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Research Article

Effect of Li(I) and TiO_2 on the Upconversion Luminance of Pr:Y_2SiO_5 and Its Photodegradation on Nitrobenzene Wastewater

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Based on the substrate of Pr:Y_2SiO_5 upconversion nanomaterials, lithium ion Li(I) doped Pr:Y_2SiO_5 and TiO_2 nanofilm coated Li,Pr:Y_2SiO_5 composites were prepared by using a sol-gel method. X-ray diffractometer, SEM, and fluorescence spectrometer have been employed to test the crystal structure, microimages, and upconversion luminescence performances. The doping of Li(I) affects highly the crystal transition of Pr:Y_2SiO_5 and X2-Y_2SiO_5 phase was well formed by doping 8% Li(I). Furthermore, the doping of Li(I) also brings high luminance intensity of Pr:Y_2SiO_5 and contributes to a maximum intensity of 9.76×10^6 cps doped 8%. Too much of Li(I) doping would result in big crystal size and fluorescence quenching of Pr:Y_2SiO_5 material. However, the coating of TiO_2 nanofilm is not helping in increasing the upconversion fluorescence of Li,Pr:Y_2SiO_5 but is promoting the full use of the fluorescence. The luminescence intensities of TiO_2/Li,Pr:Y_2SiO_5 composites are getting down sharply with the coating amount since the luminescence emitted by Li,Pr:Y_2SiO_5 is quickly adsorbed in situ by the TiO_2 coating film. With the optimum coating concentration of 1%, the TiO_2/Li,Pr:Y_2SiO_5 composite shows excellent photodegradation performances on nitrobenzene wastewater, though it shows a low luminescence intensity. For 5 mg/L nitrobenzene wastewater, the composite presents a photodegradation rate of 97.08% in 4 hours.

1. Introduction

Currently, rare earth luminescent materials have been widely studied and used in information display, lighting, and other areas of optoelectronic devices supporting material [1–5], since its phosphor high luminous intensity and good shape can effectively improve the microscopic performance of the display. However, researches focused on the luminescence application in other fields, which the fluorescent materials emitted, are not as much as in the display fields. Some reports aimed at biological application, such as antibacterials [6, 7], and some researchers focus on environmental application of the luminescent materials [8, 9].

As one of the most researched luminescent material, yttrium silicates Y_2SiO_5 has a great potential application in many fields because of its high stability and good luminescence properties. Activated Y_2SiO_5 luminescent material which is usually doped with other metal ions or activating agents is widely researched because of its much higher luminescence intensity than that of nonactivated material [10, 11]. Yttrium silicates Y_2SiO_5 has a particular geometry which leads to a possible replace of Y by other element ions, especially rare earth ions [12]. For example, Ce(III) doped Y_2SiO_5 can replace ZnS:Ag and can be used as blue phosphors for field emission display (FED); Tb(III) doped Y_2SiO_5 is a kind of cathode luminescence materials. Praseodymium ion Pr(III) has a similar ionic radius with Y ion but more suitable energy levels and longer excited state lifetimes than Y. As a result, higher energy photons and higher luminescence intensity could be emitted. Because of the small ionic radius, lithium ion Li(I) can easily get into the crystal lattice and replace the host atoms of Y_2SiO_5.

The photocatalytic behavior of TiO_2 has been studied extensively, because of the ability of nanoscale TiO_2 to

decompose a wide variety of inorganic and organic pollutants and toxic material in both liquid and gas phase systems [13–15], as well as the photocatalysis of nanoscale TiO_2 and its application for water purification [16, 17]. However, only ultraviolet light wavelength less than 387 nm, which is about 4% of the solar light, can be absorbed by pure anatase TiO_2, since the energy gap of pure anatase TiO_2 is about 3.2 eV [18]. This became the main barrier which is limiting the wide use of TiO_2 as a photocatalyst. Many methods can be used to develop TiO_2 as a promising photocatalyst for wastewater treatment, such as surface modification [19, 20], doping with other metal ions, nonmetal ions and semiconductors [21–25], and oxygen vacancy generating [26].

