

Research Article

Visible Light Excited Catalysis and Reusability Performances of $\text{TiO}_2@\text{Pr:Y}_2\text{SiO}_5$ Upconversion Materials

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To get high efficiency photodegradation on pollutants under visible light, Pr(III) doped Y_2SiO_5 upconversion materials and anatase TiO_2 nanofilm coated Pr: Y_2SiO_5 composite have been prepared by using a sol-gel method. XRD and SEM test results indicated that TiO_2 nanofilm was well coated on Pr: Y_2SiO_5 to form $\text{TiO}_2@\text{Pr:Y}_2\text{SiO}_5$ composite particles with the sizes of 0.5–1.0 μm . To avoid secondary pollution resulting from incomplete recovery of catalyst particles, $\text{TiO}_2@\text{Pr:Y}_2\text{SiO}_5$ was loaded on the glass fiber filters by using a dip-coating method. It is found that the catalyst particles were embedded into the carrier firmly, even after having been reused for 6 times. The luminescence intensities of $\text{TiO}_2@\text{Pr:Y}_2\text{SiO}_5$ were getting down sharply with the coating contents of TiO_2 increased, which was attributed to the adsorption of the luminescence by the TiO_2 film in situ. As a result, $\text{TiO}_2@\text{Pr:Y}_2\text{SiO}_5$ with 4% TiO_2 , which presented lowest luminescence intensity, showed the highest efficiency on the photodegradation of nitrobenzene wastewater. The catalysts loaded on glass fiber filters showed excellent reusability on the photodegradation of nitrobenzene and presented a photodegradation rate of 95% at the first time and up to 75.9% even after 6 times of reusing by the treatment time of 12 h.

1. Introduction

Photocatalysts responding to visible light have been studied in environment for many years, and lots of interesting research results are booming out on the photodegradation of pollutants. As one of the best photocatalyst, TiO_2 has been studied extensively on the decomposition of inorganic and organic pollutants and toxic materials [1–3], as well as the application for water purification [4, 5]. Since the energy gap of anatase TiO_2 is about 3.2 eV, only high energy UV light with wavelength less than 387 nm can excite the electron transition of TiO_2 [6]. However, only about 4% in the solar light of UV light can be absorbed by nanometer anatase TiO_2 . Many studies focus on decreasing energy gap of anatase TiO_2 , including surface modification [7, 8], doping with other metal ions, nonmetal ions and semiconductors [9–13], and oxygen vacancy generating [14], which have been researched to develop TiO_2 as a visible light responding photocatalyst.

Upconversion material, such as Yttrium Silicates (Y_2SiO_5), is a kind of material which can convert lower frequency light to upper frequency light. This unique property enables upconversion material with a great potential application in many fields. To get high luminescence intensity, activation methods were widely researched for Y_2SiO_5 luminescent material, including doping with other metal ions or activating agents [15, 16]. Y_2SiO_5 has a particular geometry which leads to a possible replacement of Y by other element ions, especially by rare earth ions [17]. Praseodymium ion Pr(III) was doped into Y_2SiO_5 and high luminescence intensity was gotten, because praseodymium ion has more suitable energy levels and longer excited state lifetimes than Y [18]. This means that, under the irradiation of visible light, UV light could be excited out by upconversion materials, which can be used by nanometer TiO_2 . Therefore, the combination of nanometer 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. Furthermore, with the combination of TiO_2 , lithium ion (Li^+) has been used to dope $\text{Pr:Y}_2\text{SiO}_5$ upconversion materials and high photocatalysis performances on nitrobenzene wastewater were gotten under visible light [18].

However, it was found that upconversion materials were seldom used as a photocatalyst independently for wastewater treatment. In order to improve the photocatalysis ability of TiO_2 excited by visible light or solar, based on the upconversion materials, various forms of TiO_2 and support materials have been reported in recent years. Hydrogen is produced efficiently from aqueous methanol solution by using Pt supported TiO_2 combined with upconversion luminescence agent ($\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}$) as the visible light photocatalysts [19, 20]. Er^{3+} doped TiO_2 thin films can present better response to infrared light upconversion [21]. With the assist of upconversion luminescent materials, TiO_2 solar photocatalysts were applied to degrade contaminants to purify water [22]. For the degradation of organic dyes, TiO_2 coating upconversion luminescence agent [23] and rutile TiO_2 catalyst doped with upconversion luminescence agent [24] both showed excellent performances under visible light irradiation.

