template-assisted method	(1) The scale of nanotube can be moderately controlled by applied template	(1) Complicated fabrication process (2) Tube morphology may be destroyed during fabrication process	Ordered arrays (powder form)
Electrochemical anodic oxidation method	(1) More desirable for practical applications (2) Ordered alignment with high aspect ratio (3) Feasible for extensive applications	(1) Mass production is limited (2) Rapid formation kinetics is subjected to the utilization of HF (3) Highly expense of fabrication apparatus	Oriented arrays (thin film)
Hydrothermal treatment	(1) Easy route to obtain nanotube morphology (2) A number of modifications can be used to enhance the attributes of titanium nanotubes (3) Feasible for extensive applications	(1) Long reaction duration is needed (2) Highly concentrated NaOH must be added (3) Difficult in achieving uniform size	Random alignment (powder form)

FIGURE 2: Schematic diagram of TiO₂ nanotube photoanode architecture and SEM cross-sectional view of sample fabricated by anodization method. Reprinted with permission from [60].

they found that Gd-doped titanium dioxide showed better photocatalytic activity than cerium-doped sample possibly because Gd³⁺ ions have better stability [62].

2.4. Other Methods. Nowadays, there are also some other routes to fabricate TiO₂ NCs. For example, Liang et al. had studied the effects brought by doping these ions of La, Y, Yb, Eu, Dy into TiO₂ NCs with the plasma way [63]. And they found that the effects of pH, sample flow rate and volume, elution solution, and interfering ions on the separation of analytes all have influence on the photocatalytic activity. Wu et al. systematically explored the effects for lanthanum-ions-doped TiO₂ NCs by plasma spray as well [64].

Template-assisted method is one of the most popular ways to fabricate such material. Attar et al. successfully prepared well-aligned anatase and rutile TiO₂ nanorods and nanotubes with a diameter of about 80–130 nm via sol-gel template method [65]. Also, magnetron sputtering method, electrophoretic deposition (EPD), and many other methods

TABLE 2: Proposed chemical structures of TNTs and their corresponding lattice parameters. Reprinted with permission from [32].

Chemical structure	Lattice parameters
Anatase TiO ₂	Tetragonal; $a = 3.79$ nm, $b = 3.79$, $c = 2.38$
N ₂ Ti ₃ O ₇ , Na ₂ Ti ₃ O ₇ , Na _x H _{2-x} Ti ₃ O ₇	Monoclinic; $a = 1.926$ nm, $b = 0.378$, $c = 0.300$, $\beta = 101.45^\circ$
H ₂ Ti ₂ O ₄ (OH) ₂ , Na ₂ Ti ₂ O ₄ (OH) ₂	Orthorhombic; $a = 1.808$ nm, $b = 0.379$, $c = 0.299$
H _x Ti _{2-x/4} □ _{x/4} O ₄ (H ₂ O)	Orthorhombic; $a = 0.378$ nm, $b = 1.874$, $c = 0.298$
H ₂ Ti ₄ O ₉ (H ₂ O)	Monoclinic; $a = 1.877$ nm, $b = 0.375$, $c = 1.162$, $\beta = 104.6^\circ$

□: Vacancy.

are employed to fabricate TiO₂ NCs doped with RE ions [66–70]. All above methods also could create nanomaterial with perfect morphology and high photocatalytic activity.

3. The Effect Caused by RE Ions

In this section, we mainly discuss the change of optical properties and the morphology caused by the RE ions doped or codoped with RE and other non-RE.

3.1. The Theory of the Effect Caused by RE Ions. The energy transfer from TiO₂ NCs to RE may easily take place since RE ions have a plenty of energy levels. For example, ⁵D₁ → ⁷F₁, ⁵D₀ → ⁷F_{*j*} ($j = 1, 2, 3, 4$) transitions of Eu³⁺ ions will cause visible luminescence peaking at 543, 598, 620, 665, and 694 nm [71]. In addition, the RE-doped TiO₂ NCs almost have the capacity to enhance photocatalytic activity due to

TABLE 3: Structural parameters of rare-earth-doped TiO₂ after template removal. Reprinted with permission from [35].

Sample	Percentage of anatase phase	Specific surface area (m ² /g)	Modal pore diameter (nm)	Total pore volume (cm ³ /g)
TiO ₂ ⁻²	83.17	165	1.6	0.11
[0.3%]	95.18	220	1.4	0.14
Nd-doped TiO ₂				
[0.3%]	90.22	200	1.6	0.15
Pr-doped TiO ₂				
[0.3%]	86.35	289	1.6	0.11
La-doped TiO ₂				
[0.3%]	83.71	175	1.4	0.11
Y-doped TiO ₂				

following properties of as-prepared RE³⁺/TiO₂ composites: (i) quantum size effect; (ii) unique textural properties (mesoporosity with larger BET surface areas and pore sizes); (iii) interesting surface compositions (more hydroxyl oxygen and adsorbed oxygen and some Ti³⁺ species existed at the surface of the products with respect to pure TiO₂) [72], while some thought that the increase in photoactivity is probably due to the higher adsorption, red shifts to a longer wavelength, and the increase in the interfacial electron transfer rate [41, 51].