The combination of anatase TiO_2 with upconversion materials could hopefully make more efficient use of solar energy in practical applications and provide a wide use of TiO_2 in photodegradation fields. In this study, Li(I) doped Pr:Y_2SiO_5 upconversion materials and anatase TiO_2 nanofilm coated Li,Pr:Y_2SiO_5 composite have been prepared and the luminescence intensities they emitted were tested. Nevertheless, the photodegradation performances of the as-prepared materials have been tested on the target pollutant of nitrobenzene wastewater.

2. Materials and Methods

2.1. Preparation of Samples. Praseodymium ion Pr(III), 1%, doped Y_2SiO_5 upconversion nanomaterials were prepared by following [8]. First, 0.1 mol/L praseodymium nitrate solution was added to the mixture (1 : 1, vol) of HNO_3 and H_2O dissolving 0.663 g Y_2O_3. Heating was followed until the solution became a viscous mixture. A number of crystals were seed out after cooling down. The crystal was collected and dissolved in ethanol. Tetraethyl orthosilicate (TEOS) was added and mixed with the ethanol solution of the crystals. The obtained mixture was put into a water bath of 70°C until a gel was formed. The gel was dried in an oven at 104°C and then ground into powder. At last, the powder was calcined at a temperature of 950°C for 3 h in a muffle furnace to get the product Pr:Y_2SiO_5 upconversion nanomaterials.

Lithium ion Li(I) doped Pr:Y_2SiO_5 nanomaterials were prepared by adding 0.1 mol/L lithium nitrate to the praseodymium nitrate solution at the first step during the preparation of Pr:Y_2SiO_5. Then, sol-gel process and heat treatment parameters were followed as in the preparation of Pr:Y_2SiO_5 nanomaterials. The lithium ion doping concentrations, 2%, 6%, 8%, and 10%, were adjusted by changing the added volume of lithium nitrate solution. These products were called as Li,Pr:Y_2SiO_5.

The composite catalysts of TiO_2/Li,Pr:Y_2SiO_5 were prepared by adding the as-prepared Li,Pr:Y_2SiO_5 powder, which was ground and ultrasonic-dispersed in absolute alcohol for 30 min, to the mixture of titanium tetrabutoxide, absolute alcohol, and distilled water with a volume ratio of 1 : 7 : 2. The mixture was adjusted to pH 2.5 by using nitric acid. After stirring for 1 h, the suspension was put into a water bath at 70°C to form a white gel. Then, the gel was dried in an oven at 80°C and ground into powder. At last, the powder was calcined at a temperature of 500°C for 2 h in a muffle furnace to get the product TiO_2/Li,Pr:Y_2SiO_5 composite catalyst. The TiO_2 concentrations, 0.3%, 0.5%, 1.0%, and 2.0%, were adjusted by changing the added volume of titanium tetrabutoxide.

2.2. Property Testing of Samples. A scanning electron microscopy (Hitachi S4800, SEM, Japan) was employed to characterize the microimages and particle size of the samples. X-ray diffractometer (D8 Advance, Bruker Corporation, German) was used to characterize the crystal form of the samples. The upconversion luminescence of the nanomaterials was tested by using a fluorescence spectrometer (FL3-TCSPC, Horiba Jobin Yvon Corporation, France). The exciting parameters were selected as 488 nm of the excitation wavelength, 370 nm of the optical filters, and 1 nm of the slit [27, 28].

Nitrobenzene wastewater, which was from a TNT factory and was diluted to 5 mg/L, was used as a target pollutant to test the photodegradation performances of the as-prepared upconversion nanomaterials. Triphosphor tube light, 100 W, was used as the exciting light source for the upconversion nanomaterials. The treatment time lasted for 1 h to 6 h. The degradation rate of nitrobenzene was calculated by comparing the ultraviolet absorption values at the wavelength of 267 nm to the original values of the nitrobenzene solution. The ultraviolet absorption values were tested by using an ultraviolet-visible spectrophotometer. The relationship of the nitrobenzene concentrations (x), in the range of 0.5–10 mg/L, with the ultraviolet absorption value (y), was determined by a linear equation $y = 9.06x - 0.312$, with a correlation R^2 of 0.99982.