In the treatment process, photocatalysts powders were usually dispersed in wastewater directly [18]. Although this process enables full contact and high degradation efficiency of the catalysts particles on the pollutants, the recovery of the catalyst powder becomes a new problem [18, 25]. In fact, incomplete recovery of the catalyst particles would lead to secondary pollution for water treatment. Nevertheless, it is very difficult to recover those catalyst particles totally from the treated water, especially for nanometer particles. Reasonably, catalysts carrier in bulk size were used to load catalyst particles and made reusing of catalysts possible [26, 27].

The doping of Li^+ was very limited to enhance the photocatalysis for $\text{Pr:Y}_2\text{SiO}_5$ upconversion materials; the degradation rate was only about 80% after 6 h of treatment. On the other hand, at the same treatment time, the upconversion material without Li^+ had gotten a degradation rate of 78%, as shown in Figure 6 in [18]. In this study, Pr(III) doped Y_2SiO_5 upconversion materials and anatase TiO_2 nanofilm coated $\text{Pr:Y}_2\text{SiO}_5$ composite have been prepared to get high photodegradation efficiency on pollutants. Furthermore, glass fiber filters, which are inert, inexpensive, and easily available, have been applied to load the upconversion composite materials by using a simple dip-coating method. The degradation performances and reusability of obtained catalysts under visible light have been tested by using nitrobenzene as typical waste in water.

2. Materials and Methods

2.1. Samples Preparation. Praseodymium ion Pr(III) doped Y_2SiO_5 upconversion nanomaterials, namely, $\text{Pr:Y}_2\text{SiO}_5$, were prepared by using a sol-gel method with the raw materials of praseodymium nitrate, Y_2O_3 , and tetraethyl orthosilicate (TEOS), which were reported by [28].

The composite catalysts of $\text{TiO}_2@\text{Pr:Y}_2\text{SiO}_5$, named as TPY, were prepared by adding the as-prepared $\text{Pr:Y}_2\text{SiO}_5$ 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 pH of mixture was adjusted to 2.5 by using nitric acid. After stirring for 1 h, the sol suspended $\text{Pr:Y}_2\text{SiO}_5$ particles were 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 milled 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 $\text{TiO}_2@\text{Pr:Y}_2\text{SiO}_5$ (TPY) composite catalyst. The TiO_2 ratios, 1%, 2%, 3%, 4%, and 5%, were adjusted by changing the added volume of titanium tetrabutoxide. We note here that when the sample name $\text{TiO}_2@\text{Pr:Y}_2\text{SiO}_5$ (TPY) is mentioned in this paper, it mainly means 4% TiO_2 in the materials except for the comparing study on the content of TiO_2 . Titanium dioxide powder was prepared by following the same procedure preparing $\text{TiO}_2@\text{Pr:Y}_2\text{SiO}_5$ except for adding $\text{Pr:Y}_2\text{SiO}_5$ particles in the sol.

The glass fiber filter (GFF) loaded $\text{TiO}_2@\text{Pr:Y}_2\text{SiO}_5$ or TiO_2 , named as TPY@GFF and $\text{TiO}_2@\text{GFF}$, respectively, was prepared by using a dip-coating method through dipping GFF into the sol suspended $\text{Pr:Y}_2\text{SiO}_5$ particles or the sol of TiO_2 precursor. Then the coated GFFs were heat-treated by drying at 80°C and calcining at 500°C sequentially. Before the dip-coating process, the glass fiber filters were washed by HNO_3 (1 : 1, vol) and diluted water for three times in turns to eliminate impurities in GFF and make the coating firmly.

2.2. Property Testing of Samples. X-ray diffractometer (D8 Advance, Bruker Corporation, German) was used to characterize crystal form and grain size of the samples. A scanning electron microscopy (Hitachi S4800, SEM, Japan) was employed to characterize the microimages and particle size of the samples. The BET specific surface areas of samples were tested after evacuating for 6 h at 160°C by using a specific surface area and pore size analyzer (V-Sorb2800P, Gold APP Instruments Corporation, China). The upconversion luminescence of the materials 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 [29, 30]. All the samples are cut into small pieces or milled into powder to fit the sample cell of the fluorescence spectrometer.

Nitrobenzene wastewater, 5 mg/L, was used as a target pollutant to test the photodegradation performances of the as-prepared upconversion composite nanomaterials. After dipping the GFF loaded with catalysts into the wastewater or dispersing the photocatalysts powder into the wastewater, half an hour of dark environment was experienced to reach an adsorbing balance of the pollutants on the catalysts materials. Then, a triphosphor tube light 100 W with an ultraviolet filter was turned on as a visible light source to excite the upconversion nanomaterials and photocatalysts. 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.