3.2. The Effect Caused by RE Ions Doped Only. TiO₂ NCs doped with RE ions can concentrate organic pollutants on the semiconductor surface just because lanthanide ions can form complexes with various Lewis bases including organic acids, amines, aldehydes, alcohols, and thiols by the interaction of the functional groups with their f orbital, which can enhance the efficiency of separation between electrons and holes and prohibit the transformation from anatase to rutile [27, 28, 73]. Accordingly, it can prolong the photoresponse in visible region. Du et al. studied the effect of surface OH population on the photocatalytic activity of RE-doped P25-TiO₂ systematically [74], listed in Table 4. It can be seen that Pr, La, Ce, Y, and Sm ions in TiO₂ Ncs have a significant inhibition of phase transformation, especially at 800°C or above. And the anatase fraction follows the decreasing order Pr > La > Ce > Y > Sm. At the meantime, we can also know that the photocatalytic degradation of methylene blue over RE oxide-modified TiO₂ is mainly dependent on the quantity of a specific anatase—OH group. Cacciotti et al. successfully prepared La-, Eu-, and Er-doped TiO₂ NCs via electrospinning technique [75], which also can raise the transformation temperature up to 900°C. Wang et al. also synthesized TiO₂ NCs doped with Eu, Er, Ce, Pr by this method [76]. And the particles obtained had

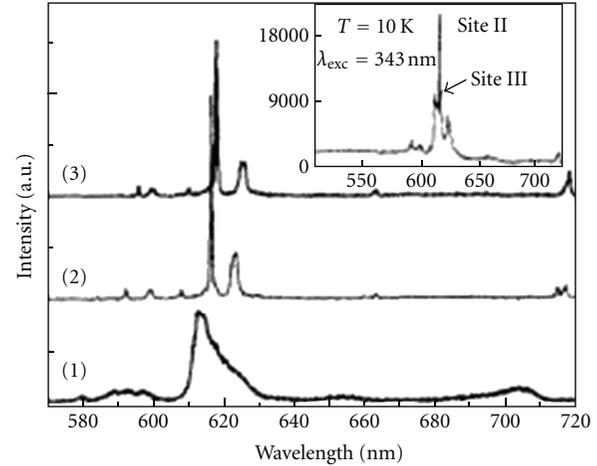


FIGURE 3: Site-selective emission spectra of the Eu_{3n}:TiO₂ nanocrystals at 10 K, with curves (1) $\lambda_{\text{exc}} = 464.7$ nm for Site I; (2) $\lambda_{\text{exc}} = 470.6$ nm for Site II; and (3) $\lambda_{\text{exc}} = 472.0$ nm for Site a, respectively. The inset shows the 10 K emission spectrum under the band gap excitation at 343.1 nm. Reprinted with permission from [81].

an average diameter of 10 nm with remarkable luminescent properties. It can be clearly seen that most of the RE ions have the ability to inhibit the transformation from anatase to rutile. Li et al. reported that the luminescent intensity can be enhanced through energy transfer from Eu³⁺ to TiO₂ NCs [77]. Jeon and Braun synthesized Er³⁺-doped TiO₂ nanoparticles (~50 nm) through a simple hydrothermal method starting from sol-gel precursors with anatase phase [78]. They observed obviously enhanced luminescence from thin films of the nanoparticles by annealing at 500°C. A sharp emission peak at 1532 nm with a full width at half maximum (FWHM) of 5 nm was observed, which excludes the possibility that Er³⁺ ions exist under a free oxide form in the TiO₂ matrix, with contrast with the emission band of erbium oxide nanoclusters synthesized through a microemulsion technique centered at 1540 nm with an FWHM of 22 nm [79]. Patra et al. also studied the upconversion luminescence of Er doped into TiO₂ NCs under 975 nm excitation [80].

However, there are two major controversies still exist [81]. One is whether the lifetime of transition metal or RE ions-doped TiO₂ semiconductor NCs can be shortened by orders of magnitude caused by quantum size effects. The other is that lanthanide ions incorporate into the lattice sites of the host or be adsorbed on the surface because of the different radius and valence between RE ions and cationic of host. Chen et al. prepared TiO₂:Eu anatase NCs (8–12 nm) by a hydrothermal method and proved that Eu³⁺ occupy three sites in NCs host through site selective spectra at 10 K [81], as shown in Figure 3. By means of site selective spectra, at least three kinds of luminescence sites of Eu³⁺ are identified and separated from each other. Two sites (Sites II and IU) exhibit sharp emission and excitation peaks, which are ascribed to the lattice site with ordered crystalline environment (inside). The other site (Site I) associated with

TABLE 4: Characterization of samples. Reprinted with permission from [74].

