Hollow Sr/Rh-codoped TiO$_2$ photocatalyst for efficient sunlight-driven organic compound degradation†

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Sunlight-driven photocatalysis has emerged as a potential technology to address organic pollutant issues. Here, we report the first Rh-doped hollow-structured TiO$_2$ photocatalyst, which is highly active in the photocatalytic decomposition of organic pollutants under solar light. We achieved this by introducing Sr$^{2+}$ as a co-doping agent, which stabilized the hollow structure at high temperatures and enabled us to control the oxidation state of Rh. The designed photocatalyst exhibited strong visible light absorption (up to 600 nm), and a very high surface area (up to 140 m$^2$ g$^{-1}$). As a result, the Sr/Rh-doped TiO$_2$ hollow photocatalysts demonstrated a photocatalytic efficiency (PE) of 0.242%, which was at least 8 times higher than that of commercial TiO$_2$ (0.03%) and 25 times higher than that of bulk Sr/Rh–TiO$_2$ (0.01%), in the photocatalytic decomposition of isopropanol under solar light irradiation.

Introduction

As a consequence of rapid global economic growth, environmental pollution by organic compounds has become one of the most critical issues for human society over the past four decades. Photocatalytic decomposition of organic species in air and water offers an efficient solution to solve this problem through the utilization of solar energy and high performance photocatalysts. Among the various photocatalysts developed to date, TiO$_2$-based photocatalysts continue to receive considerable attention because of their abundance, nontoxicity, and stability under photochemical conditions, which makes them highly suitable for scale-up in environmental remediation.

Currently, most TiO$_2$ photocatalysts are based on the anatase phase, which is generally the most active phase of TiO$_2$. Compared to the anatase phase, the rutile phase is often overlooked due to its relatively low specific surface area originating from its high temperature synthesis, and its poor light absorption. Nevertheless, it has been demonstrated that the rutile phase is a promising candidate for the degradation of organic pollutants because of its strong reduction potential and high O$_2$ adsorption capacity.$^3,4$

One of the biggest limitations of TiO$_2$ is its large bandgap (>3 eV), which makes it active only in the UV region, which accounts for less than 5% of the solar spectrum. There have been numerous attempts to overcome the poor light absorption of TiO$_2$ under sunlight by methods including the sensitization of TiO$_2$ with dyes or small bandgap semiconductors, doping, and coupling TiO$_2$ with plasmonic nanostructures.$^7$ Among them, doping TiO$_2$ with Rh has emerged as a viable technique for the enhancement of visible light absorption.$^8,12$ Both Rh$^{3+}$ and Rh$^{4+}$ introduce sub-bands into the forbidden band of TiO$_2$. Rh$^{3+}$ contributes a donor level to the valence band, thus reducing the band energy and shifting light absorption to the visible region, whereas Rh$^{4+}$ introduces an electron acceptor level below the conduction band, which serves as a recombination site, reducing the activity of the materials, as shown in Fig. SI 1.$^1,14,63$ Therefore, controlling the oxidation state of Rh in Rh-doped TiO$_2$ is critical to the photocatalytic enhancement of TiO$_2$.

Another approach to improve the performance of TiO$_2$ photocatalysts is through nanostructuring.$^{14}$ For example, photocatalysts based on hollow structures have attracted considerable attention because they improve the photoactivity of the catalyst by enhancing the separation of photogenerated charge carriers, shortening the charge diffusion length, and increasing the accessibility of active sites for reactants.$^{15}$ In addition, multiple reflections within the hollow cavity could improve the efficiency of light absorption, leading to the generation of additional electron–hole pairs.$^{16}$

It is reasonable that combining the aforementioned approaches (i.e., Rh doping and a hollow structure) would result in an efficient TiO$_2$-based photocatalyst with strong visible light absorption, good charge separation, and high surface active area. However, the design of such materials remains challenging because the introduction of Rh into the TiO$_2$ lattice requires high temperatures (>1000 °C), at which the hollow structure collapses because high surface energy induces...
sintering effects. Therefore, using a stabilizer to maintain the surface area is critical and so far has not been explored in the development of high performance photocatalysts.

