Effect of Erbium on the Photocatalytic Activity of TiO$_2$/Ag Nanocomposites under Visible Light Irradiation

Natarajan Prakash, Rajan Karthikeyan, Dheivasigamani Thangaraju, Mani Navaneethan, Mukannan Arivanandhan, Tadanobu Koyama, and Yasuhiro Hayakawa*

Erbium co-doped TiO$_2$/Ag catalysts are synthesized by using a simple, one-step solvothermal method and characterized by X-ray diffraction, field-emission scanning electron microscopy, transmission electron microscopy, Raman analysis, X-ray photoelectron spectroscopy, and diffuse reflectance spectroscopy. The catalysts exhibit anatase crystal structures with increased visible light absorption compared with pure TiO$_2$. Enhanced photocatalytic activity is observed with Er co-doped TiO$_2$/Ag nanocomposites for Rhodamine B degradation under visible light irradiation. The photocatalytic activity of 1% Er co-doped TiO$_2$/Ag is much higher than that of TiO$_2$/Ag, TiO$_2$/Er, pure TiO$_2$, and commercial Degussa P25. The kinetics of the degradation process are studied and the pseudo-first-order rate constant ($k$) and half-life time ($t_{1/2}$) of the reaction are calculated. The enhanced activity might be accredited to the efficient separation of electron–hole pairs by silver and higher visible light absorption of TiO$_2$ induced by Er.

1. Introduction

Semiconductor metal oxides have drawn great attention because of their rich range of photocatalytic properties for environmental applications.$^{[1]}$ Enormous research efforts have been dedicated to the development of semiconductor photocatalysts.$^{[2–4]}$ TiO$_2$ has been used widely as a photocatalyst since the discovery of its ability to split water under the irradiation of UV light, which is popularly known as the Honda–Fujishima effect.$^{[5]}$ Outstanding properties such as its electronic structure, optical properties, photostability, chemical stability, and environmentally friendly nature make TiO$_2$ a most suitable photocatalyst in many environmental applications.$^{[6–9]}$ The wide band gap of TiO$_2$ semiconductors (3.2 eV) makes them very limited to activity only in UV ($\leq$ 385 nm) light absorption. In addition, the very short life time (ca. 30 ps) of photogenerated electron–hole pairs leads to fast recombination.$^{[10]}$ To solve these major problems, several strategies for the modification of TiO$_2$ have been proposed.$^{[11]}$ Several investigations have indicated that the doping of noble metal nanoparticles (Ag,$^{[11,12]}$ Au,$^{[13]}$ Pt,$^{[14]}$ and Pd$^{[15]}$) onto the surface of TiO$_2$ enhances its photocatalytic activity. Noble metals can act as reservoirs for photogenerated electrons and promote interfacial charge transfer because of their high Schottky barrier.$^{[11]}$ Among the noble metals, silver has been of great interest for doping TiO$_2$ because of its electron–hole separation and its antibacterial effects, which are very useful in waste treatment and in medical applications.$^{[16]}$

Several modification strategies have been adapted to enhance the visible light response of TiO$_2$ using plasmonic metals,$^{[17]}$ transition metals (Fe,$^{[18]}$ Co,$^{[19]}$ and V$^{[20]}$), and nonmetals,$^{[21,22]}$ coupling with small band gap semiconductors (CdS/ TiO$_2$,$^{[23]}$ In$_2$O$_3$/TiO$_2$,$^{[24]}$) dye sensitization,$^{[25,26]}$ and luminescent phosphors.$^{[27,28]}$ Doping of lanthanide into semiconductors has been studied extensively because of its significant role in altering the absorption edge of semiconductors, which enhances the absorption of low energy photons and increases thermal stability.$^{[29–32]}$ In addition, the lanthanide ions can readily form complexes with various Lewis bases, such as acids, amines, aldehydes, and alcohols, through their 4f orbitals. Therefore, organic molecules can be easily adsorbed on the surface of lanthanide-doped titania, demonstrating the enhancement of photocatalytic activity.$^{[33]}$ Erbium is a popular element for doping photocatalytic semiconductors (TiO$_2$) because of its up-conversion ability; that is, the ability to convert infrared light into visible light.$^{[34]}$ Co-doping of two different ions in a TiO$_2$ matrix results in a higher photocatalytic activity than single dopant TiO$_2$.$^{[35]}$ Single-step synthesis of nanoparticles produces more uniform distribution of nanoparticles than multistep synthesis, which tends not to yield a uniform distribution.

