

Research Article

Upconversion Luminescence and Photodegradation Performances of Pr Doped Y_2SiO_5 Nanomaterials

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Yttrium silicates Y_2SiO_5 upconversion nanomaterials with different doping concentrations of praseodymium ion Pr are prepared by using a sol-gel method. X-ray diffractometer, SEM, Fourier transform infrared spectrometer, and fluorescence spectrometer have been employed to test the crystal structure and upconversion luminescence performances. The results indicate that samples calcined higher than 950°C present fine crystal structures, of which Si-O-Si band at $757\text{--}1048\text{ cm}^{-1}$ splits into three fine peaks. The crystal size of the samples calcined at 950°C and 1000°C is 29.1 nm and 66.7 nm, respectively. The luminescence intensities of the samples are increasing at first and then decreasing, with the increasing of the doping concentrations of 0.47%, 0.77%, 0.96%, 2.95%, and 4.93%. Nanomaterial sample doped 0.96% Pr emits the highest upconversion luminescence intensity of 6.43×10^6 cps and shows the best photodegradation performance for nitrobenzene wastewater. It demonstrates that too much of Pr doping concentration would result in quenching of the fluorescence. Nevertheless, as the degradation time expands, sample doped 0.96% Pr shows much faster increasing of photodegradation rate than samples of other doping concentrations and reaches to a high photodegradation rate of 97.14% in 6 hours for 10 mg/L nitrobenzene wastewater.

1. Introduction

Upconversion nanomaterials are known for its efficient emission of ultraviolet fluorescence under the exciting visible light [1]. It has been extensively studied since mid-1960s and widely applied in many areas [2–4]. The emission of short wavelength light excited by long wavelength light is called anti-stokes luminescence, namely, upconversion luminescence. Upconversion nanomaterials and upconversion luminescence can be widely used in the degradation of organic pollutants in environmental governance [5] and the killing of harmful bacteria in medical treatment or biological areas [6–8], because of the ultraviolet light emitted in the upconversion processes. The upconversion nanomaterials, which is differ from ultraviolet lamp, can be excited by visible light, such as sun light, instead of electricity.

In the past decades, high-quality rare earth-doped upconversion nanomaterials have been successfully synthesized with the rapid development of nanotechnology and are becoming more prominent in biological and environmental

sciences [9–11]. However, till now, the low luminescence efficiency is still one of the main limiting factors for upconversion materials. A suitable host material with lower phonon energy is one of the most important factors to obtain high upconversion luminescence efficiency. Up to now, host materials, including fluoride, chloride, and bromide, have been shown to enhance upconversion luminescence intensity. As a substrate for upconversion materials, yttrium silicates Y_2SiO_5 show high thermal stability, good optical performance, simple manufacture process, and has been widely used in fluorescent technique, optical information storage, and anticounterfeit technology [12].

To get the highest upconversion luminescence efficiency, another critical factor is doping with other ions to occupy or replace the ions in the host material [13–15]. In the molecular geometry of yttrium silicates Y_2SiO_5 , yttrium ion Y is located on two different positions and its corresponding coordinate numbers are 7 and 9 in X1 molecular configuration, while 6 and 7 in X2 molecular configuration [16]. The particular geometry leads to a possible replace of Y by other element

ions. Praseodymium ion has a similar ionic radius with Y ion, but more suitable energy levels and longer excited state lifetimes than Y. This leads to the transition of Pr to a lower energy band after absorbing two photons continuously. As a result, higher energy photons could be emitted. Therefore, Praseodymium ion is a potential doping element ion for the Y_2SiO_5 system to obtain high energy photons and excellent upconversion performances.

Besides the host materials and doping ions, the synthetic methods are also critical for the high quality upconversion nanomaterials to obtain high luminescence efficiency. The synthesis methods are usually phase-based processes. So far, three kinds of methods are commonly used to synthesize upconversion nanomaterials, including thermal decomposition [17–19], hydrothermal synthesis [20, 21], and ionic liquids-based synthesis [22]. In addition, sol-gel method has potential for synthesizing high quality upconversion nanomaterials of high luminescence efficiency and usually used as the first choice to doping ions since it provides a way of mixing in molecular level of the reactants [23, 24], which has also been used in this study.