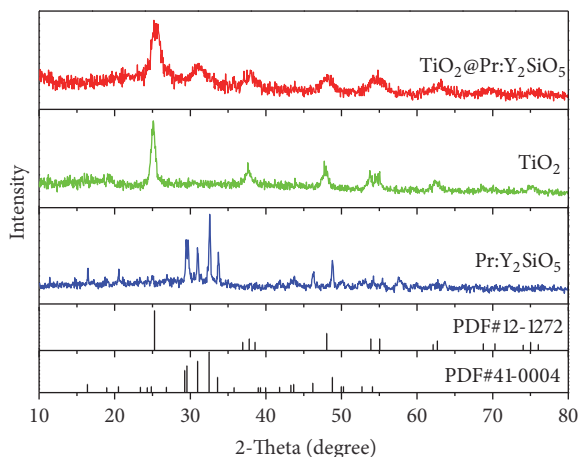


FIGURE 1: XRD patterns of samples.

The ultraviolet absorption values were tested by using an ultraviolet-visible spectrophotometer. When treated for a certain time, about 3 ml of the solution was taken out from the reaction vessel and injected into the cuvette of the ultraviolet-visible spectrophotometer and put back to the vessel after test. 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. Physical Properties Testing for the Samples. The crystal structure and crystal size play important roles in the photocatalysis properties for TiO_2 particles, as well as the light conversion performances for upconversion nanomaterials [28, 31]. Figure 1 shows the XRD patterns of the as-prepared samples $\text{TiO}_2@Pr:Y_2SiO_5$, $Pr:Y_2SiO_5$, and TiO_2 . The patterns of $Pr:Y_2SiO_5$ and TiO_2 present good accordance with the standard PDF card of #41-0004 and #21-1272, respectively. These also insist that sample $Pr:Y_2SiO_5$ is of low temperature phase X1 molecular configuration and TiO_2 belongs to anatase phase, of which the two kinds of crystal structures are both suitable for light response. Meanwhile, $TiO_2@Pr:Y_2SiO_5$ shows all the characteristic patterns of anatase phase TiO_2 and along with a peak at about 2θ of 31° in which most of characteristic patterns of $Pr:Y_2SiO_5$ are located. It indicates that TiO_2 and $Pr:Y_2SiO_5$ are two independent materials coexisting in the composite of $TiO_2@Pr:Y_2SiO_5$. Titanium dioxide probably in film form coats the surface of $Pr:Y_2SiO_5$ particles, which also can be suggested by the SEM photos of the samples, as shown in Figure 2.

According to the XRD patterns in Figure 1, the crystal size of $Pr:Y_2SiO_5$ is 41.7 nm at 2θ angle 30.83° , which are calculated by the Scherrer equation [17]: $D = K\lambda/(\beta \cos \theta)$, 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 ($^\circ$); 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. Meanwhile, the crystal sizes of TiO_2 and TiO_2 in the $TiO_2@Pr:Y_2SiO_5$ composite sample are calculated, 33.1 nm and 22.5 nm, respectively, at 2θ angle 25.1° .

However, as shown in Figure 2, SEM particle sizes are much bigger than those crystal sizes calculated by XRD. It indicates that every single particle is composed of several crystals which makes it difficult to disperse the $Pr:Y_2SiO_5$ powders fully in the preparation process. The grains are about 0.5 to 1.0 μm in both of the two images of Figure 2. The particle sizes in image (b) are a little bigger than that in image (a), which insists on the coating of TiO_2 on the surface of $Pr:Y_2SiO_5$ grains. Nevertheless, energy dispersive X-ray spectrometer (EDS) testing on the sample surface of Figure 2(b) shows that Ti and O are the majority elements, while Si and Y are the minority elements. It also suggests that TiO_2 film gives intact coating on $Pr:Y_2SiO_5$ particles. Furthermore, it is difficult to find element information of Pr in the EDS testing, which probably has gotten into the crystal lattice and replaced the host atoms of Y_2SiO_5 [17].

Figure 3 shows SEM photos of glass fiber filters (GFF) before and after loading the photocatalysts. In the microimage of $TiO_2@GFF$, small TiO_2 particles are well loaded in the interspace of GFF, as shown in Figure 3(b). However, although many small particles are also loaded in the interspace of GFF, there are some big particles present on the GFF surface, as shown in Figures 3(c) and 3(d). It is no doubt that these big particles would drop out firstly during the treatment process, because the adhesive forces of big particles on the surface are less than that of small particles in the interspace. Despite that, there are still many big particles loading on the surface firmly even after having been reused for 6 times, as shown in Figure 3(d). It suggested that the simple combination of sol-gel method and dip-coating method could be useful for loading photocatalysts precursor on carrier.