In this work, we report the synthesis of silver and erbium co-doped TiO$_2$ nanocomposites by using a simple solvothermal route without using any capping or reducing agents. The photocatalytic effects of Er and Ag co-doping on TiO$_2$ were investigated for the photocatalytic degradation of Rhodamine B dye in aqueous solutions and compared with those of pure TiO$_2$.
and TiO$_2$-P25. Our results reveal that Er and Ag co-doping of TiO$_2$ led to improved photocatalytic ability under visible light.

**Experimental Section**

**Materials**

Titanium(IV) isopropoxide (Ti(OCH(CH$_3$)$_2$)$_4$, 95%, Wako), silver nitrate (AgNO$_3$, Wako), butanol (C$_4$H$_{10}$O, 99%, Wako), hydrochloric acid (HCl, 37%, Wako), and TiO$_2$ (Degussa P25, Aeroxide) were used as purchased. Erbium oxide (Er$_2$O$_3$, 99.9%, Wako) was dissolved in nitric acid to form erbium nitrate, which was then dried at 80 °C and kept in an airtight glass bottle. Deionized water was used for all the experiments and treatment processes. Rhodamine B (C$_{28}$H$_{31}$ClN$_2$O$_3$, Wako) dye was used as a model system to demonstrate the photocatalytic activity.

**Solvothermal Synthesis of TiO$_2$:Ag:Er Nanocomposites**

Ag and Er co-doped TiO$_2$ nanocomposites were prepared by using a simple solvothermal procedure, as shown in Figure 1. Titanium(IV) isopropoxide (0.5 M) was dissolved in n-butanol. Appropriate amounts of silver nitrate and erbium nitrate were dissolved in deionized water (20 mL). These two solutions were mixed together and stirred for 60 min for the complete hydrolysis of titanium(IV) isopropoxide. The resulting solution was placed in a 100 mL Teflon-lined stainless steel autoclave, and growth was carried out at 150 °C for 25 h. The resulting product was dried at 150 °C to remove superfluous liquid and further annealed at 350 °C for 2 h. TiO$_2$ nanocomposites with various molar concentrations (%) of silver and erbium were prepared by using the above procedure. The appropriate concentration (mol%) of precursors is given in Table 1.

**Photocatalytic Degradation of Rhodamine B**

The photocatalytic performance of TiO$_2$ nanocomposites was evaluated with respect to the degradation of Rhodamine B dye molecules in aqueous solution. Photocatalytic experiments were carried out in a laboratory-made borosilicate glass reactor (76 mm height and 74 mm diameter with water-circulating outer jacket); the distance between the reactor bottom and light source was 15 cm. The measured power intensity of light was 8000 ± 50 lux. In a typical experiment, the synthesized catalyst (75 mg) was dispersed in Rhodamine B solution (10 mg L$^{-1}$, 50 mL) and stirred constantly for 45 min at room temperature in the dark to the attain adsorption–desorption equilibrium of the dye with the catalyst. The system was then irradiated with a visible light source (500 W Toshiba, daylight color). At constant time intervals, 2.5 mL of solution was withdrawn from the mixture and centrifuged to remove the suspended catalyst. The concentration of Rhodamine B was then measured from the absorbance value at 557 nm using a UV/Vis spectrophotometer (Jasco, V-670).