Many researches focused on the optical properties, luminescence properties, and fluorescence quenching mechanisms of Pr doped Y_2SiO_5 crystals [25–27]. Also, a number of studies report the application of Pr doped Y_2SiO_5 nanomaterials in biological, medical, sensing, optical areas, and so on [2, 3, 5–8]. In particular, the upconversion nanomaterials unique property of emitting visible light under NIR irradiation makes them a suitable candidate both for in vivo and in vitro bioimaging [28, 29]. However, the research and application of Pr doped Y_2SiO_5 nanomaterials on environment or pollutants degradation are seldom reported. In this study, nitrobenzene wastewater, which is from a TNT factory, has been used as the target pollutant to test the photodegradation performances of the prepared Pr(III) doped Y_2SiO_5 upconversion nanomaterials.

2. Materials and Methods

Praseodymium ion Pr(III), doped Y_2SiO_5 upconversion nanomaterials were prepared by using a sol-gel method. First, 0.1 mol/L praseodymium nitrate solution was added into the mixture (1:1, vol) of HNO_3 and H_2O dissolved 0.663 g Y_2O_3 . Heating was followed until the solution becomes 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 $70^\circ C$ until a gel was formed. The gel was dried in an oven of $104^\circ C$ and then grinded into powder. At last, the powder was calcined at a temperature of $900^\circ C$, $950^\circ C$, and $1000^\circ C$ for 3 h in a muffle furnace to get the final product of Pr(III) doped Y_2SiO_5 upconversion nanomaterials. The Pr (III) doping concentrations, 0.47%, 0.77%, 0.96%, 2.95%, and 4.93%, which were confirmed by using inductively coupled plasma (ICP) spectrometer, were adjusted by changing the adding volume of the 0.1 mol/L praseodymium nitrate solution at the first stage.

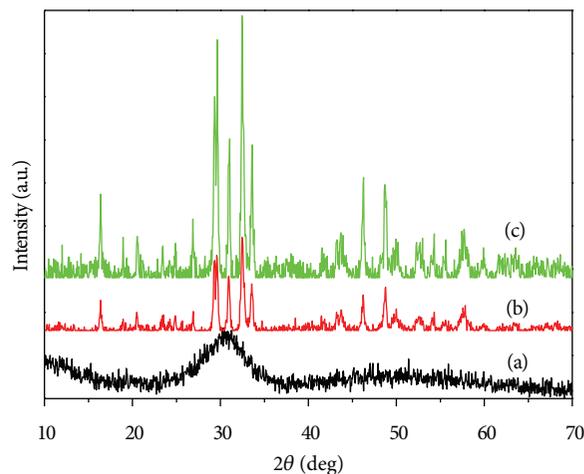


FIGURE 1: XRD patterns of Pr(III) doped samples calcined at different temperatures: (a) $900^\circ C$, (b) $950^\circ C$, (c) $1000^\circ C$.

X-ray diffractometer (D8 Advance, Bruker Corporation, German) was used to characterize the crystal form of the samples. A scanning electron microscopy (Hitachi S4800, SEM, Japan) was employed to characterize the particle size of the samples. Fourier transform infrared spectrometer (FTIR, MB154S, ABB BOMEN Corporation, Canada) was employed to check the crystal and groups of 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 425 nm of the excitation wavelength, 370 nm of the optical filters, and 2 nm of the slit.

Nitrobenzene wastewater, 10 mg/L, which was from a TNT factory, was used as a target pollutant to test the photodegradation performances of the prepared Pr(III) doped Y_2SiO_5 upconversion nanomaterials. Filament lamp, 52 W, was used as the exciting light source for the upconversion nanomaterials. The treatment time was lasting for 1 h to 6.5 h. The degradation rate of nitrobenzene was tested by comparing the ultraviolet absorption values to the original value of the wastewater. The ultraviolet absorption values were tested by using an ultraviolet-visible spectrophotometer. The relationship of the nitrobenzene concentrations (x), in the range of 0–15 mg/L, with the ultraviolet absorption values (y), was determined by a linear equation: $y = 0.072x + 0.012$, with a correlation R^2 of 0.9987.

3. Results and Discussion

3.1. Heat Treatment on the Crystal of Upconversion Nanomaterials. The heat treatment temperature is an important parameter for the crystal structure and crystal size of many kinds of nanomaterials, as well as upconversion nanomaterials. Figure 1 shows the XRD patterns of Pr(III) doped samples at the heat treatment temperature of $900^\circ C$, $950^\circ C$, and $1000^\circ C$.