Generally, the specific surface area is a key parameter on the adsorption properties of porous materials. As a result, it highly affects the degradation performances of catalysts since the pollutants must be adsorbed onto or be getting very close to the catalysts before the start of the degradation process. The adsorption isotherm linear graphs of the as-prepared catalysts and the GFF before and after loading TPY catalysts are shown in Figure 4. All the three curves in Figure 4(a) show the characteristics of type I adsorption isotherm, which suggests that the adsorption performances of the catalysts, TiO_2 , $Pr:Y_2SiO_5$, and $TiO_2@Pr:Y_2SiO_5$, are mainly attributed to micropores. The specific surface areas of the three catalysts are 231.58 m^2/g , 12.34 m^2/g , and 127.85 m^2/g , respectively, which show good accordance with the curves in Figure 4(a). On the other hand, the specific surface area of GFF is only 4.61 m^2/g , and its adsorption isotherm line shows adsorption isotherm characteristics of type V. Nevertheless, after loading TPY catalyst, the adsorption line of TPY@GFF is changed to type II adsorption isotherm. It is interesting that this line is very similar to the curve of TPY in the relative pressure range of 0–0.15, while presenting similar characteristics of GFF curve in the relative pressure range of 0.15–0.30. This suggests that the adsorption performances of TPY@GFF

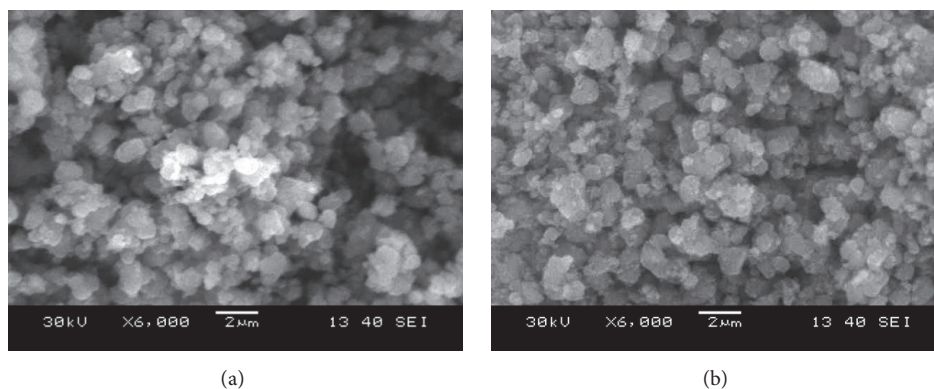


FIGURE 2: SEM photos of (a) $\text{Pr:Y}_2\text{SiO}_5$ and (b) $\text{TiO}_2@\text{Pr:Y}_2\text{SiO}_5$.