**Characterization**

The crystal structures of the prepared TiO$_2$ nanocomposites were analyzed by X-ray powder diffraction (XRPD) (scan rate of 0.04° s$^{-1}$ in the 2θ range of 20° to 80°) with a RINT-2200 Rigaku X-ray diffractometer (Cu-K$_\alpha$ radiation, λ = 1.54178 Å). The surface morphology of synthesized composites was analyzed with a JEOL JSM6320F field-emission scanning electron microscope (FESEM). High-resolution transmission electron microscope (HRTEM) images were recorded with a JEOL JEM 2100F microscope at an accelerating voltage of 200 kV. The chemical states of the synthesized materials were analyzed with X-ray photoelectron spectroscopy (XPS) (Shimadzu ESCA 3100). The ultraviolet visible (UV/Vis) diffuse reflectance spectra and UV/Vis absorption spectra were recorded in the range of 200–800 nm with a JascoV-670 UV/Vis-NIR spectrophotometer. Raman spectra were recorded in the range of 100–1000 cm$^{-1}$ with a Jasco NRS-7100 Raman spectrophotometer.

**Table 1.** Various concentrations of Ag and Er co-doped TiO$_2$ and their synthesis parameters and bandgap values.

<table>
<thead>
<tr>
<th>Exp. no.</th>
<th>Sample name</th>
<th>Titanium isopropoxide [mL]</th>
<th>AgNO$_3$ [mM]</th>
<th>Er(NO$_3$)$_3$ [mM]</th>
<th>Butanol [mL]</th>
<th>Water [mL]</th>
<th>Growth time [h]</th>
<th>Band Gap [eV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>TiO$_2$</td>
<td>0.5</td>
<td>0.000</td>
<td>0.00</td>
<td>70</td>
<td>20</td>
<td>25</td>
<td>3.23</td>
</tr>
<tr>
<td>2</td>
<td>TiO$_2$:0.8 Ag</td>
<td>0.5</td>
<td>0.004</td>
<td>0.00</td>
<td>70</td>
<td>20</td>
<td>25</td>
<td>3.17</td>
</tr>
<tr>
<td>3</td>
<td>TiO$_2$:1.0 Er</td>
<td>0.5</td>
<td>0.000</td>
<td>0.005</td>
<td>70</td>
<td>20</td>
<td>25</td>
<td>3.15</td>
</tr>
<tr>
<td>4</td>
<td>TiO$_2$:0.8 Ag:0.5 Er</td>
<td>0.5</td>
<td>0.004</td>
<td>0.0025</td>
<td>70</td>
<td>20</td>
<td>25</td>
<td>3.13</td>
</tr>
<tr>
<td>5</td>
<td>TiO$_2$:0.8 Ag:1.0 Er</td>
<td>0.5</td>
<td>0.004</td>
<td>0.005</td>
<td>70</td>
<td>20</td>
<td>25</td>
<td>3.13</td>
</tr>
<tr>
<td>6</td>
<td>TiO$_2$:0.8 Ag:1.5 Er</td>
<td>0.5</td>
<td>0.004</td>
<td>0.075</td>
<td>70</td>
<td>20</td>
<td>25</td>
<td>3.09</td>
</tr>
<tr>
<td>7</td>
<td>TiO$_2$:0.8 Ag:2.0 Er</td>
<td>0.5</td>
<td>0.004</td>
<td>0.100</td>
<td>70</td>
<td>20</td>
<td>25</td>
<td>3.09</td>
</tr>
<tr>
<td>8</td>
<td>TiO$_2$:3.0 Ag:1.0 Er</td>
<td>0.5</td>
<td>0.015</td>
<td>0.015</td>
<td>70</td>
<td>20</td>
<td>25</td>
<td>3.14</td>
</tr>
</tbody>
</table>
2. Results and Discussion

