

## Research Article

# Synthesis of $\text{TiO}_2/\text{Pd}$ and $\text{TiO}_2/\text{PdO}$ Hollow Spheres and Their Visible Light Photocatalytic Activity

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A series of  $\text{TiO}_2$ ,  $\text{TiO}_2/\text{Pd}$ , and  $\text{TiO}_2/\text{PdO}$  hollow sphere photocatalysts was successfully prepared *via* a combination of hydrothermal, sol-immobilization, and calcination methods. The structure and optical properties of the as-prepared samples were characterized by X-ray diffraction, field emission scanning electron microscopy, transmission electron microscopy, Brunauer-Emmett-Teller analysis, Barrett-Joyner-Halenda measurement, and UV-Vis diffuse reflectance spectroscopy. The photocatalysis efficiencies of all samples were evaluated through the photocatalytic degradation of rhodamine B under visible light irradiation. Results indicated that  $\text{TiO}_2/\text{PdO}$  demonstrated a higher photocatalytic activity (the photocatalytic degradation efficiency could reach up to 100% within 40 min) than the other samples and could maintain a stable photocatalytic degradation efficiency for at least four cycles. Finally, after using different scavengers, superoxide and hydroxyl radicals were identified as the primary active species for the effectiveness of the  $\text{TiO}_2/\text{PdO}$  photocatalyst.

## 1. Introduction

Semiconductor materials have been received and extensively applied as photocatalysts in photocatalytic water splitting and photodegradation of organic pollutants.  $\text{TiO}_2$  is an important semiconductor in wide applications, such as in photocatalysts [1, 2], solar cells [3], electrorheology [4, 5], and antibacterial agents [6]. It has been exhaustively explored for its merits of environment friendliness, chemical inertness, high stability, nontoxicity, and low cost when utilized as a photocatalyst for environment remediation and photodegradation of organic pollutants [7–9].

Xiang et al. [10] successfully synthesized 3D urchin-like  $\text{TiO}_2$  microspheres for photocatalytic applications. Lai et al. [11] prepared hierarchical  $\text{TiO}_2$  and hierarchical nanosheet-assembled yolk-shell  $\text{TiO}_2$  microspheres for dye adsorption and photocatalysis, respectively. Sarkar and Chattopadhyay [12] synthesized a large-scale mesoporous  $\text{TiO}_2$  microsphere for photocatalysis degradation. However, these  $\text{TiO}_2$  photocatalysts exhibit high photocatalytic activity only under UV irradiation. This finding can be ascribed to the intrinsic prop-

erties of  $\text{TiO}_2$ : a wide band gap (3.2 eV), which limits its use in the UV region of the solar spectrum, which accounts for a very small fraction of solar energy [13]. Therefore significant efforts have been devoted to modify the band gap of  $\text{TiO}_2$ . Doping to extend the optical absorption of  $\text{TiO}_2$  into the visible spectrum is an effective method. In recent decades, doping with metals or nonmetals has been performed to shift the optical response of the catalytically active  $\text{TiO}_2$  from the UV to the visible light region. For example, mordenite [14], graphene [15, 16], F [17], Sm [18], Ni [19], Pt [20], Au [21], Ag [22], and Pd [23, 24] have been used to extend the photoresponse range of  $\text{TiO}_2$ . Similar to Pd, doped PdO can form a certain number of heterojunctions with  $\text{TiO}_2$ , thereby inhibiting the recombination of photogenerated carriers, improving the light utilization efficiency and catalytic activity.

In this study, we successfully synthesized  $\text{TiO}_2/\text{Pd}$  and  $\text{TiO}_2/\text{PdO}$  hollow sphere photocatalysts following the methods of Li et al. [25]. The methods combined hydrothermal, sol-immobilization, and calcination. We selected rhodamine B (Rh B) as the dye template for studying the

photocatalytic degradation efficiency of the as-prepared samples under visible light [26]. The results exhibited that  $\text{TiO}_2/\text{PdO}$  demonstrated a higher photocatalytic activity than previously reported photocatalysts [27, 28] because  $\text{TiO}_2/\text{PdO}$  possessed a wide range of optical absorption, high crystallinity, and a large pore size. Moreover, the photocatalytic reaction mechanism was also discussed on the basis of trapping experiments of active species.

## 2. Experimental Section

**2.1. Materials.** Titanium butoxide (TBOT), palladium chloride ( $\text{PdCl}_2$ ), and rhodamine B (Rh B) were purchased from Aladdin Regent Company. Absolute ethanol, N, N-dimethylformamide (DMF), trifluoroacetic acid (TFA), P-benzoquinone (BQ), isopropanol (IPA), and potassium iodide (KI) were obtained from Kelong Chemical Reagent Company.

**2.2. Synthesis of  $\text{TiO}_2$  Hollow Spheres.** We followed the methods of Li et al. to prepare the  $\text{TiO}_2$  hollow spheres [25]. In a typical procedure, a homogeneous solution including 51 mL of  $\text{H}_2\text{O}$ , 14.1 mL of DMF, and 6.9 mL of TFA was dropped to 2.04 mL of TBOT in a Teflon-lined autoclave, and then the mixture solution was heated to  $180^\circ\text{C}$  and maintained this temperature for 24 h. After cooling to room temperature, the white precipitate was obtained and washed with absolute ethanol and distilled water three times, respectively. Then, the obtained  $\text{TiO}_2$  hollow spheres were dried in a vacuum at  $60^\circ\text{C}$  and calcined at  $450^\circ\text{C}$  for 3 h in air. The  $\text{TiO}_2$  hollow spheres before and after calcination were denoted  $\text{TiO}_2$  and  $\text{TiO}_2\text{-T}$ , respectively.