Sample	Anatase fraction ^a [nm]	Anatase crystal size ^a [nm]	Rutile crystal size ^a [nm]	Band gap energy [eV]	S _{scr} [m ² /g]
P25	0.70	22	37	3.25	51
P25_600	0.70	25	36	3.23	47
P25_0, 2La_600	0.71	28	41	3.23	46
P25_0, 2Ce_600	0.71	27	50	3.19	47
P25_0, 2Y_600	0.72	28	39	3.16	46
P25_0, 2Pr_600	0.71	27	50	3.14	47
P25_0, 25m_600	0.71	26	47	3.16	46
P25_800	0.05	—	43	3.04	16
P25-0.2La-800	0.22	31	43	3.03	23
P25-0.2Ce-800	0.15	35	45	3.04	19
P25-0.2Y-800	0.13	30	50	3.02	20
P25-0.2Pr-800	0.31	35	47	3.02	24
P25-0.25m-800	0.08	29	50	3.01	17
P25-1La-800	0.31	35	45	3.05	25
P25-1Ce-800	0.48	31	47	3.07	30
P25-1Y-800	0.05	—	50	3.04	16
P25-1Pr-800	0.15	31	45	3.03	21
P25-15m-800	0.37	33	50	3.06	29
P25_2La_800	0.14	34	47		21
P25_2Ce_800	0.15	35	49		18

^a Determined from XRD.

the distorted lattice sites near the surface shows significantly broadened fluorescence lines. very strong Eu^{3+} luminescence from major Sites II and III plus other minor sites can be seen under the band gap excitation at 343.1 nm. The energy transfer from the host to Eu^{3+} confirms that Eu^{3+} ions have been effectively incorporated into the TiO_2 NCs. But it should be noted that there may be some RE ions locating at surface sites. So it always has a long way to explore the function caused by lanthanide ions doped.

3.3. The Effect Caused by Codoped RE Ions and Other Ions. Besides, Xu et al. and Ma et al. had prepared the TiO_2 NCs codoped with RE ions and nonmetal ions by the sol-gel method [82, 83], which had better adsorption activity than those doped with RE ions only. Xu et al. reported that Eu-, N-codoped TiO_2 NCs exhibited a significant red shift to the visible area [82], as shown in Figure 4. It is obvious that Eu-, N-codoped TiO_2 NCs show the highest adsorption activity. And we could also know that Eu-, N-codoped TiO_2 NCs have a smaller particle with a good inhibition from anatase to rutile. Besides, Ma et al. also obtained Sm-, N-codoped TiO_2 NCs by a similar way [83], which was similar to the result of Eu-, N-codoped TiO_2 NCs. Thus, we can conclude the absorption of TiO_2 NCs could be modulated from UV light to visible light because of the addition of RE ions, which can meet the application. It is thought that the metal ions (such as lanthanide ions) doped TiO_2 NCs will expand the photoresponse area. Meantime, the nonmetal ions will inhibit the combination

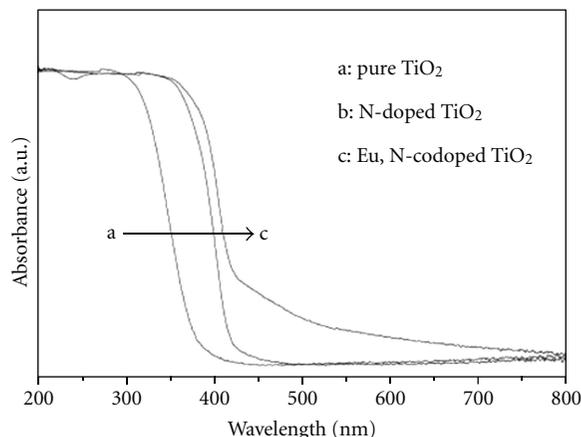


FIGURE 4: DRS spectra of Eu, N-codoped titania, N-doped titania, and pure titania. Reprinted with permission from [82].

of photogenerated electrons and holes. And it also has the ability to suppress the transformation from anatase to rutile. So it is hopeful to improve the photocatalytic activity by adding the metal ions with nonmetal elements.

4. Conclusion

In conclusion, TiO_2 NCs are chosen as one of the most potential candidates to purify polluted water and air, to solve the environmental problems, and to be host in the field of

solar cell and other relative areas for its excellent stability, low cost, and friendliness to environment. Adding RE ions to TiO₂ can suppress the transformation to rutile from anatase, absorb the organic pollutant on the surface of the base, then improving the photocatalytic activity. So RE-doping nano-TiO₂ has been studied extensively, but the application situation is not that affirmative. The author suggested that the development orientation include these aspects below.

- (1) explore the influent theory about the co-doping ions into nano-TiO₂, such as metal and metal, metal and nonmetal, nonmetal and nonmetal, especially the area of metal and nonmetal coexists,
- (2) investigate the way to improve the catalytic properties, without sacrificing the oxidation activity, especially adjusting the absorption range,
- (3) search for the ideal ways to manufacture RE-doped TiO₂ NCs so as to modulate the absorption to visible region and to meet its industrial needs.

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