The crystal structures of Ag and Er co-doped TiO_2 samples were analyzed by XRPD; the obtained patterns of the pure TiO_2, TiO_2:0.8 mol\% Ag, TiO_2:1.0 mol\% Er (TiO_2:1.0Er), and TiO_2:0.8 mol\% Ag:1.0 mol\% Er (TiO_2:0.8Ag:1.0Er) are compared in Figure 2a. The reflections were well matched with the anatase phase of titania (JCPDS Card No. 21-1272). There were no significant peaks related to silver at low silver concentration (0.8 mol\%). The crystalline phases of various TiO_2 samples showed higher absorption in the visible region. The oxidation states of elements present in the prepared TiO_2:3.0Ag:3.0Er catalyst were evaluated by XPS measurements. The different chemical states of Ti2p, O1s, Ag3d, and Er4d are shown in Figure 3a-d. Figure 3a shows peaks at 459.45 and 465.05 eV, which correspond to Ti2p_3/2 and Ti2p_1/2 peaks, respectively. The separation between the peaks was 5.6 eV, which was in good agreement with the Ti^{4+} of anatase titania. Another peak at 457 eV revealed the +3 charge state of Ti ions in the TiO_2 lattice and had lower intensity than the Ti^{4+} peak. Figure 3b shows the O1s peak with a binding energy of 530.9 eV, which was attributed to the lattice oxygen in anatase titania. Hydroxyl oxygen and adsorbed oxygen were also identified at band energies of 532.6 and 534.2 eV, respectively. The binding energies of Ag 3d_5/2 and Ag 3d_3/2 corresponded to 368.8 and 374.8 eV (Figure 3c), respectively, and the energy separation value (6.0 eV) indicated the metallic silver presence over the TiO_2 surface, which agreed well with XRPD results. The small sub-peak at 367.7 eV corresponded to silver oxide. Figure 3d shows a peak of the 4d energy state of erbium as native erbium oxide.

The Raman spectra of pure TiO_2 and TiO_2 nanocomposites are shown in Figure 4. Raman peaks observed at 147, 398.5, and 641.5 cm^{-1} indicated the anatase phase of titania. The Raman peak of the E_g band [147 cm^{-1} (TiO_2)] shifted toward higher wavenumbers [147.5 (TiO_2:0.8Ag), 149.5 (TiO_2:1.0Er), 149.5 (TiO_2:0.8Ag:1.0Er), and 151 cm^{-1} (TiO_2:3.0Ag:3.0Er)] in doped TiO_2. This indicates that increasing the amount of Ag and Er dopants led to high lattice defects in the nanocomposites. Diffused reflectance spectra were measured to study the optical properties of TiO_2 and TiO_2 composites. The corresponding Kubelka–Munk functions as functions of light energy are shown in Figure 5a,b. The pure TiO_2 nanoparticles absorbed very low amounts of visible light because of their wide band gap (3.23 eV). However, the Ag-doped and Er/Ag co-doped TiO_2 samples showed higher absorption in the visible region.
The characteristic Er absorptions located at 2.53, 2.37, and 1.89 eV corresponded to the excitation from $4I_{15/2}$ to $4F_{7/2}$, $2H_{11/2}$, and $4F_{9/2}$, respectively. [28, 41] Ag and Er co-doped TiO$_2$ showed lower band gap values than pure titania (3.23 eV) and TiO$_2$:0.8Ag (3.17 eV). A significant decrease in the band gap values of TiO$_2$ was observed when loading Ag and Er as co-dopants. The redshift of TiO$_2$ confirmed the existence of Ag and Er bonds with TiO$_2$. This redshift towards the visible region is due to the charge transfer between TiO$_2$ and the 4f electrons of Er.[31, 41] The Ag and Er dopants essentially modify the absorption of titania and allow enhancement in the visible region, which, in turn, yields a higher photocatalytic activity of the nanocomposite under visible light.