Without obvious diffraction peak appears on the XRD pattern of sample calcined at $900^\circ C$, except for a broad curve at the 2-theta angle about 30° . It means that Y_2SiO_5 under

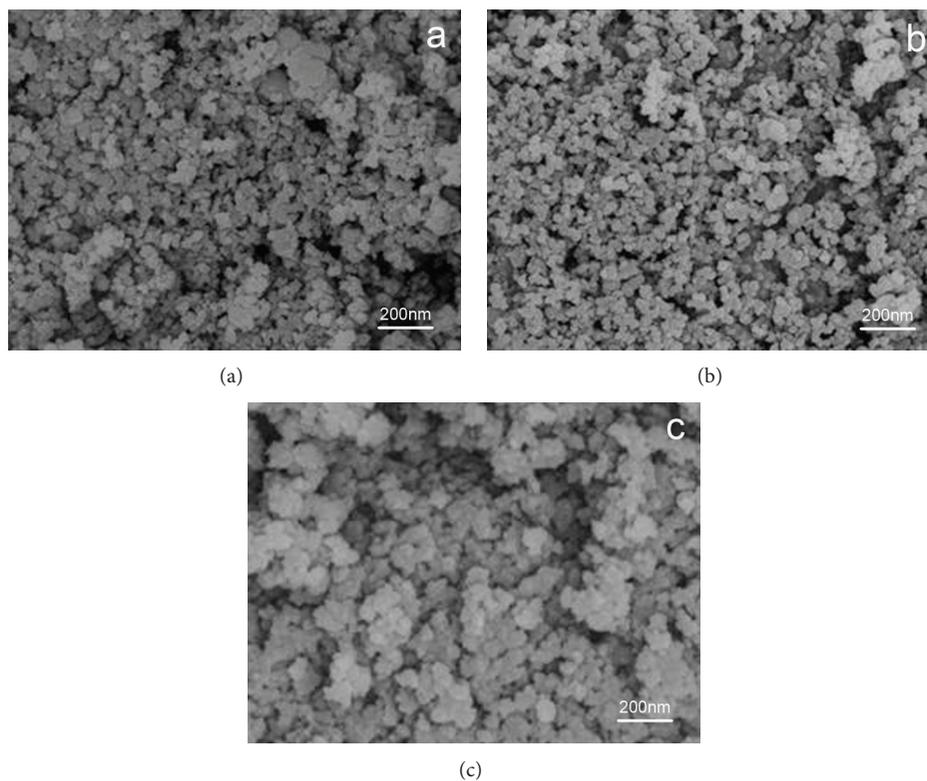


FIGURE 2: SEM images of Pr(III) doped samples calcined at different temperature (a) 900°C; (b) 950°C; (c) 1000°C.

the heat treatment temperature of 900°C is amorphous. Meanwhile, a higher heat treatment temperature of 950°C or 1000°C leads to good crystal forms of the Pr(III) doped Y_2SiO_5 upconversion nanomaterials, of which diffraction peak positions show high consistency with that of $X1-Y_2SiO_5$ phase [30]. The temperature is further lower than the report postanneal temperature 1373 K for $X1-Y_2SiO_5$ phase [30]. However, sample calcined at 1000°C shows much higher diffraction peaks than that of sample calcined at 950°C. This phenomenon states a conclusion that the crystal size of the later is smaller than that of the former, 29.1 nm and 66.7 nm at 2θ angle 32.67° , respectively, which are calculated by the Scherrer equation: $D = K\lambda/(\beta \cos \theta)$, where D is the crystal size (nm); K is 0.89, the Scherrer constant; β is the full width at half maximum (FWHM) of the main diffraction peaks (rad); θ is the diffraction angle which the diffraction peaks located ($^\circ$); λ is 0.154056 nm, the X-ray wavelength.

It indicates that the crystal structure transition temperature of Pr (III) doped $X1$ pattern Y_2SiO_5 is about 950°C, heat treatment temperature higher than 950°C is not good for the forming of small crystal size for the materials.