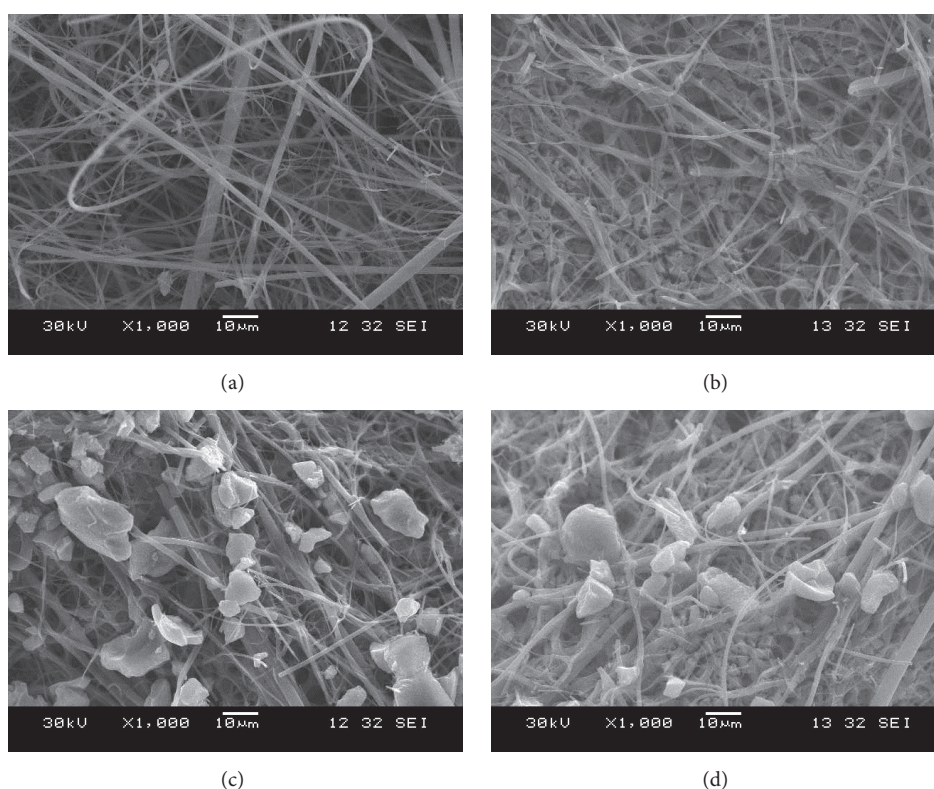


FIGURE 3: SEM photos of samples. (a) GFF; (b) $\text{TiO}_2@\text{GFF}$; (c) $\text{TPY}@\text{GFF}$; and (d) $\text{TPY}@\text{GFF}$ used 6 times.

are composed of two stages: micropore adsorption of TPY catalysts dominated at the stages of low relative pressure and macropore adsorption of GFF is mainly at the stage of high relative pressure. The same features also can be found on the adsorption isotherm line of $\text{TPY}@\text{GFF}$ used 6 times, as shown in Figure 4(b). It is easy to be understood that, because of the dropping out of the catalysts particles in the treatment procedures, the specific surface area of $\text{TPY}@\text{GFF}$ used 6 times would be a little less than that unused, which are $12.58 \text{ m}^2/\text{g}$ and $13.07 \text{ m}^2/\text{g}$, respectively. This presents good evidence on the excellent recycle usability performances of the $\text{TPY}@\text{GFF}$, which also has been suggested by the SEM images in Figure 3.

3.2. Upconversion Luminescence of Samples. Figure 5 shows the upconversion emission spectra of $\text{Pr:Y}_2\text{SiO}_5$ with different concentrations of TiO_2 , which are excited by light with the wavelength of 488 nm. Each of the samples shows an obvious upconversion emission peak in the wavelength range of 290 nm to 340 nm with a peak value at 312 nm.

It can be found that the upconversion luminescence intensities are decreasing with the coating ratios of TiO_2 , 0%, 1%, 2%, 3%, 4%, and 5%. 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,

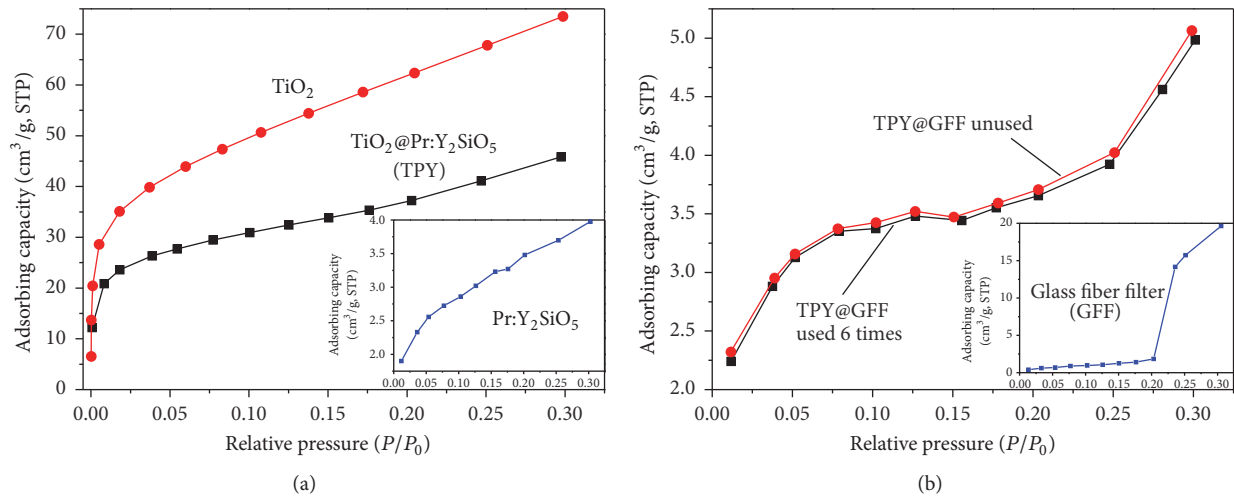


FIGURE 4: The adsorption isotherm linear graphs of the samples. (a) As-prepared catalyst powders; (b) GFF before and after loading TPY catalysts.