**2.3. Synthesis of  $\text{TiO}_2/\text{Pd}$  and  $\text{TiO}_2/\text{PdO}$  Hollow Spheres.** Pd nanoparticles were supported on  $\text{TiO}_2$  hollow spheres by using the methods of Li et al. [25]. An aqueous solution of  $\text{PdCl}_2$  (10 mL) and polyvinyl alcohol (PVA, 1 wt%, 0.72 mL) were diluted with water (120 mL). After stirring for 30 min, 1.98 mL  $\text{NaBH}_4$  solution (0.1 M) was added to form a dark brown solution. Subsequently, sulfuric acid solution was added to adjust the pH to 1. Then, 0.2 g  $\text{TiO}_2$  was ultrasonically dispersed in this mixture and rapidly stirred for 2 hours. The resulting slurry was filtered, washed with absolute alcohol, and distilled water, respectively. The obtained  $\text{TiO}_2/\text{Pd}$  hollow spheres were dried in a vacuum at  $60^\circ\text{C}$  and calcined at  $450^\circ\text{C}$  for 3 h in air. The  $\text{TiO}_2/\text{Pd}$  hollow spheres before and after calcination were denoted  $\text{TiO}_2/\text{Pd}$  and  $\text{TiO}_2/\text{PdO}$ , respectively.

**2.4. Characterization.** X-ray diffraction (XRD, Philips X'Pert PRO, Netherlands) on a diffractometer equipped with  $\text{Cu K}\alpha$  radiation ( $k = 0.15418 \text{ nm}$ ) from  $20^\circ$  to  $80^\circ$  at a scanning speed of  $2^\circ \text{ min}^{-1}$ . The morphology and detailed structural information of the samples were observed using a field emission scanning electron microscope (FESEM, Ultra 55, CARL ZEISS in Germany) and transmission electron microscopy (TEM, Libra 200 PE, operated at 200 kV, Germany). The nitrogen adsorption-desorption isotherms were measured at 77 K using a Micromeritics ASAP 2000 system, and the surface area and pore size distribution were calculated using the Brunauer-Emmett-Teller (BET) and Barrett-Joyner-

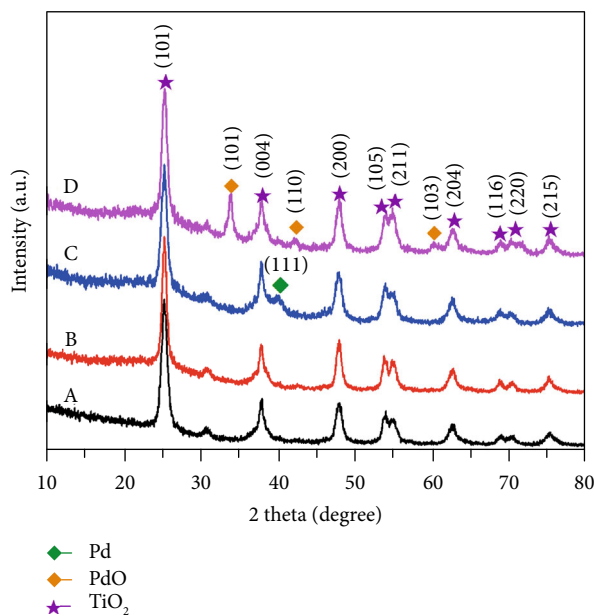


FIGURE 1: Typical XRD patterns of (a)  $\text{TiO}_2$ , (b)  $\text{TiO}_2\text{-T}$ , (c)  $\text{TiO}_2/\text{Pd}$ , and (d)  $\text{TiO}_2/\text{PdO}$ .

Halenda (BJH) methods, respectively. The optical spectra were examined by using a Hitachi U-4100 UV-Vis diffuse reflectance spectra (UV-Vis DRS) in the wavelength range of 200–800 nm equipped with the integrating sphere accessory for diffuse reflectance spectra.

**2.5. Photocatalytic Activity Measurement.** Photocatalytic activities of the as-synthesized products were studied using Rh B as a model pollutant under visible light irradiation. The photocatalytic reactor (Beijing NBT Technology Co., Ltd.) consisted of quartz glass with a circulating water jack and a light source (A 500 W xenon lamp). There is circulating water between the reaction system and the xenon lamp to remove the thermal effect of light. The experiments were performed at room temperature. For each photocatalytic activity measurement, 30 mg of photocatalyst was added to 50 mL of Rh B aqueous solution with the concentration of 30 mg/L. Before irradiation, the reaction mixture was stirred in the dark at  $25^\circ\text{C}$  for 20 min to ensure the establishment of absorption/desorption equilibrium between the photocatalysts and Rh B solution. After the absorption equilibrium, the suspension solution was irradiated by the visible light with continuous stirring. At the given intervals, 5 mL of reaction mixture was centrifuged and then analyzed by recording variations of the maximum absorption spectra by UV1600 spectrometer [29].

## 3. Results and Discussion

**3.1. X-Ray Diffraction (XRD) Analysis.** Figure 1 shows the typical XRD patterns of  $\text{TiO}_2$ ,  $\text{TiO}_2\text{-T}$ ,  $\text{TiO}_2/\text{Pd}$ , and  $\text{TiO}_2/\text{PdO}$ . The main diffraction peaks at  $2\theta = 25.3^\circ$ ,  $37.9^\circ$ ,  $48.1^\circ$ ,  $53.8^\circ$ ,  $55.0^\circ$ ,  $62.7^\circ$ ,  $68.8^\circ$ ,  $70.2^\circ$ , and  $75.1^\circ$  in the spectrum of  $\text{TiO}_2$  and the composite samples were identified and attributed to the diffraction faces of (101), (004), (200),