The particle size of the samples characterized by a scanning electron microscopy also shows high dependence on the heat treatment temperature, as shown in Figure 2. With the increasing of heat treatment temperature, the particle sizes of the samples are increasing gradually, 42 nm, 55 nm, and 96 nm for the treatment temperature of 900°C, 950°C, and 1000°C, respectively. It shows a good consistent tendency to the crystal size of samples. Particle sizes in SEM bigger than its

crystal size of the corresponding sample are reasonable, since a particle in SEM is always composed by several crystals, not to mention the congregating of particles themselves.

It has been proved that the crystal structures and bond groups of phosphor materials show high dependence on the heat treatment or thermal annealing temperature [31]. An FTIR spectrometer is employed to test the effect of heat treatment temperature on the crystal structure of the Pr(III) doped Y_2SiO_5 upconversion nanomaterials, as shown in Figure 3. Sample calcined at 900°C shows two big absorption bands on the FTIR spectrum curve, in the range of 757–1048 cm^{-1} and 1260–1620 cm^{-1} , which can be roughly identified to the vibration absorption of Si-O-Si bond and the bending vibration of O-H bond, respectively. When heat treatment temperature is increased to 950°C or 1000°C, both of the two absorption bands show a great change: the lower wavenumber absorption band splits into three absorption peaks, and the higher wavenumber absorption band disappears thoroughly.

High heat treatment temperature is believed to be beneficial to the forming of fine crystal structures of the nanomaterials. Therefore, as a result, when the upconversion nanomaterials are calcined at the temperature of 950°C and 1000°C, the absorption band at 757–1048 cm^{-1} splits into three fine peaks at 849.7 cm^{-1} , 933.8 cm^{-1} , and 1008.3 cm^{-1} , which result from the bending vibration absorption of Si-O bond, the symmetric vibration absorption of Si-O-Si bond, and the asymmetric vibration absorption of Si-O-Si bond, respectively, as curves (b) and (c) shown in Figure 3. It further demonstrates that samples calcined at 950°C have been converted

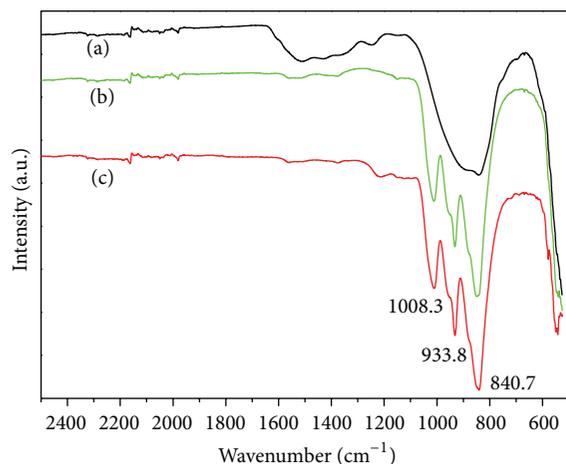


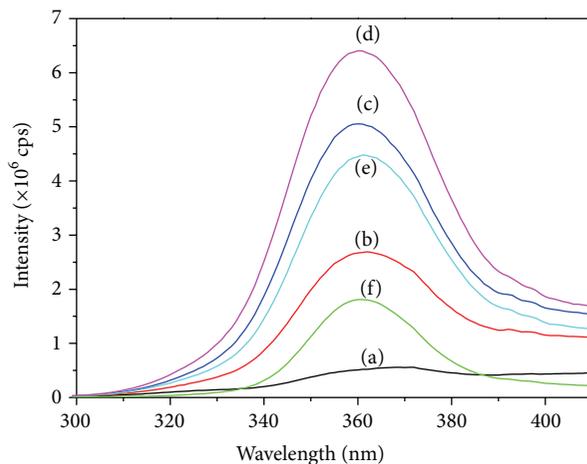
FIGURE 3: FTIR spectra of Pr(III) doped samples calcined at different temperatures: (a) 900°C, (b) 950°C, (c) 1000°C.

from amorphous state to crystal structure, which shows high consistency with the results of Figure 1.

The absorption bands at 1260–1620 cm^{-1} are attributed to the bending vibration of O-H bond or H_2O , which is adsorbed on the internal holes surface of the nanomaterials or bonded with the nanomaterials in other forms. The bonded H_2O in the materials is difficult to desorb at 900°C. A higher heat treatment temperature is usually beneficial to the desorption of the bonded or adsorbed H_2O in the materials, and lead to the disappearing of the absorption bands at 1260–1620 cm^{-1} at the temperature of 950°C or 1000°C, as curves (b) and (c) shown in Figure 3.