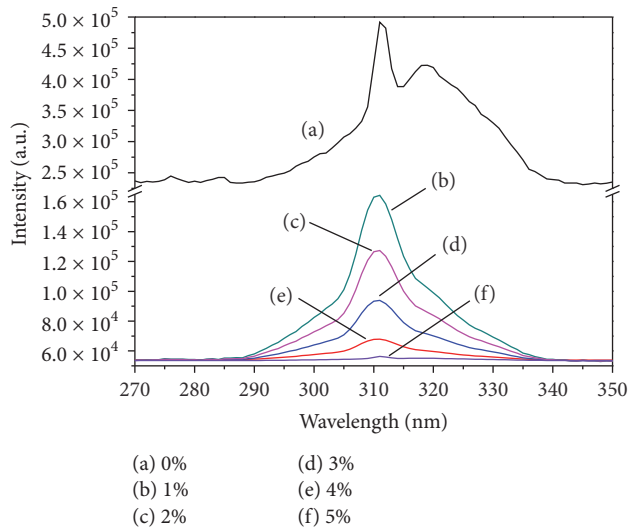


FIGURE 5: Emission spectra of Pr:Y₂SiO₅ coating with different ratios of TiO₂. (a) 0%; (b) 1%; (c) 2%; (d) 3%; (e) 4%; and (f) 5%.

energy would be added to valence electron and it would be excited by photon and the electrons 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 [32]. As a result, a hole is left behind in the valence band. On the occasion of nanoscale TiO₂ coating on the upconversion material Pr:Y₂SiO₅, the luminescence emitted by Pr:Y₂SiO₅ is absorbed in situ by the TiO₂ coating film which led to a sharp decreasing of the luminescence intensities. The more of TiO₂ film is coated, the less of the luminescence intensity can be tested. When the coating amount of TiO₂ film is up to 4%, the intensity of the emission spectra is very low, as shown in Figure 5. The luminescence peaks almost cannot be found on the emission spectra of the sample with 5% of TiO₂. It means that too thick TiO₂ coating film would not only block the transmission of light onto the upconversion material

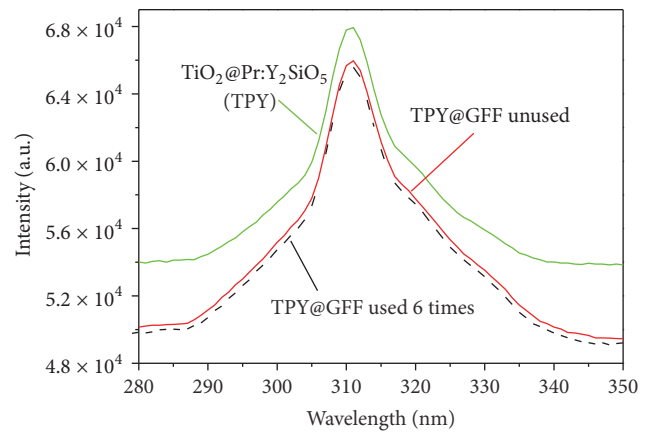


FIGURE 6: Emission spectra of the samples.

but also absorb out the luminescence that the upconversion material Pr:Y₂SiO₅ emitted. Therefore, the coating amount of 4% could be a balance point or an optimum value for the composite of TiO₂@Pr:Y₂SiO₅ nanomaterials.

After being loaded on the GFF, the catalyst TiO₂@Pr:Y₂SiO₅, with 4% of TiO₂, shows notable decreasing on the upconversion emission intensity, as shown in Figure 6. This could be attributed to the penetrating of the catalyst particles into the interspace of glass fiber filter during the dip-coating process, which decreases the emission intensity what can be detected. Besides, the upconversion emission spectra of TYP@GFF before and after being used 6 times have also been tested, as shown in Figure 6, to check the recycle usability performances of the sample. After being used 6 times, little decreasing of the upconversion emission intensity of the TYP@GFF materials can be seen. It could be verified that TYP@GFF would probably have excellent reusing performances, which also have been suggested by the SEM photos in Figure 3 and the adsorption isotherms in Figure 4.