3. Results and Discussion

3.1. Pr:Y_2SiO_5 with Different Li(I) Concentrations. Doping ions are known for changing crystal structure and crystal size, as well as light conversion performances for upconversion nanomaterials [8, 9]. Figure 1 shows the XRD patterns of Pr:Y_2SiO_5 with different Li(I) concentrations, 0%, 2%, 6%, 8%, and 10%.

It is known that Y_2SiO_5 has two types of crystal structure, low-temperature (X1) and high temperature (X2), when taking high temperature structure, with better emission performances. It is very interesting that the doping amount of Li(I) contributes a great effect to the crystal transition of Y_2SiO_5 materials. When the doping amounts of Li(I) are not bigger than 6%, the crystal form of samples belongs to low-temperature phase X1 molecular configuration (X1-Y_2SiO_5), which is corresponding to the PDF card number of #52-1810. However, when the doping amounts are high as 8%, the crystal forms of Y_2SiO_5 materials transfer from X1-Y_2SiO_5 to X2-Y_2SiO_5 phase, which is corresponding to the PDF card number of #21-1458, as shown in Figure 2. Generally, for X2-Y_2SiO_5 materials, heat treatment temperature up to 1350°C is needed [12], instead of 950°C in this study. It indicates that the doping of Li(I) can effectively decrease the crystallization temperature of Y_2SiO_5 and promotes the crystallization of X2-Y_2SiO_5 at a lower temperature. When the doping amount

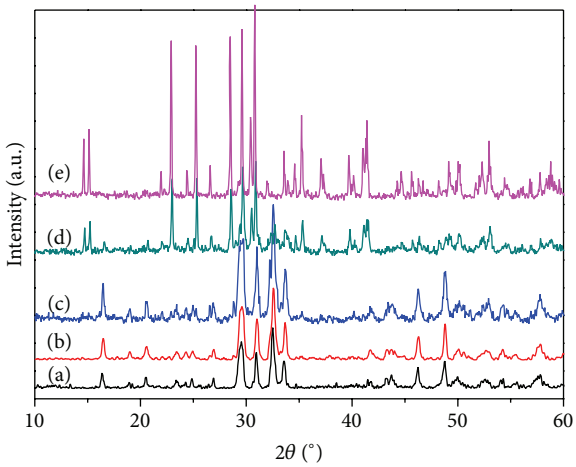


Figure 1: XRD patterns of Pr:Y_2SiO_5 doped different concentrations of Li(I). (a) 0%; (b) 2%; (c) 6%; (d) 8%; (e) 10%.

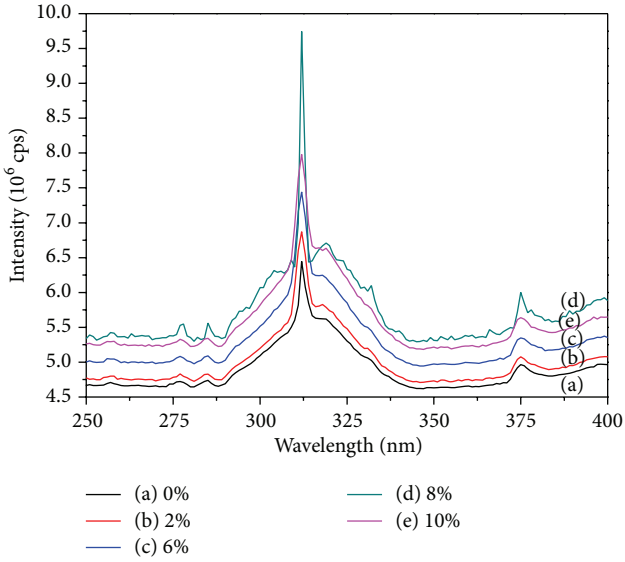
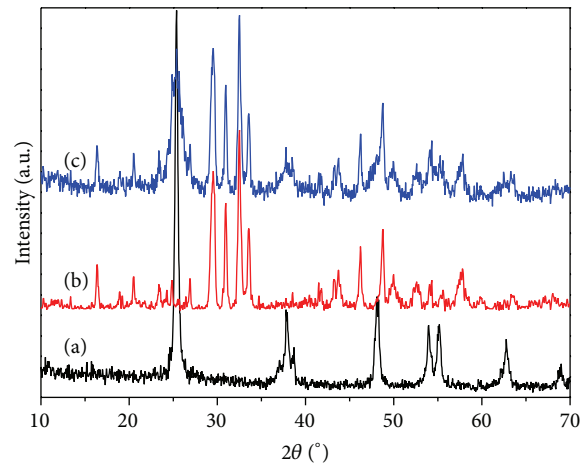