3.2. The Upconversion Luminescence of Y_2SiO_5 Nanomaterials. Since the ionic radius of Pr(III) and Y(III), 113 pm and 104 pm, respectively, is very close [32], the lattice parameter of Y_2SiO_5 nanomaterials would not change a lot when Pr(III) dopes in and replaces the position of Y(III) in the lattice. Therefore, X-ray diffraction patterns of Y_2SiO_5 upconversion nanomaterials show little dependence on the dope concentrations of Pr(III). However, the segregation of doped ions strongly modifies the luminescence properties of nanocrystals [33]. It means that the doping concentrations of Pr(III) play an important role on the upconversion luminescence of Y_2SiO_5 nanomaterials, as shown in Figure 4.

The blank sample, the sample without doped Pr(III), shows relative low luminescence intensity. On the other hand, those samples doped Pr(III) emit obvious luminescence spectra at the wavelength of 360 nm. With the increasing of the dope concentration of Pr(III), the emission luminescence intensities are also enhanced obviously to a maximum of 6.43×10^6 cps (count per second) with the Pr(III) doping concentration of 0.96%. It shows an excellent enhancement of Pr(III) doping for the emission luminescence of Y_2SiO_5 nanomaterials. However, further increasing of Pr(III) doping concentration leads to a sharp decrease of the emission luminescence intensity. It is believed that too high of doping



Peak values:

(a) 0.57×10^6 cps	(d) 6.43×10^6 cps
(b) 2.67×10^6 cps	(e) 4.49×10^6 cps
(c) 5.06×10^6 cps	(f) 1.83×10^6 cps

FIGURE 4: Emission spectra of Y_2SiO_5 doped different concentrations: of Pr(III), (a) 0.0%, (b) 0.47%, (c) 0.77%, (d) 0.96%, (e) 2.95% and (f) 4.93%.

concentration of Pr(III) would result in luminescent quenching [34]. As a result, the highest doping concentration of 4.93% Pr(III) results in the lowest luminescence intensity, 1.83×10^6 cps, of all the samples except for the blank sample, as shown in Figure 4.

3.3. Photodegradation of Nitrobenzene Wastewater. As a typical environmental priority control pollutant, nitrobenzene wastewater usually comes from the factories manufacturing medicines, pesticides, plastics, explosives. It is difficult to degrade by normal methods because of its particular molecular structures [35]. In this study, 10 mg/L nitrobenzene wastewater is used to test the photodegradation performances of Pr(III) doped Y_2SiO_5 upconversion nanomaterials. The doping concentrations of Pr(III), 0.47%, 0.96%, 4.93%, and the degradation time, 1 h to 6.5 h, have been taken into account to learn the degradation rate of nitrobenzene in the water, as shown in Figure 5.

Sample doped 0.96% Pr(III) shows much higher photodegradation rate at all the time than the samples of the other two doping concentrations, 0.47% and 4.93%. It can be concluded that higher luminescence emission sample, such as Y_2SiO_5 nanomaterials doped 0.96% Pr(III) as shown in Figure 4, would show a higher photodegradation rate on the pollutant. Too much of doping concentration is not a benefit to the increasing of photodegradation rate. On the other hand, as the time expands, the degradation rates of all the upconversion nanometer samples are increasing obviously at different rate. It is interesting that the slopes of the fitting lines show the same tendency with the degradation rates of the doping concentrations. That is to say, higher degradation rate of the sample is also corresponding to higher slope of fitting line and showing faster photodegradation on the nitrobenzene.

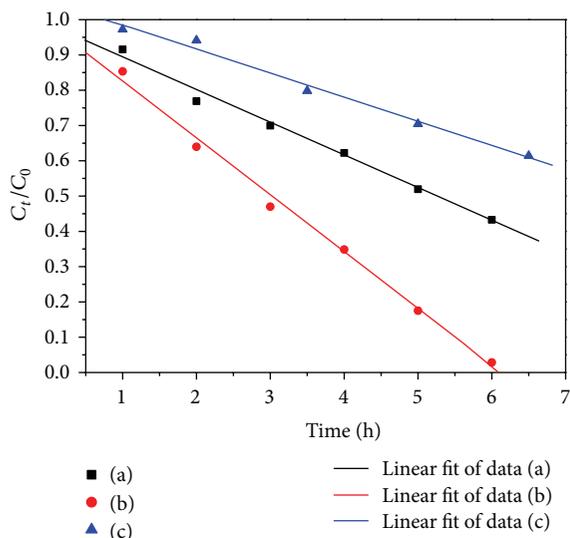


FIGURE 5: The photodegradation performances of Pr(III) doped Y_2SiO_5 nanomaterials (a) 0.47%, (b) 0.96% and (c) 4.93%.