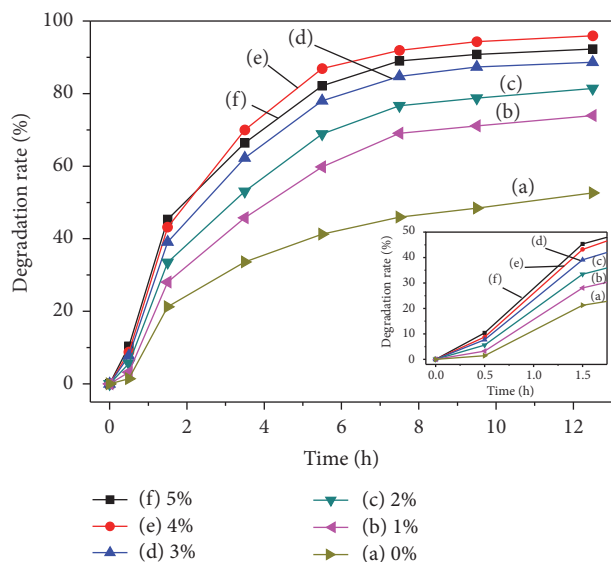


FIGURE 7: Photodegradation performances of TPY with different content of TiO₂. (a) 0%; (b) 1%; (c) 2%; (d) 3%; (e) 4%; and (f) 5%.

3.3. Visible Light Photodegradation on Nitrobenzene Wastewater. Coating on the surface would hopefully improve catalysis performances of base particles because of the synergistic effects of the coating materials and base materials, although the process would not change the crystal structure or crystal size of base particles. The synergistic effects improvement of TiO₂ with Pr:Y₂SiO₅ has been tested, as shown in Figure 7. For these five samples, the photodegradation performances show high consistency with the intensities of upconversion luminescence which they emitted, as shown in Figure 5. Meanwhile, the photodegradation rates increase gradually with the TiO₂ coating rate increase from 0% to 4%. It can be deduced that too less coating of TiO₂ film on the Pr:Y₂SiO₅ particles would lead to inadequate use of violet light that the upconversion materials converted. For the sample of Pr:Y₂SiO₅ (0% of TiO₂), it shows much more poor photodegradation performances than those samples coated with TiO₂. It is because of the absence of TiO₂ which is the media converting ultraviolet light or/and high energy photons into hydroxyl radical (*OH) [33]. Meanwhile, it is believed that hydroxyl radical is one of the most strong oxidability matters. On the other hand, too much coating of TiO₂ film would not only increase the barrier of visible light to Pr:Y₂SiO₅ nanomaterials, which weakens the intensity of incident light, but also decrease the proportion of Pr:Y₂SiO₅ in the composite, in which the conversion of visible light to ultraviolet light is provided. As a result, the sample containing 5% TiO₂ presents a lower degradation rate comparing to the sample with 4% of TiO₂.

The degradation curves of samples treated for 2 h are shown with an insert map at the right corner of Figure 7. Since an adsorbing balance of half an hour in a dark environment has been pretreated before the photocatalysis, the degradation data mainly resulted from the adsorbing capability of the samples, which are highly in accordance

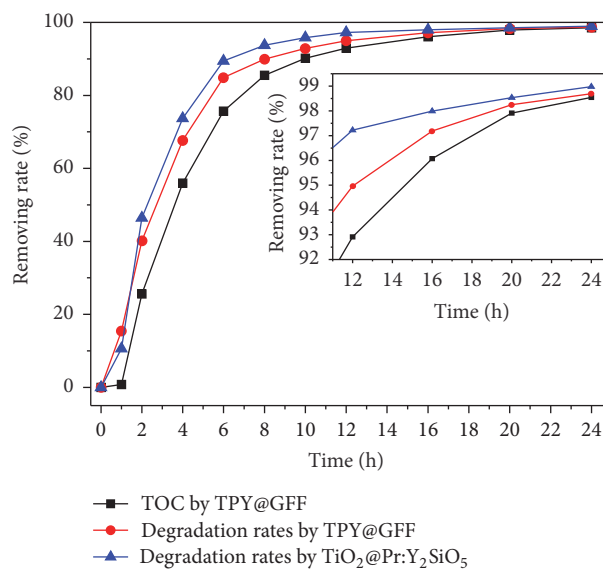


FIGURE 8: The degradation rates and TOC removing rates of nitrobenzene.

with the coating content of TiO₂, as shown in Figure 7. The photodegradation performances of the samples in the next 1 h are highly affected by the adsorbing results which have the same tendency in the first half an hour. However, as the treatment time goes by, the photodegradation is dominant gradually which presents good evidence on the function of the upconversion materials in visible light.

The visible light excited photodegradation performances of TiO₂@Pr:Y₂SiO₅ before and after being loaded on GFF have been compared with the same content of composite catalyst, as shown in Figure 8. The sample TPY@GFF shows lower removing rates of pollutant than that of TiO₂@Pr:Y₂SiO₅ powder at all the treatment time except for at the first 2 hours which is attributed to the adsorption effect of GFF. The lower removing performances of TPY@GFF could be resulting from the embedding of the catalyst particles into the interspace of glass fiber filter and, as a result, lower contact surface of catalyst particles with pollutants than that of TiO₂@Pr:Y₂SiO₅ particles used directly.