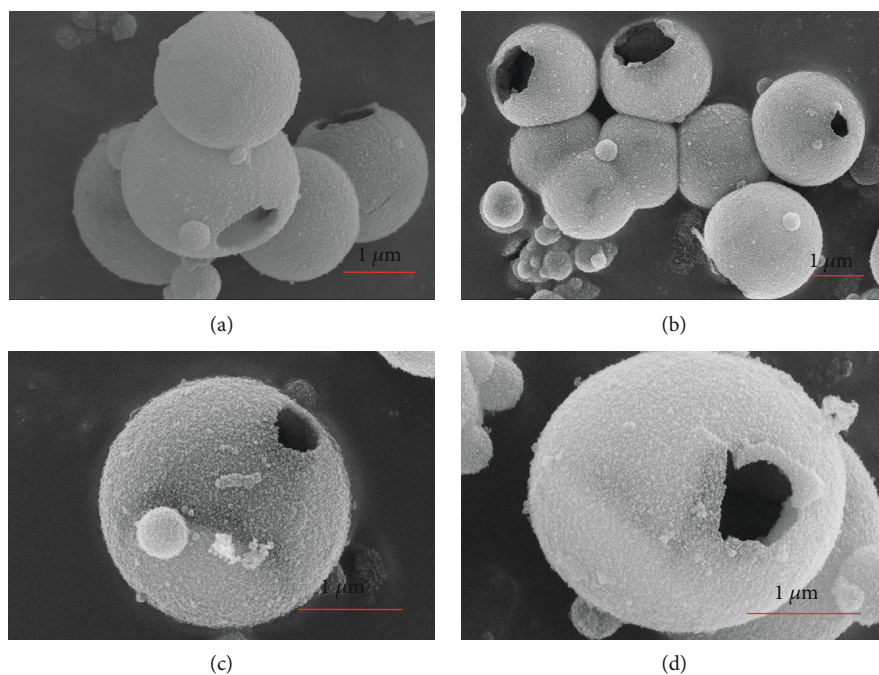


FIGURE 2: FESEM images of (a)TiO<sub>2</sub>, (b)TiO<sub>2</sub>-T, (c)TiO<sub>2</sub>/Pd, and (d)TiO<sub>2</sub>/PdO.

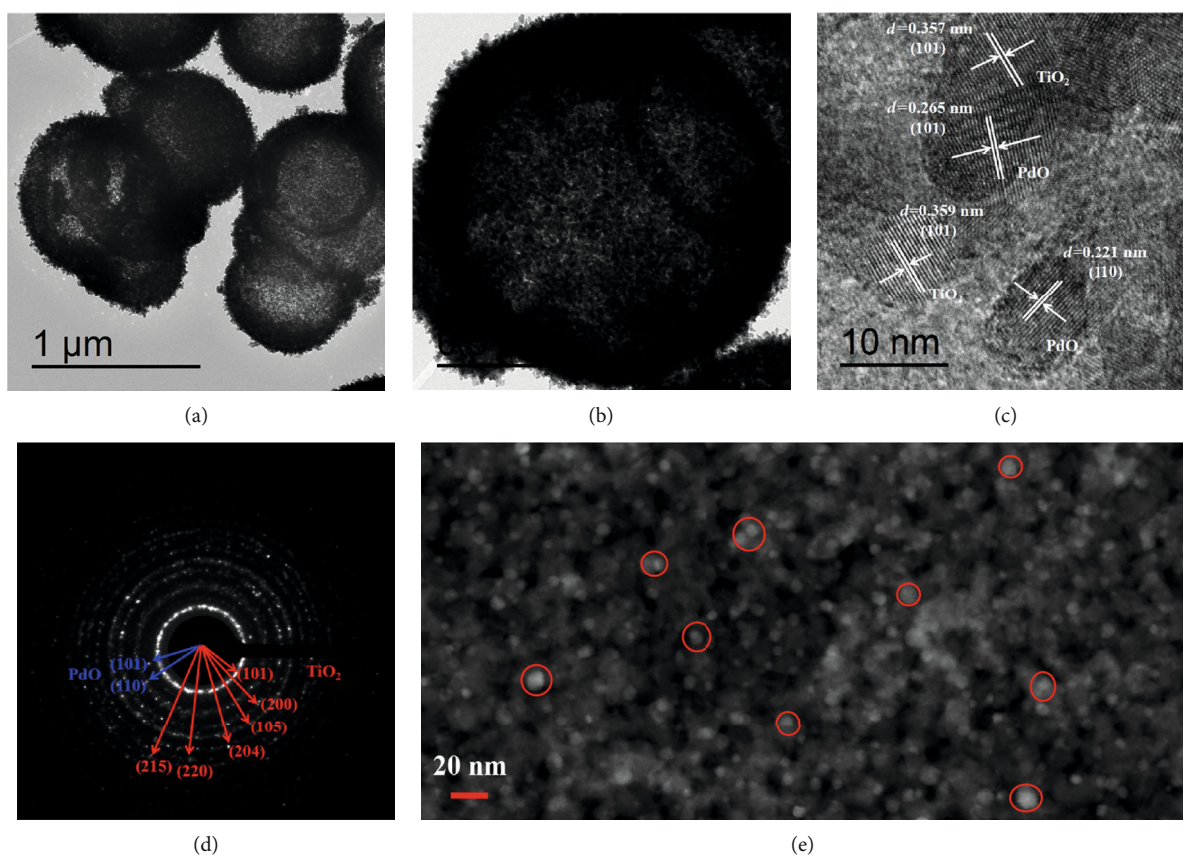


FIGURE 3: TEM (a, b), HRTEM (c), SAED (d), and STEM (e) images of TiO<sub>2</sub>/PdO.