Here, we report the first Rh-doped hollow-structured TiO₂ photocatalyst, which is highly active in the photocatalytic decomposition of organic pollutants under sunlight. We achieved this by introducing simultaneous rhodium and strontium. We found that Sr²⁺ is as a codoping agent which stabilized the hollow structure at high temperatures, and contribute to control the chemical state of Rh in doped material.¹⁶–¹⁸ The designed photocatalyst exhibited strong visible light absorption (up to 600 nm), and a very high surface area (up to 140 m² g⁻¹). As a result, the photocatalysis of the photocatalyst was at least 8 times higher than those of commercial TiO₂ and bulk Sr/Rh–TiO₂ powders in the decomposition of isopropanol under solar radiation.

Results and discussion

Traditional methods for the synthesis of Rh-doped TiO₂ photocatalysts mainly focus on improving the doping of Rh in the TiO₂ lattice to enhance the visible light response of TiO₂. However, high-temperature calcination requirements for the substitution of Rh for Ti⁴⁺ in the TiO₂ matrix results in a photocatalyst with a very low surface area, which increases the charge recombination and decreases the number of active sites. Also, Rh³⁺, which serves a critical role in the photocatalytic activity of Rh-doped TiO₂ under visible light irradiation, cannot be obtained by conventional methods. Therefore, Rh³⁺-doped TiO₂ materials with high surface areas are highly desired. Compared to traditional bulk Rh-doped TiO₂ photocatalysts, Sr/ Rh-codoped TiO₂ offer several advantages. First, they exhibit a high surface area, owing to the presence of nanoparticles on the hollow wall. Therefore, the reaction can proceed inside and outside of the hollow spheres. Second, the co-incorporation of Sr cations enabled us to control the oxidation state of Rh, which leads to a significant enhancement in the visible light absorption and charge separation. Third, the homogeneous distribution of dopants significantly lowers the doping temperature as compared to conventional synthetic routes.

Hollow Sr/Rh–TiO₂ was prepared via a multistep pathway (Scheme 1) comprised of the following steps: (i) the one-pot synthesis of carbon colloidal spheres@Sr,Rh (C@Sr,Rh); (ii) coating C@Sr,Rh with TiO₂ by controlling the hydrolysis of tetraethyl titanium butoxide to obtain core–shell carbon sphere@Sr,Rh–TiO₂ microspheres (C@Sr,Rh–TiO₂); (iii) two-step calcination at 550 °C for 5 h to obtain anatase Sr/Rh–TiO₂-500, followed by calcination at 900 °C for 10 h to form rutile Sr/Rh–TiO₂-900. The calcination steps are critical for the substitution of Sr/Rh ions for Ti⁴⁺ in the TiO₂ crystal lattice and for the formation of the hollow structure with high porosity.

Fig. 1 shows the scanning electron microscopy (SEM) images of C@Sr,Rh–TiO₂, hollow Sr/Rh–TiO₂-550, and hollow Sr/Rh–TiO₂-900. The size of the C@Sr,Rh–TiO₂ microspheres was in the range of 500 nm to 2 μm prior to the two-step calcination (Fig. 1A). After calcination at 550 °C, the hollow structure was

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**Scheme 1** Schematic illustration of the synthesis of hollow Sr/Rh-doped TiO₂ nanospheres: (1) one-pot synthesis of carbon colloidal spheres@Sr,Rh³⁺, (2) loading of TiO₂ from the titanium alkoxide precursor, and (3) calcination at 550 °C for 5 h followed by calcination at 900 °C for 10 h.

**Fig. 1** SEM images of (A) carbon colloidal spheres@Sr,Rh@TiO₂ and hollow Sr/Rh–TiO₂ after calcination at (B) 550 °C and (C) 900 °C.
Rh3+ cations, which resulted in a homogeneous distribution of these elements. Fig. 2A shows the Ti, O, Rh, and Sr contents of 2.0 and 2.3%, respectively, confirmed the successful synthesis of the hollow Rh/Sr-doped TiO2 structure.