Figure 2: Emission spectra of Pr:Y_2SiO_5 doped different concentrations of Li(I). (a) 0%; (b) 2%; (c) 6%; (d) 8%; (e) 10%.

of Li(I) is increased to 10%, the diffraction peaks show much more sharp than that of 8%. The crystal sizes of Pr:Y_2SiO_5 with 8% and 10% Li(I) are 47.8 nm and 62.5 nm at 2θ angle 30.83°, respectively, which are calculated by the Scherrer equation [29]: $D = K\lambda/(\beta \cos\theta)$, where D is the crystal size (nm); K is 0.89, the Scherrer constant; θ is the diffraction angle at which the diffraction peaks are located (°); β is the full width at half maximum (FWHM) of the main diffraction peaks (rad), which is located at the 2θ angle of 30.83° in this situation; λ is 0.154056 nm, the X-ray wavelength.

Figure 2 shows the upconversion luminescence emission spectra of Pr:Y_2SiO_5 doped with different concentrations of Li(I). Since the excitation wavelength is set on 488 nm, the peaks of the upconversion luminescence emission spectra are located at 312 nm, instead of 425 nm and 360 nm of



(a) TiO_2 (anatase)
(b) Li,Pr:Y_2SiO_5
(c) TiO_2/Li,Pr:Y_2SiO_5

Figure 3: XRD patterns of samples. (a) Commercial anatase TiO_2; (b) Li,Pr:Y_2SiO_5; (c) TiO_2/Li,Pr:Y_2SiO_5.

the excitation wavelength and the emission spectra peaks, respectively [8].

As the Li(I) doping amount increases, the intensity of the emission spectra is increasing gradually but is getting down at the doping amount of 10%, as shown in Figure 2. Sample doped with 8% Li(I) shows the strongest luminescence intensity of 9.76×10^6 cps (count per second), which is about 1.5 times of the blank sample Pr:Y_2SiO_5 (0% Li) emitted at the wavelength of 312 nm. Compared to lower doping samples, sample doped with 8% Li(I) emits much stronger upconversion luminescence, which has more intact X2-Pr:Y_2SiO_5 structures according to the test results in Figure 1. On the other hand, too much of Li(I) doping amount, as shown in Figure 1, would result in big crystal size of Pr:Y_2SiO_5 nanomaterials. For upconversion luminescence nanomaterials, a smaller crystal size hopefully contributes to higher upconversion efficiency. However, it is believed that too high doping concentration of exotic ions would result in luminescent quenching [30]. As a result, the doping concentration of 10% Li(I) results in a low luminescence intensity, as shown in Figure 2. Therefore, Pr:Y_2SiO_5 upconversion nanomaterial doping 8% Li(I), which has a smaller crystal size and less fluorescence quenching, emits much stronger luminescence than that of doping 10% Li(I), as shown in Figure 2.

3.2. Testing of TiO_2/Li,Pr:Y_2SiO_5 Composites. It is different with doping of ions; doping of nanomaterials would seldom change the crystal structure of the host material. Figure 3 shows the XRD patterns of three kinds of samples, commercial nanometer TiO_2 (anatase), as-prepared Li,Pr:Y_2SiO_5 (8% Li), and as-prepared TiO_2/Li,Pr:Y_2SiO_5 (1% TiO_2).