(105), (211), (204), (116), (220), and (215), respectively, showing the crystal phase of anatase (JCPDS no. 21-1272) and implying that calcination and the doping of Pd (the dif-

fraction peak at  $2\theta = 40.1^\circ$ , JCPDS no. 87-0639) and PdO (the diffraction peaks at  $2\theta = 33.8^\circ$ ,  $42.2^\circ$ , and  $60.2^\circ$ , JCPDS no. 43-1024) did not change the structure of TiO<sub>2</sub>. These

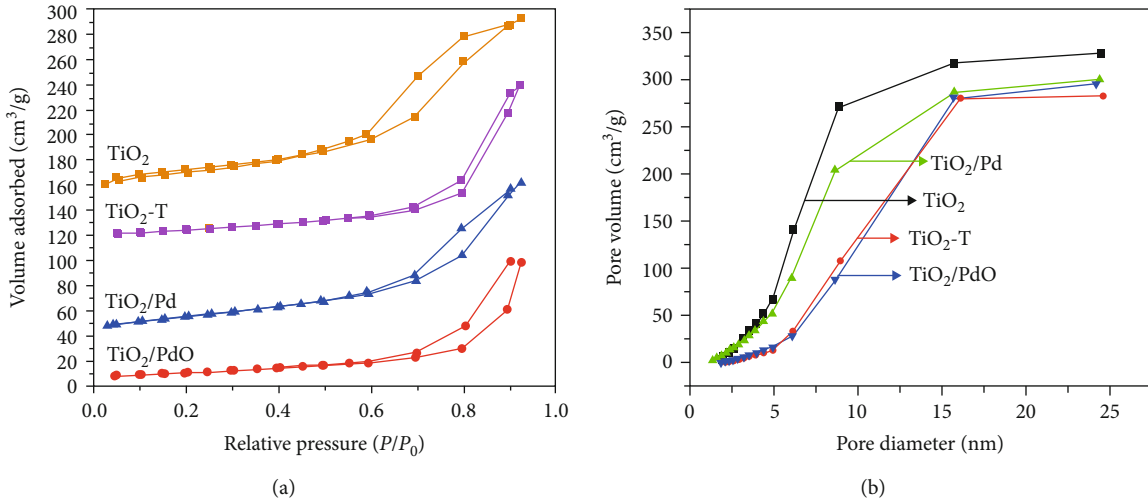


FIGURE 4: (a)  $N_2$  adsorption-desorption isotherms and (b) pore size distribution of  $TiO_2$ ,  $TiO_2$ -T,  $TiO_2$ /Pd, and  $TiO_2$ /PdO.

TABLE 1: Microstructure of  $TiO_2$ ,  $TiO_2$ -T,  $TiO_2$ /Pd, and  $TiO_2$ /PdO.

Samples	$TiO_2$	$TiO_2$ -T	$TiO_2$ /Pd	$TiO_2$ /PdO
$S_{BET}$ ( $m^2/g$ )	112.316	63.919	96.796	65.506
Average pore size (nm)	9.9017	15.8853	10.7378	16.5032

TABLE 2: Photoabsorption edge and band gap energy of  $TiO_2$ ,  $TiO_2$ -T,  $TiO_2$ /Pd, and  $TiO_2$ /PdO.

Samples	Absorption edge (nm)	Band gap (eV)
$TiO_2$	380	3.26
$TiO_2$ -T	397	3.12
$TiO_2$ /Pd	406	3.05
$TiO_2$ /PdO	503	2.47

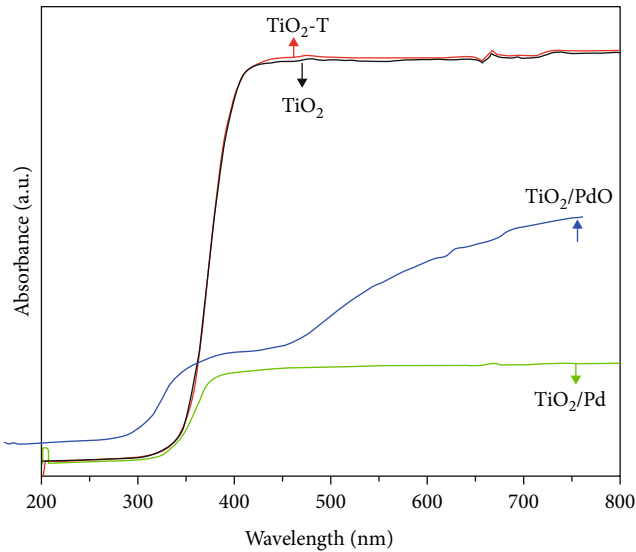


FIGURE 5: UV-Vis diffusive reflectance spectra of  $TiO_2$ ,  $TiO_2$ -T,  $TiO_2$ /Pd, and  $TiO_2$ /PdO.

results show that the diffraction peaks of  $TiO_2$ -T and  $TiO_2$ /PdO were stronger and narrower than those of  $TiO_2$  and  $TiO_2$ /Pd, indicating that the crystallinity of  $TiO_2$ -T and  $TiO_2$ /PdO improved through calcination.

**3.2. Scanning Electron Microscopy (SEM) Analysis.** The morphology of  $TiO_2$ ,  $TiO_2$ -T,  $TiO_2$ /Pd, and  $TiO_2$ /PdO was characterized by SEM and is shown in Figure 2. The result implies that samples with an average diameter of approximately 2-3  $\mu m$  were successfully synthesized. The

hollow spheres obtained exhibited thin and coarse shells with a large cavity space, which can be observed from the fragment. Most of the hollow sphere shells had holes, which may be caused by the collision during the hydrothermal reaction or the centrifugation step [30].

**3.3. Transmission Electron Microscopy (TEM) Analysis.** The morphology and crystal structure of  $TiO_2$ /PdO were examined by TEM, as shown in Figure 3. Figures 3(a) and 3(b) are different magnification TEM images showing that  $TiO_2$ /PdO has hollow structures, which is consistent with the results of SEM.  $TiO_2$ /PdO displayed clear lattice fringes, suggesting its crystalline nature as shown in Figure 3(c). The lattice fringes were measured to be 0.357 and 0.221 nm, which correspond to the (101) and (110) planes of  $TiO_2$  (JCPDS no. 21-1272) and PdO (JCPDS no. 43-1024), respectively. Further analysis of the crystal structure was performed by selected area electron diffraction (SAED) pattern as shown in Figure 3(d). The rings of the SAED patterns can be indexed to the crystalline phases of PdO and  $TiO_2$ . The SAED results indicate the presence of the (101) and (110) planes for crystalline PdO as derived from the lighter ring and the (101), (200), (105), (204), (220), and (215) planes from the brighter ring for crystalline  $TiO_2$ . The planes obtained from the HRTEM and SAED pattern for both PdO and  $TiO_2$  matched the XRD results well. The STEM image of  $TiO_2$ /PdO is shown in Figure 3(e). The white spots in the STEM image are the homogenous dispersion of PdO particles on the  $TiO_2$  [31, 32].