First-order fitting of the $\ln(C_0/C)$ versus time for the photodegradation of pollutants, such as methyl orange and methylene blue, is usually used to study the reaction kinetics [36]. Based on the photodegradation rates of nitrobenzene with time, the photodegradation reaction kinetics lines are drawn out, as shown in Figure 6.

The best photodegradation belongs to the upconversion nanomaterials doped 0.96% of Pr(III), and too much of doping concentrations of Pr(III) would not show high photodegradation of upconversion nanomaterials, which confirms high consistency with the test results indicated in Figure 5. On the other hand, linear relationships appear between the degradation time and the value of $\ln(C_t/C_0)$, where C_t is the concentration of nitrobenzene in the water at a time (t) and C_0 is the original concentration of nitrobenzene 10 mg/L, as shown in Figure 6. Each of the doping concentration of Pr(III), 0.47%, 0.96%, and 4.93%, is according to a reaction kinetics linear equation and correlation indexes: $\ln C_t/C_0 = -0.14399t + 0.05826$, $R = -0.99414$, $\ln C_t/C_0 = -0.29939t + 0.14481$ ($t = 1$ to 4 h), $R = -0.99992$, and $\ln C_t/C_0 = -0.08688t + 0.08227$, $R = -0.99486$, respectively. It can be concluded that the degradation reaction of nitrobenzene under the visible light follows the first-order kinetic law by the photodegradation of Pr(III) doped Y_2SiO_5 upconversion nanomaterials. However, as shown in Figure 6, the fit line for the sample doped 0.96% Pr is linearly only at the first 4 hours. After that, the degradation reaction of nitrobenzene would not follow the first-order kinetics law.

4. Conclusions

Praseodymium ion, Pr(III), doped Y_2SiO_5 upconversion nanomaterials are prepared by using a sol-gel method. The doping concentrations of Pr(III) play important roles on the upconversion of the nanomaterials. The emission luminescence intensity of the nanomaterial reaches a maximum of

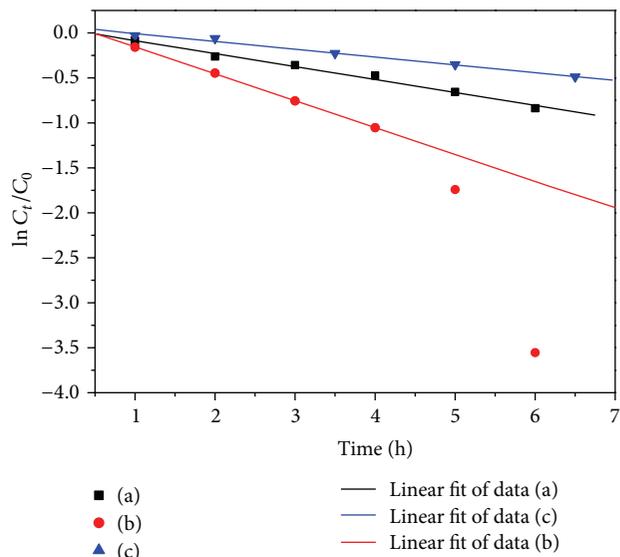


FIGURE 6: The photodegradation reaction kinetics data of nanomaterials (a) 0.47%, (b) 0.96% and (c) 4.93%.

6.43×10^6 cps (count per second) with the Pr(III) doping concentration of 0.96%. In addition, the optimized doping sample shows the best photodegradation performance in all the samples. For 10 mg/L of nitrobenzene wastewater, the photodegradation rate is up to 97.14% in 6 hours. The photodegradation reaction kinetics data indicated that the degradation reaction of nitrobenzene under the visible light follows the first-order kinetic law at the first 4 hours.

Acknowledgment

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