The surface morphology of the synthesized TiO$_2$ nanocomposite was investigated by SEM analysis; the acquired micrographs are shown in Figure 6a–f. The SEM images of pure TiO$_2$ particles (Figure 6a) showed self-assembled, sphere-like nanostructures with diameters ranging between 50 and 400 nm. TiO$_2$/Ag and TiO$_2$/Er showed rough-surfaced spheres with diameters between 20 and 300 nm (Figure 6b,c). The self-assembling nature of TiO$_2$ completely disappeared in the Er co-doped TiO$_2$/Ag sample (Figure 6d). Further increasing the Ag (3.0%) and Er (2.0, 3.0%) dopant concentrations resulted in micrometer-sized particles with irregular shapes, as shown in Figure 6e,f. This indicated that increasing the amount of Er (above 1.5%) prevents silver ion diffusion onto the TiO$_2$ surfaces. Heavily agglomerated metallic silver particles were formed by increasing the Ag percentage because of the high surface energy of silver. Similar results were obtained by Mogal et al.[43]

Figure 7a–d shows TEM images of TiO$_2$, TiO$_2$:0.8Ag, TiO$_2$:1.0Er, TiO$_2$:0.8Ag:1.0Er, and TiO$_2$:3.0Ag:3.0Er nanocomposites. The TEM images of pure TiO$_2$ particles (Figure 6a) showed spherical particles with diameters in the range of 100 to 300 nm and a grain size distribution in the range of 5 to 13 nm (Figure 6a inset); the self-assembled sphere size agreed well with the SEM results. Figure 7b,c shows that the morphology of self-assembled TiO$_2$ spheres changed from spherical to irregular because of the Ag and Er dopants. The TEM image (Figure 7d) of TiO$_2$:3.0Ag:3.0Er clearly confirmed the presence of silver and TiO$_2$ particles by their lattice fringe values. The calculated lattice fringes 0.35 nm (Figure 7a inset) and 0.23 nm (Figure 7d inset) can...
be attributed to TiO$_2$ (101) and Ag (111) planes, respectively.[37, 40]

The photocatalytic activity of the pure TiO$_2$ and modified TiO$_2$ nanocomposites was evaluated by degradation (decolorization) of Rhodamine B under visible light irradiation. Dye degradation experiments were carried out under identical experimental conditions. The dye degradation (%) was calculated by using Equation (1):

\[
\text{Dye degradation} \, (\%) = \frac{A_0 - A_t}{A_0} \times 100
\]

Here, $A_0$ is the initial absorbance of Rhodamine B solution and $A_t$ is the absorbance of Rhodamine B solution at time $t$. The degradation (%) is plotted against time to derive the catalytic efficiency of the nanocomposite catalysts.

The direct photolysis of Rhodamine B in the absence of a catalyst did not show any considerable degradation. Absorbance of Rhodamine B gradually decreased with a constant interval of time with synthesized TiO$_2$ nanocomposites, as shown in Figure 5.

Figure 5. Kubelka–Munk function as a function of light energy for a) pure TiO$_2$, TiO$_2$-0.8 Ag, TiO$_2$-1.0 Er, TiO$_2$-0.8 Ag:1.0 Er, and TiO$_2$-3.0 Ag:3.0 Er nanocomposites, b) TiO$_2$:0.8 Ag:0.5 Er, TiO$_2$:0.8 Ag:1.0 Er, TiO$_2$:0.8 Ag:1.5 Er, and TiO$_2$:0.8 Ag:2.0 Er nanocomposites. PA: primary absorption (onset near 3.1 eV), SA: secondary absorption (onset near 1.65 eV).