As shown in Figure 3, the XRD pattern of sample (c) is seemly the combination of that of sample (a) and sample (b), which clearly corresponds to the XRD diffraction peaks

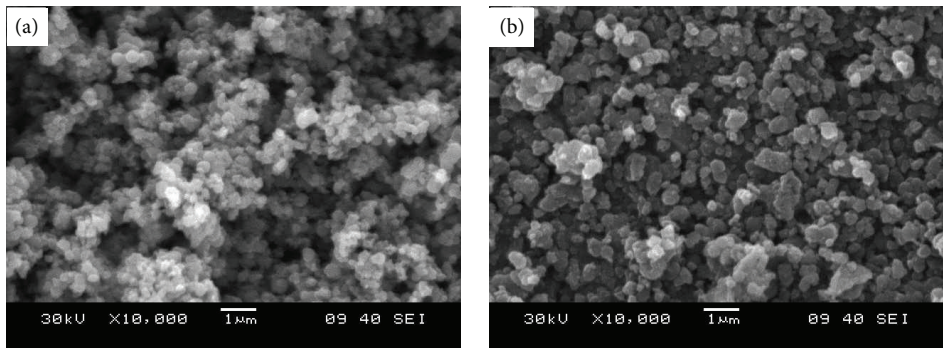


Figure 4: SEM photos of (a) Li,Pr:Y_2SiO_5 and (b) TiO_2/Li,Pr:Y_2SiO_5 nanomaterials.

of TiO_2 and Li,Pr:Y_2SiO_5. However, comparing the intensities of diffraction peaks belonging to TiO_2, the diffraction intensities of sample (c) are much lower than those of sample (a), commercial anatase TiO_2. On the other hand, the diffraction intensities belonging to Li,Pr:Y_2SiO_5 do not show big differences between Li,Pr:Y_2SiO_5 and its composite. It indicates that TiO_2 and Li,Pr:Y_2SiO_5 are two independent materials coexisted in the composite of TiO_2/Li,Pr:Y_2SiO_5. Titanium dioxide probably in the form of films exists on the surface of Li,Pr:Y_2SiO_5 particles, which also can be suggested by the SEM photos of the samples, as shown in Figure 4.

Figure 4(a) shows SEM photo of Li,Pr:Y_2SiO_5 particles, which presents regular but partially reunited spherical particles in the diameter of 300 nm to 500 nm. A little different from Li,Pr:Y_2SiO_5 sample, TiO_2/Li,Pr:Y_2SiO_5 nanoparticles show good dispersibility and are a little big in size, which is in the range of 500 nm to 800 nm, as shown in Figure 4(b). Much bigger particle sizes in SEM than those of XRD indicate that every single particle is composed of several crystals which makes it difficult to disperse the Li,Pr:Y_2SiO_5 powders fully in the preparation process. Energy dispersive X-ray spectrometer (EDS) testing on the sample surface of Figure 4(b) shows that Ti and O are the majority of elements, while Si and Y are the minority of elements. It is difficult to find element information of Li and Pr in the EDS testing. It suggests that TiO_2 film gives intact coating for Li,Pr:Y_2SiO_5 particles in a thickness of about 100 nm to 150 nm.

Figure 5 shows the upconversion emission spectra of Li,Pr:Y_2SiO_5 with different concentrations of TiO_2. It is very different to the situation of doping with Li(I) and Pr(III); the upconversion luminescence intensities are decreasing with the coating amount of TiO_2, instead of increasing by the doping amount of Li(I) and Pr(III). This should be attributed to the semiconductor characteristics of TiO_2. It is known that titanium dioxide is a kind of *n*-type semiconductor material with a band gap of 3.2 eV (for anatase). When it is exposed to ultraviolet light whose wavelength is less than 387.5 nm, energy would be added to valence electron and it would be excited by photon and would leap from the valence band (VB) to the conduction band (CB), where it can move freely around the crystal in the form of photoelectron [31]. As a result, a hole is left behind in the valence band. On the occasion