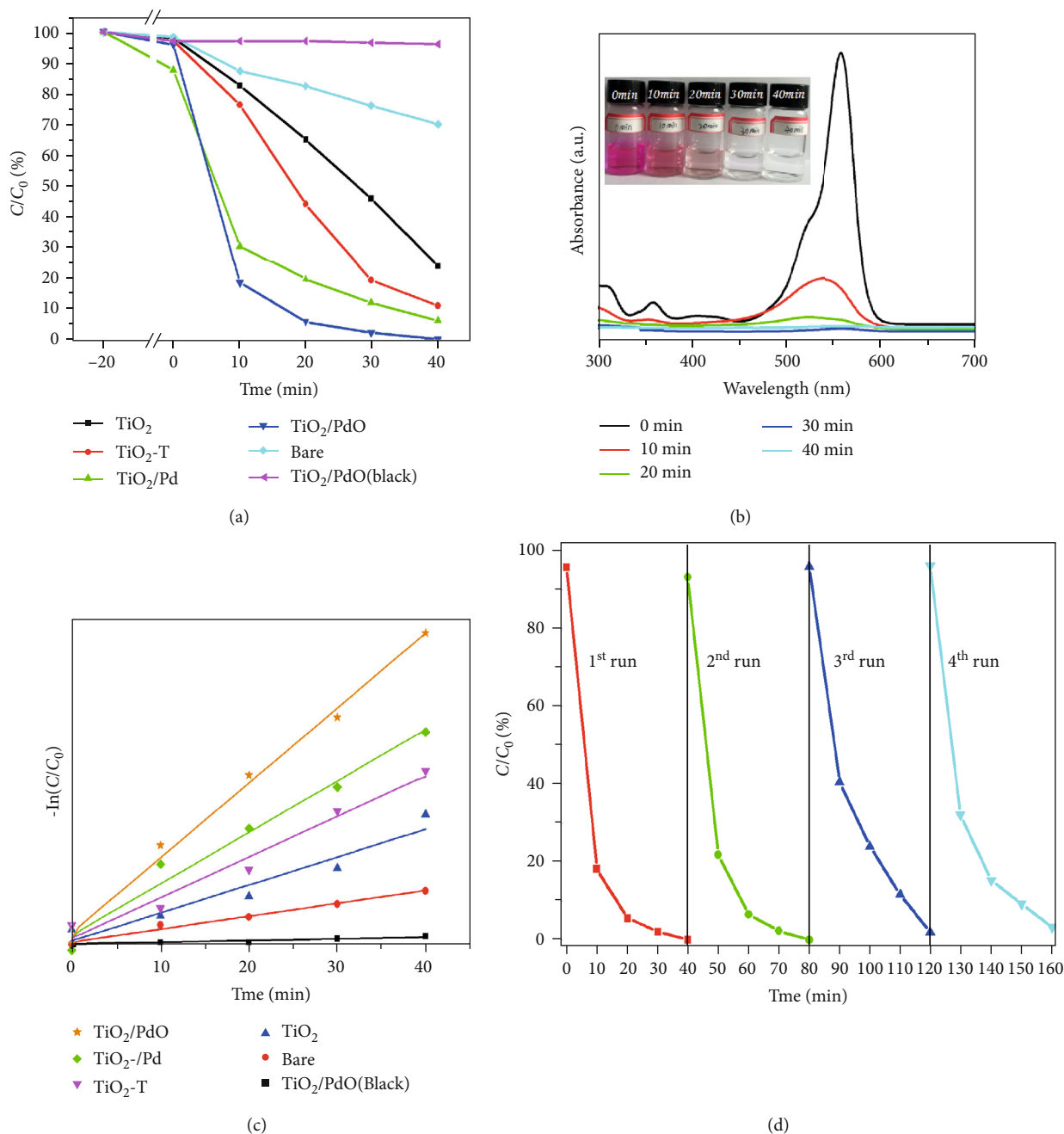


FIGURE 6: (a) Photocatalytic degradation of Rh B solution with TiO<sub>2</sub>, TiO<sub>2</sub>-T, TiO<sub>2</sub>/Pd, and TiO<sub>2</sub>/PdO under visible light irradiation. (b) UV-Vis absorption spectra of Rh B in the presence of TiO<sub>2</sub>/PdO at different photocatalytic degradation times. (c) Kinetics of Rh B photocatalytic degradation over TiO<sub>2</sub>, TiO<sub>2</sub>-T, TiO<sub>2</sub>/Pd, and TiO<sub>2</sub>/PdO under visible light irradiation. (d) Recycling of TiO<sub>2</sub>/PdO for photocatalytic degradation of Rh B.