The Ag and Er co-generation results of various TiO$_2$ composites were compared with the commercially available TiO$_2$-P25 catalyst as a reference. The Rhodamine B degradation efficiencies of TiO$_2$, TiO$_2$-P25, TiO$_2$:0.8 Ag, TiO$_2$:1.0 Er, TiO$_2$:0.8 Ag:1.0 Er, and TiO$_2$:3.0 Ag:3.0 Er were 65, 85, 89, 91, 98, and 70%, respectively, estimated at 30 min, as shown in Figure 9. The Ag and Er co-
doped sample showed higher activity than other synthesized catalysts. The observed photocatalytic enhancement of TiO$_2$ in the presence of Ag and Er can be explained with respect to electron–hole pair generation and separation, as shown in the schematic diagram (Figure 10). The catalytic activity depends on the number of electron–hole pairs involved during photoreaction in a semiconductor photocatalyst. The optimum amount of silver acted as an electron sink, which trapped the photogenerated electrons from the conduction band of TiO$_2$ and facilitated the electron–hole pair separation in TiO$_2$/Ag catalysts. The photogenerated holes remained at the valence band of TiO$_2$. During this process, more OH and \( \cdot \)O radicals were produced and increased the photocatalytic activity of the TiO$_2$/Ag catalyst.[11] Among the various percentages of Ag loading in TiO$_2$, TiO$_2$:0.8Ag showed the highest degradation of dye, as shown in Figure 11.

The dye degradation curves of various Er-doped TiO$_2$/Ag are presented in Figure 12. TiO$_2$:0.8Ag:1.5Er and TiO$_2$:0.8Ag:2.0Er catalysts showed lower degradation efficiency than TiO$_2$:0.8Ag:1.0Er because they had partly aggregated particles. The optimum Ag and Er concentration and improved properties of the TiO$_2$:0.8Ag:1.0Er composite produced high degradation ability, when compared with those of other Er compositions in TiO$_2$/Ag. The high Ag and Er loadings in TiO$_2$:3.0Ag:3.0Er led to the heavy aggregation of TiO$_2$ as micrometer-sized particles, which reduced the number of available photocatalytic sites for dye molecule absorption and hence led to lower photocatalytic activity. However, the UV/Vis absorption spectra of Er co-doped TiO$_2$ revealed improved visible light absorption of TiO$_2$. Doping with Er enhanced the for-

Figure 8. Degradation of Rhodamine B versus time by TiO$_2$:0.8Ag:1.0Er. Rhodamine dye concentration: 10 mg L$^{-1}$, dye volume: 50 mL, catalyst: 75 mg, pH3.

Figure 9. Percentage degradation of Rhodamine B by a) TiO$_2$:0.8Ag:1.0Er, b) TiO$_2$:1.0Er, c) TiO$_2$:0.8Ag, d) TiO$_2$:P25, e) TiO$_2$:3.0Ag:3.0Er, f) pure TiO$_2$, and g) without catalyst. Rhodamine dye concentration: 10 mg L$^{-1}$, dye volume: 50 mL, catalyst: 75 mg, pH3.

Figure 10. Schematic diagram of photocatalytic Rhodamine B degradation by Ag and Er co-doped TiO$_2$ nanocomposites.

Figure 11. Percentage degradation of Rhodamine B by various Ag-doped TiO$_2$ nanocomposites, Rhodamine dye concentration: 10 mg L$^{-1}$, dye volume: 50 mL, catalyst: 75 mg, pH3.
formation of electron–hole pairs under visible light irradiation. The excited electrons reduced the surface Er$^{3+}$ into Er$^{2+}$ upon light irradiation, which enhanced O$_2$ adsorption.[28] This process favors electron–hole pair separation in TiO$_2$. Er$^{3+}$ ions also created crystal defects and oxygen vacancies in the TiO$_2$ lattice, as identified by Ti$^{3+}$ formation in the XPS spectrum (Figure 3 a). These crystal defects further trap higher numbers of electrons. Hence, Er played a vital role in enhancing the photocatalytic ability through interfacial charge transfer and effective prevention of electron-hole pairs. Thus, doping of Ag and Er generates more ‘OH and ‘O$_2^-$ radicals, which ultimately increases the photocatalytic activity.