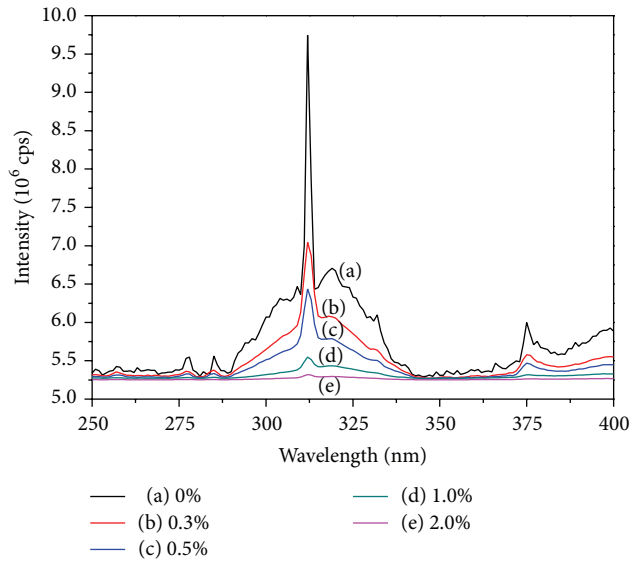


Figure 5: Emission spectra of Li,Pr:Y_2SiO_5 with different concentrations of TiO_2. (a) 0%; (b) 0.3%; (c) 0.5%; (d) 1.0%; (e) 2.0%.

of nanoscale TiO_2 coating on the upconversion material Li,Pr:Y_2SiO_5, the luminescence emitted by Li,Pr:Y_2SiO_5 is absorbed in situ by the TiO_2 coating film. When more of TiO_2 film is coated, less of the luminescence intensity can be tested. When the coating amount of TiO_2 film is up to 1%, the intensity of the emission spectra is very low. There almost can not be found luminescence peaks on the emission spectra of the sample with 2% of TiO_2, as shown in Figure 5. It means that too much of coating TiO_2 would absorb out all the luminescence that the upconversion material Li,Pr:Y_2SiO_5 emitted. Therefore, the coating amount of 1% could be a balance point or optimum value for the composite of TiO_2/Li,Pr:Y_2SiO_5 nanomaterials.

3.3. Photodegradation of Nitrobenzene Wastewater. Nitrobenzene wastewater, which is an environmental priority control pollutant, usually comes from the factories manufacturing medicines, pesticides, plastics, and explosives. The

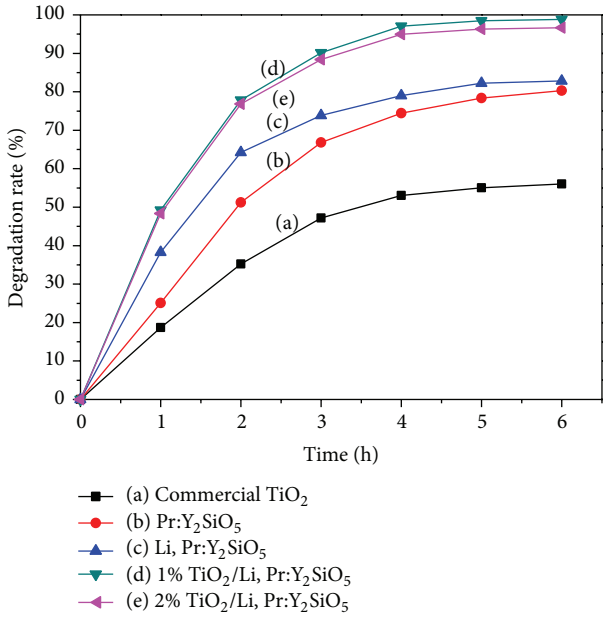


Figure 6: The photodegradation performances of nanomaterial samples. (a) Commercial TiO_2; (b) Pr:Y_2SiO_5; (c) Li,Pr:Y_2SiO_5; (d) 1% TiO_2/Li,Pr:Y_2SiO_5; (e) 2% TiO_2/Li,Pr:Y_2SiO_5.