Before the mineralization of those macromolecular compounds or refractory organics, such as benzene and its compounds, several degradation steps are needed and intermediate products would normally be produced. Total organic carbon (TOC), which has been tested by using a Shimadzu TOC analyzer (TOC-V_{CPH}) in this paper, is always used to characterize the organic carbon content and naturally the mineralization of organic pollutants in wastewater. Since the forming of the intermediates during the degradation of nitrobenzene, there always have been gaps between the TOC removing rates and the degradation rates which are tested by using the ultraviolet absorption testing method. However, these intermediates are still a kind of pollutant which can be tested by TOC. Therefore, the degradation rates are always a little bit higher than the removing rates of TOC, as shown in Figure 8. An interesting phenomenon

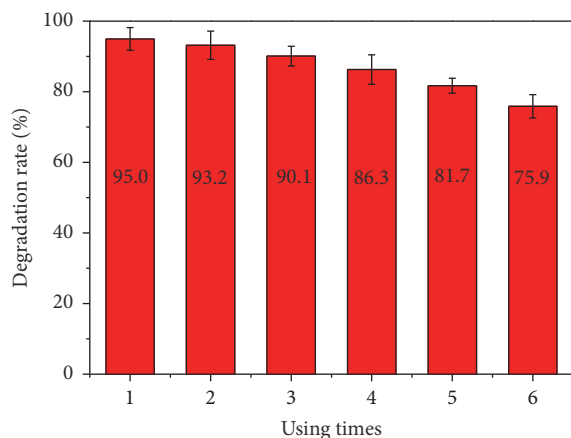


FIGURE 9: Recycling degradation performances of TPY@GFF samples.

is that more than 92% of nitrobenzene has been degraded and mineralized after 12 hours of photodegradation under visible light. When the treatment time comes to 24 hours, the photodegradation rate and mineralization rate are up to 98.9% and 98.5%, respectively. This suggested that the as-prepared upconversion materials show excellent photocatalysis on the degradation of nitrobenzene under the exciting of visible light.

The best performance sample TPY@GFF, where the TiO_2 coating content is 4% in TPY material, has been used to study its reusability performance. The degradation time of each recycle degradation process has been set to 12 hours since the photodegradation rates are not increasing significantly after that, as shown in Figure 8. Therefore, after lasting for 12 hours of photodegradation, TPY@GFF samples are pulled out and heat-treated by drying at 80°C for 1 h and calcining at 500°C for 2 h sequentially to get rid of the impurities and renew the samples. The recycle degradation performances of TPY@GFF after 6 times of reusing are shown in Figure 9. As the reusing times increase, the degradation rates are getting down gradually from 95.0% of the first time to 75.9% of the sixth time. It is well known that, by the reusing times, the active sites of the catalysts would be decreasing inevitably and the catalysts particles loaded on the carrier would be dropping down more or less, no matter how advanced or careful the renew process is. However, the photodegradation rate is still more than 90% at the 3rd time and up to 75.9% even after reusing for 6 times, as shown in Figure 9. It suggests that the TPY@GFF materials have excellent visible light excited photodegradation, as well as good reusability performances.

4. Conclusions

Titanium dioxide TiO_2 coated $\text{Pr:Y}_2\text{SiO}_5$ upconversion materials, $\text{TiO}_2@\text{Pr:Y}_2\text{SiO}_5$, have been prepared by using a sol-gel method. The composite upconversion materials have been loaded on the glass fiber filter by using a dip-coating method. The luminescence intensities of the composite

$\text{TiO}_2@\text{Pr:Y}_2\text{SiO}_5$ are decreased sharply by the coating contents of TiO_2 nanofilm, which could be attributed to the adsorbing of the luminescence emitted by the upconversion material $\text{Pr:Y}_2\text{SiO}_5$ by the TiO_2 coating film in situ. As a result, the $\text{TiO}_2@\text{Pr:Y}_2\text{SiO}_5$ composite with 4% TiO_2 , which presents low luminescence intensity apparently, shows high efficiency on the photodegradation of nitrobenzene wastewater. Though a little bit lower photodegradation than that of $\text{TiO}_2@\text{Pr:Y}_2\text{SiO}_5$ powder used directly, the composite upconversion materials loaded on glass fiber filter, namely, TPY@GFF, show excellent reusability performances on the photodegradation of nitrobenzene and present 75.9% degradation rate by the treatment time of 12 h even after having been reused for 6 times.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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