3.4. Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) Analyses. Figure 4 presents the nitrogen adsorption-desorption isotherms and pore size distribution curve of TiO<sub>2</sub>, TiO<sub>2</sub>-T, TiO<sub>2</sub>/Pd, and TiO<sub>2</sub>/PdO. The isotherms of these samples could be attributed to type IV, and the curves exhibited hysteresis loops at high relative pressures, indicating a mesoporous structure. Furthermore, the specific surface areas and average pore sizes of these samples are summarized in Table 1. As calculated by the BET method, TiO<sub>2</sub>-T and TiO<sub>2</sub>/PdO resulted in BET surface areas of

63.919 and 65.506 m<sup>2</sup>/g and relatively large average pore sizes of 15.8853 and 16.5032 nm, respectively. However, the BET surface areas of TiO<sub>2</sub>-T and TiO<sub>2</sub>/PdO were smaller than those of TiO<sub>2</sub> (112.316 m<sup>2</sup>/g) and TiO<sub>2</sub>/Pd (96.796 m<sup>2</sup>/g), and the average pore sizes of TiO<sub>2</sub>-T and TiO<sub>2</sub>/PdO were larger than those of TiO<sub>2</sub> (9.9017 nm) and TiO<sub>2</sub>/Pd (10.7378 nm). This result may be because the average pore size is related to the crystallite size of a sample [33]. When the hollow spheres were calcining, the crystallites located in the inner cores were easier to dissolve than the exterior

nanoparticles, the exterior nanoparticles could serve as the new starting site for the subsequent recrystallization process, and continued crystal growth could lead to the increased crystallite size of the sample [30]. Therefore, the average pore sizes of  $\text{TiO}_2$ -T and  $\text{TiO}_2/\text{PdO}$  after calcinations were larger than those of  $\text{TiO}_2$  and  $\text{TiO}_2/\text{Pd}$  without calcination. The specific surface area of the catalyst is mainly determined by the pore wall area in the crystal. Due to the high-temperature calcination process, the hollow spheres dissolved and grew, which would cause the pores in the crystal to collapse and lose fine voids. Therefore, the BET specific surface areas of the calcined  $\text{TiO}_2$ -T and  $\text{TiO}_2/\text{PdO}$  were smaller than that of the uncalcined  $\text{TiO}_2$  and  $\text{TiO}_2/\text{PdO}$  [34].

**3.5. UV-Vis Diffusive Reflectance Spectra (UV-Vis DRS) Analysis.** Figure 5 shows the UV-Vis adsorption spectra of  $\text{TiO}_2$ ,  $\text{TiO}_2$ -T,  $\text{TiO}_2/\text{Pd}$ , and  $\text{TiO}_2/\text{PdO}$ . The corresponding absorption edge wavelengths and band gaps are summarized in Table 2. The band gap energy can be estimated by using the equation  $E_g = 1240/\lambda_g$ , where  $E_g$  is the band gap energy (eV) and  $\lambda_g$  is the wavelength (nm) of the absorption edge in the spectrum, respectively. The absorption spectra of  $\text{TiO}_2$  and  $\text{TiO}_2$ -T were only in the ultraviolet region and can be ascribed to the intrinsic band gap absorption of  $\text{TiO}_2$ . Compared with those of  $\text{TiO}_2$  and  $\text{TiO}_2$ -T, the absorption spectra of  $\text{TiO}_2/\text{Pd}$  and  $\text{TiO}_2/\text{PdO}$  showed more absorption in the visible range (400-700 nm). The absorption intensities in the visible light region decreased in the order of  $\text{TiO}_2/\text{PdO} > \text{TiO}_2/\text{Pd} > \text{TiO}_2$ -T  $> \text{TiO}_2$ . In other words, the band gap energies decreased in the order of  $\text{TiO}_2 > \text{TiO}_2$ -T  $> \text{TiO}_2/\text{Pd} > \text{TiO}_2/\text{PdO}$ . Numerous previous studies indicated that  $\text{TiO}_2$  doping with a noble metal can effectively increase absorption and significantly enhance the visible light photocatalytic properties of  $\text{TiO}_2$  [35].

**3.6. Photocatalytic Activity and Recycled Photocatalytic Degradation Performance.** The photocatalytic activities of  $\text{TiO}_2$ ,  $\text{TiO}_2$ -T,  $\text{TiO}_2/\text{Pd}$ , and  $\text{TiO}_2/\text{PdO}$  were evaluated in terms of the decolorization of Rh B under visible light irradiation as shown in Figure 6(a). The photocatalytic performances of a blank Rh B solution without photocatalysts and  $\text{TiO}_2/\text{PdO}$  without visible light irradiation are also included in Figure 6(a) for comparison. The chart clearly shows that the photocatalytic degradation rate of Rh B increased with the intensity of irradiation and the relative photocatalytic activity of the catalysts decreased in the order  $\text{TiO}_2/\text{PdO} > \text{TiO}_2/\text{Pd} > \text{TiO}_2$ -T  $> \text{TiO}_2 > \text{Bare} > \text{TiO}_2/\text{PdO}$  (black) (Table 3). First, the final photocatalytic degradation rate of Rh B during self-degradation and adsorption was lower than that under visible light and with the presence of photocatalysts, thereby revealing the photocatalytic activity of these samples. Second,  $\text{TiO}_2/\text{PdO}$  and  $\text{TiO}_2/\text{Pd}$  exhibited higher activities than  $\text{TiO}_2$  and  $\text{TiO}_2$ -T. The higher activities of  $\text{TiO}_2/\text{PdO}$  and  $\text{TiO}_2/\text{Pd}$  could be explained in terms of the enhancement of UV-Vis absorbance spectra due to Pd and PdO doping (as shown in Figure 5) [35]. The enhancement of UV-Vis absorbance spectra of the doped samples represents their optical absorption property, offering a higher photocatalytic activity. Third, the visible light photocatalytic

TABLE 3: Photocatalytic degradation activity for  $\text{TiO}_2$ ,  $\text{TiO}_2$ -T,  $\text{TiO}_2/\text{Pd}$ , and  $\text{TiO}_2/\text{PdO}$  and previously reported photocatalysts for Rh B degradation under visible light irradiation.