degradation-resistant pollutant, which is attributed to its particular molecular structures, is difficult to degrade by normal methods [32]. In this study, 5 mg/L nitrobenzene wastewater and 1.5 g/L photocatalysts are used to test the photodegradation performances of as-prepared samples. The photodegradation curves of nitrobenzene wastewater with the photocatalysts of commercial nanometer anatase TiO_2, Pr:Y_2SiO_5, Li,Pr:Y_2SiO_5, 1% TiO_2/Li,Pr:Y_2SiO_5 (with 1% of TiO_2, similarly hereinafter), and 2% TiO_2/Li,Pr:Y_2SiO_5, are shown in Figure 6. All the data in Figure 6 are the mean values measured 3 times.

Samples TiO_2/Li,Pr:Y_2SiO_5, curves (d) and (e), show excellent photodegradation performances, but commercial TiO_2 shows the worst in the samples. Nanoscale TiO_2 is known for its good photocatalysis performances on pollutions under ultraviolet light. However, very different situation for nanoscale TiO_2 would arise when it is exposed to visible light. Thus, in this study, compounding of TiO_2 with Li,Pr:Y_2SiO_5 nanomaterials, which can upconvert visible light to ultraviolet light, would significantly improve the photocatalysis performances of TiO_2 under visible light, as shown in Figure 6. Although the luminescence intensities of TiO_2/Li,Pr:Y_2SiO_5 composite are far lower than that of Li,Pr:Y_2SiO_5 nanomaterials, as shown in Figure 5, it does not mean that the upconversion processes of Li,Pr:Y_2SiO_5 in the composite are stopped. It is still working well in the form of promoting and strengthening the photocatalysis of TiO_2 by providing high energy photons, instead of in the form of high intensity of upconversion luminescence emit out of the materials which can be tested, as shown in Figures 5 and 6. On the other hand, too much coating of TiO_2 film would not only increase the barrier of visible light to Li,Pr:Y_2SiO_5 nanomaterials, which weakens the intensity of incident light, but also decrease the proportion of Li,Pr:Y_2SiO_5 in the composite, in which the conversion of visible light to ultraviolet light is provided. Therefore, TiO2/Li,Pr:Y_2SiO_5 coating with 2% TiO_2 shows a little bit poor photodegradation performance than that with 1% TiO_2, as shown in Figure 6.

For samples Pr:Y_2SiO_5 and Li,Pr:Y_2SiO_5, their photodegradation performances show high consistency with the intensities of upconversion luminescence which they emitted; the former is lower than the latter. Because of lack of direct or quick conversion ultraviolet light, high energy photons, to hydroxyl radical (•OH) [33], which is one of the most strong oxidizability matter, two of the upconversion nanomaterials show much more poor photodegradation performances than TiO_2/Li,Pr:Y_2SiO_5 composites.

4. Conclusions

Lithium ion Li(I) doped Pr:Y_2SiO_5 and TiO_2 nanofilm coated Li,Pr:Y_2SiO_5 composites were prepared by using a sol-gel method. The doping amount of Li(I) plays an important role on the upconversion luminescence of the nanomaterial which reaches a maximum intensity of 9.76×10^6 cps with the doping concentration of 8%. The coating of TiO_2 nanofilm leads the luminescence intensity of TiO_2/Li,Pr:Y_2SiO_5 composite to get down sharply, since the luminescence emitted by Li,Pr:Y_2SiO_5 is adsorbed in situ by the TiO_2 coating film. As a result, the TiO_2/Li,Pr:Y_2SiO_5 composite with 1% TiO_2, which presents a low luminescence intensity, shows the excellent photodegradation performance on nitrobenzene wastewater. For 5 mg/L of nitrobenzene wastewater, the photodegradation rate is up to 97.08% and 98.82% in 4 h and 6 h, respectively.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgment

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