The rate of photodegradation of dye catalyzed by titania composites depends on the concentration of Rhodamine B and follows a pseudo-first-order reaction given in Equations (2) and (3):[44]

$$\ln \left( \frac{C_0}{C} \right) = kt$$

(2)

$$t_{1/2} = \frac{\ln 2}{k}$$

(3)

Here, $k$ is the pseudo-first-order rate constant, $C_0$ is the initial concentration, $C$ is the concentration of Rhodamine B at time $t$, and $t_{1/2}$ is the half-life time of the reaction. The rate constant was calculated by measuring the Rhodamine B disappearance at 557 nm (Figure 8) at constant intervals (5 min) up to 30 min. The average rate constants of synthesized TiO$_2$ nanocomposite catalysts were compared, as shown in Table 2.

Increased photocatalytic activity was observed for TiO$_2$:0.8 Ag (0.06942 min$^{-1}$) and TiO$_2$:1.0 Er (0.08036 min$^{-1}$) composites compared with pure TiO$_2$ (0.03081 min$^{-1}$) and TiO$_2$:P25 (0.05206 min$^{-1}$) because of the efficient separation of electron-hole pairs, which increased visible light absorption. The calculated rate constant for TiO$_2$:0.8 Ag:1.0 Er was 0.13091 min$^{-1}$, which is much higher than that of the pure and other doped TiO$_2$ nanocomposites. The synergistic effect of Ag and Er in TiO$_2$ enhanced the photocatalytic ability for rapid dye degradation.

The effect of pH on the photo dye degradation ability of TiO$_2$:0.8 Ag:1.0 Er catalyst was estimated at pH values ranging from 3 to 11, as shown in Figure 13; the rate constants are given in Table 3. Maximum photocatalytic degradation efficiency (0.13091 min$^{-1}$ at 30 min) was apparent at pH 3. The degradation activity of TiO$_2$:0.8 Ag:1.0 Er gradually decreased with increasing pH up to 9 and then increased at pH 11. This photocatalytic activity change can be explained by the zero-point charge (ZPC) nature of the catalyst. The ZPC of TiO$_2$:Ag:Er composites was found to be 5.4–6.0 pH.[45]

The surface of the catast...
lyst was positively charged when the pH was below the ZPC value, and this facilitated greater Rhodamine B molecule adsorption on the surface of TiO₂, increasing degradation efficiency.

The reusability of the TiO₂:0.8Ag:1.0Er catalyst was tested for the photodegradation of Rhodamine B under the same experimental conditions; the percentage of repeatability is shown in Figure 14. After the first cycle, the TiO₂:0.8Ag:1.0Er catalyst was washed well with water several times and dried at 110 °C for 3 h. The cleaned catalyst was used for four cycles, and the degradation (%) was compared. The dye degradation percentages were 98, 95, 97, and 96% for 30 min, showing similar values of degradation. This revealed the excellent photostability of the catalyst, which can thus be used for continuous treatment of wastewater.

![Figure 14](image_url) Reusability of TiO₂:0.8Ag:1.0Er, Rhodamine dye concentration: 10 mg L⁻¹, dye volume: 50 mL, catalyst: 75 mg, pH3, irradiation time: 30 min.

3. Conclusions

Various compositions of Ag and Er co-doped TiO₂ nanocomposites were successfully synthesized by using a simple solvothermal method. The modified absorption nature of TiO₂ was observed in the presence of Ag and Er in the nanocomposite. The doping of Ag and Er affected the properties of TiO₂ photocatalysts significantly. The TiO₂:0.8Ag:1.0Er nanocomposite was demonstrated to be the best catalyst. The excellent photocatalytic ability of the catalyst originated from a combination of the electron-trapping ability of Ag and the visible light absorption associated with Er doping. TiO₂:0.8Ag:1.0Er showed similar photocatalytic activity after four cycles, and hence, could be used as a photocatalyst for industrial wastewater treatment under visible light irradiation.

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Erbium doping: Erbium co-doped TiO$_2$/Ag catalysts were synthesized by using a simple, one-step solvothermal method and characterized. Enhanced photocatalytic activity was observed with Er co-doped TiO$_2$/Ag nanocomposites for Rhodamine B degradation under visible light irradiation (see figure).