Sample	Degradation (%)	First-order kinetic equation	$k$ ( $\text{min}^{-1}$ )
Bare	28.6	$-\ln(C/C_0) = 0.0079t$	0.0079
$\text{TiO}_2/\text{PdO}$ (black)	3.4	$-\ln(C/C_0) = 0.00026t$	0.00026
$\text{TiO}_2$	76.23	$-\ln(C/C_0) = 0.034t$	0.034
$\text{TiO}_2$ -T	89.14	$-\ln(C/C_0) = 0.058t$	0.058
$\text{TiO}_2/\text{Pd}$	94.04	$-\ln(C/C_0) = 0.063t$	0.063
$\text{TiO}_2/\text{PdO}$	100	$-\ln(C/C_0) = 0.126t$	0.126
$\text{Pd}/\text{TiO}_2$ <sup>[a]</sup> [27]	94	—	—
$\text{PdO}/\text{TiO}_2$ <sup>[b]</sup> [27]	94	—	—
$\text{TiO}_2$ <sup>[c]</sup> [12]	85	$-\ln(C/C_0) = 0.013t$	0.013
P25 <sup>[d]</sup> [11]	—	$-\ln(C/C_0) = 0.023t$	0.023

Footnotes: The test conditions for [a], [b], [c], and [d] in the reference are 30 mg of the photocatalysts and 50 mL of a solution of Rh B (10 mg/L, irradiation time is 50 min), 30 mg of photocatalysts and 50 mL of a solution of Rh B (10 mg/L, irradiation time is 150 min), and 30 mg of photocatalysts and 50 mL of a solution of Rh B (4.8 mg/L, irradiation time is 120 min), respectively.

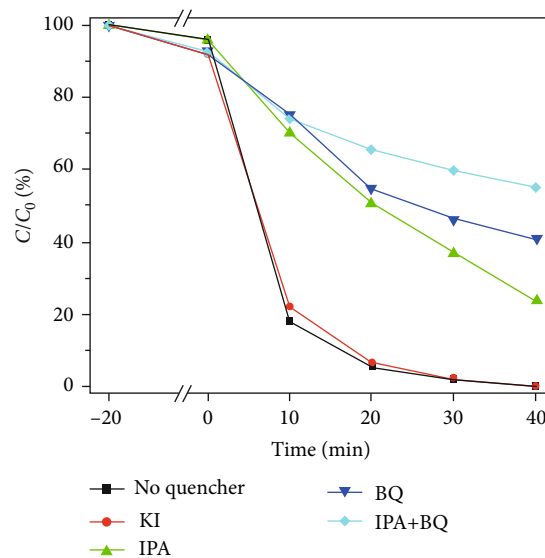


FIGURE 7: Effect of different scavengers on the degradation of Rh B by the  $\text{TiO}_2/\text{PdO}$  photocatalysts.

activities of  $\text{TiO}_2/\text{PdO}$  and  $\text{TiO}_2$ -T after calcination were higher than those before calcination ( $\text{TiO}_2$  and  $\text{TiO}_2/\text{Pd}$ ). This finding could be ascribed to the crystallinity of the samples; that is, high crystallinity indicates few defects, which could lead to the slowed recombination of photogenerated hole-electron pairs [36]. The crystallinity of  $\text{TiO}_2$ -T and  $\text{TiO}_2/\text{PdO}$  was improved by calcination (as shown in Figure 1). Thus, the photocatalytic activities of  $\text{TiO}_2/\text{PdO}$  and  $\text{TiO}_2$ -T were better than those of  $\text{TiO}_2$  and  $\text{TiO}_2/\text{Pd}$ .

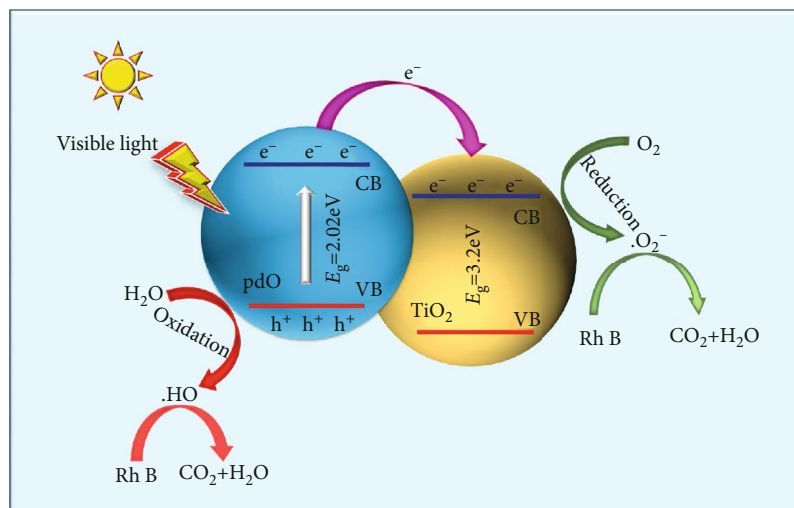


FIGURE 8: Photocatalytic mechanism of  $\text{TiO}_2/\text{PdO}$  photocatalysts under visible light irradiation.

The UV-Vis spectra changes in the dye solution over various time intervals are shown in Figure 6(b) to understand and clarify the changes in the molecular structure of Rh B in the presence of  $\text{TiO}_2/\text{PdO}$  under visible light irradiation. The absorption peak of 550 nm continuously descended with increasing exposure time and almost vanished after 40 min of irradiation. This result is consistent with the gradual color change of the reaction solution from peach to almost colorless during the different reaction times, which suggests that  $\text{TiO}_2/\text{PdO}$  exhibited an excellent photocatalytic activity for Rh B degradation. In addition, most dye degradation processes occurred in the initial minutes. Immediately after 10 min,  $\text{TiO}_2/\text{PdO}$  obtained a degradation percentage of 81.7%. Therefore, the degradation rate for  $\text{TiO}_2/\text{PdO}$  in the initial minutes was high.

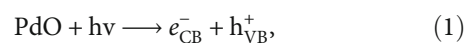
The kinetics of the photodegradation of Rh B in the presence of  $\text{TiO}_2$ ,  $\text{TiO}_2\text{-T}$ ,  $\text{TiO}_2/\text{Pd}$ , and  $\text{TiO}_2/\text{PdO}$  was also studied. The  $-\ln(C/C_0)$  of these samples presented a good linear reaction with irradiation time (shown in Figure 6(c)), which means that the photodegradation of Rh B follows the rules of the first-order reaction kinetics  $-\ln(C/C_0) = kt$ , where  $k$  is the first-order rate constant, and  $C_0$  and  $C$  are the concentrations of Rh B at irradiation times 0 and  $t$ , respectively [11]. The calculated kinetic rate constants are summarized in Table 3.  $\text{TiO}_2/\text{PdO}$  had a maximum  $k$  value of  $0.126 \text{ min}^{-1}$ , whereas the others had  $0.034 \text{ min}^{-1}$  ( $\text{TiO}_2$ ),  $0.058 \text{ min}^{-1}$  ( $\text{TiO}_2\text{-T}$ ),  $0.063 \text{ min}^{-1}$  ( $\text{TiO}_2/\text{Pd}$ ),  $0.0079 \text{ min}^{-1}$  (Bare), and  $0.00026 \text{ min}^{-1}$  ( $\text{TiO}_2/\text{PdO}$  black). Moreover, the rate constant coincides with the final degradation rate (Table 3) of the photocatalytic degradation in Figure 6(a).

The degradation (%) and rate constant ( $k$ ) of previously reported photocatalysts, such as  $\text{Pd}/\text{TiO}_2$  [27],  $\text{PdO}/\text{TiO}_2$  [27],  $\text{TiO}_2$  [12], and P25 [11], are listed in Table 3 for comparison. Notably, the degradation and rate constant of  $\text{TiO}_2/\text{PdO}$  were determined to be 100% and  $0.126 \text{ min}^{-1}$ , which were much larger than those of  $\text{PdO}/\text{TiO}_2$  and other photocatalysts. The high degradation and rate constant of  $\text{TiO}_2/\text{PdO}$  could be attributed to its wide range of optical absorption, high crystallinity, and large pore size.

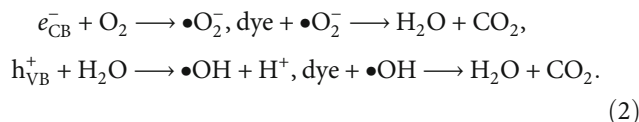
Recycling of catalysts is a key step in assessing the practical application of photocatalysts. To confirm the possibility of recycling the obtained photocatalysts, four recycling experiments were performed with a  $\text{TiO}_2/\text{PdO}$  sample in the photocatalytic degradation of Rh B. As shown in Figure 6(d), the degradation rates of four recycling instances reached up to 99.8%, 99.0%, 98.4%, and 96.6%. The results reveal that the separation of photocatalysts was effective. Thus, the photocatalyst is basically stable and therefore promising for environmental remediation.

**3.7. Active Species and Mechanism Underlying the Photocatalytic Degradation of Rh B.** The effect of different scavengers on the degradation of Rh B by the  $\text{TiO}_2/\text{PdO}$  was investigated to confirm the main active species and provide insight into the potential photocatalytic mechanism of  $\text{TiO}_2/\text{PdO}$  photocatalysts. Three different scavengers, namely, BQ (a  $\cdot\text{O}_2^-$  radical scavenger), IPA (a  $\cdot\text{OH}$  radical scavenger), and KI ( $\text{h}^+$  scavenger), were introduced into the reaction systems [37, 38]. Figure 7 shows that BQ markedly suppressed the degradation rate of Rh B, whereas the presence of KI barely inhibits the photocatalytic efficiency. Compared with KI, IPA hindered the degradation of Rh B. Thus, we conducted a set of comparative experiments. Both BQ and IPA scavengers were added to the same set of experiments to obtain the results shown in Figure 7. IPA+BQ inhibited the degradation of Rh B more strongly than BQ. Therefore, these results suggest that  $\cdot\text{OH}$  and  $\cdot\text{O}_2^-$  were the primary active species that governed the photocatalytic process, and  $\text{h}^+$  was not the main active species in the degradation of Rh B by the  $\text{TiO}_2/\text{PdO}$ .

On the basis of the above investigation and analysis, we propose the possible mechanism for the charge transfer and separation processes underlying the photocatalytic degradation of  $\text{TiO}_2/\text{PdO}$  as schematically illustrated in Figure 8. Upon visible light irradiation, PdO absorbs incident photons and generates electron-hole pairs:



where  $e_{CB}^-$  and  $h_{VB}^+$  are the electrons in the conduction band (CB) and the holes in the valence band (VB), respectively. The photogenerated electrons transfer from the CB of PdO to the CB of  $TiO_2$ , while the photogenerated holes remain in the VB of PdO. Thus, the electrons and holes can be effectively separated to inhibit their recombination [39]. Finally, the electrons reduce  $O_2$  to  $\cdot O_2^-$  radicals; the holes can react easily with the surface-bound  $H_2O$  and generate  $\cdot OH$  radicals. The powerful oxidizing agent ( $\cdot O_2^-$  and  $\cdot OH$ ) can then react with the organic dyes and produce  $CO_2$ ,  $H_2O$ , and so on [12].



#### 4. Conclusion

We have successfully synthesized  $TiO_2/Pd$  and  $TiO_2/PdO$  hollow spheres. The photocatalysis efficiencies of all as-prepared samples were evaluated through the photocatalytic degradation of Rh B under visible light irradiation. The results indicated that  $TiO_2/PdO$  demonstrated a higher photocatalytic activity than the other samples, and a Rh B of 30 mg/L could be completely (100%) degraded by  $TiO_2/PdO$  under visible light irradiation within 40 min. This result can be ascribed to the wide-range optical absorption, high crystallinity, and large pore size of  $TiO_2/PdO$ . In addition,  $TiO_2/PdO$  can be easily separated and retain its photocatalytic efficiency for at least four cycles of reaction under visible light irradiation. Thus,  $TiO_2/PdO$  is a promising photocatalyst for the decomposition of recalcitrant and emerging pollutants in water and wastewater treatments.

#### Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

#### Conflicts of Interest

The authors declare that they have no conflict of interest.

#### Acknowledgments

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