The X-ray diffraction (XRD) pattern of hollow Sr/Rh–TiO2-900 (line a) and rutile TiO2 (line b) Fig. 3A indicate the presence of rutile TiO2 in the prepared photocatalysts, as neither SrTiO3 nor Rh were detected.21,22 The XRD peaks of hollow Sr/Rh–TiO2-900 were slightly shifted to lower angles as compared to non-doped rutile-TiO2, which could be due to the substitution of Rh3+ for Ti4+, as Rh3+ ions (0.805 Å) are larger than Ti4+ ions (0.74 Å).23 Because of the higher ionic radius of Sr2+ (1.12 Å) as compared to Ti4+ (0.61 Å), Sr2+ was unable to enter the TiO2 lattice. Hence, Sr2+ could be present on the TiO2 surface as Sr–O clusters.24,25

Fig. 3B shows the ultraviolet-visible (UV-vis) spectra of hollow Sr/Rh–TiO2-550, hollow Sr/Rh–TiO2-900, and bulk rutile TiO2-900. A remarkable enhancement in the light absorption along with a color alteration from white to yellow, as shown in Fig. 3B, was observed for hollow Sr/Rh–TiO2-900 and Rh3+–TiO2-900 compared to hollow Sr/Rh–TiO2-550, indicating the effect of calcination temperature on the light absorption properties of Rh-doped TiO2 materials. Higher calcination temperatures may favor the introduction of Rh to TiO2 crystallites forming Rh-doped TiO2 with a smaller bandgap. The UV-vis spectrum of Rh–TiO2-900 revealed a discontinuous level at ~420 nm, which could be attributed to electron excitation from the donor levels formed by Rh3+ to the conduction band of rutile TiO2.26 In addition, a significant absorption band around 580–750 nm appeared in the UV-vis spectrum of this sample, indicating the presence of an acceptor level formed by Rh4+ in the TiO2 structure. Thus, both Rh3+ and Rh4+ were present in the bulk Rh–TiO2-900 sample. Compared to bulk Rh–TiO2-900, hollow Sr/Rh–TiO2-900 (in the presence of Sr) exhibited a simple absorption profile with an onset at ~420 nm, and the disappearance of the absorption band at around 580–750 nm. This suggested that only Rh3+ was present in hollow Sr/Rh–TiO2-900.26,28 The presence of Rh4+ ions in the hollow Sr/Rh–TiO2 further confirm the important role of Sr2+ in this synthesis, as it not only prevented sintering induced by high temperature.

Fig. 3 (A) XRD pattern of the hollow Sr/Rh–TiO2 sample after calcination at 900 °C and that of rutile TiO2. (B) UV-vis spectra of the various hollow samples: Sr/Rh–TiO2-550 (black line), Sr/Rh–TiO2-900 (red line), and Rh–TiO2-900 (blue line).
annealing, but also maintained the Rh\(^{3+}\) chemical state in the Rh-doped material. Fig. S17† shows the plot of (ahe)\(^2\) versus photon energy for the bandgap calculation of the samples. The band gap of hollow Sr/Rh-TiO\(_2\)-900 was calculated to be 2.25 eV, which was significantly lower than that of the hollow sample calcined at 550 °C (3.37 eV). The increased band gap of hollow Sr/Rh-TiO\(_2\)-550 as compared to anatase TiO\(_2\) alone (3.2 eV) could be ascribed to the presence of Sr\(^{2+}\) on the TiO\(_2\) surface, which reduced the particle size.\(^{29}\)

To understand the surface composition and chemical states of the elements in the samples, X-ray photoelectron spectroscopy (XPS) was carried out for the hollow Sr,Rh-doped TiO\(_2\)-900 and Rh-doped TiO\(_2\)-900. The presence of Sr, Rh, Ti, and O in Sr/Rh-TiO\(_2\)-900 was confirmed by XPS, as depicted in Fig. 4A. As shown in Fig. S18,† for the Sr 3d XP spectrum, the deconvoluted peaks centered at 133.1 and 134.87 eV could be attributed to Sr 3d\(_{3/2}\) and Sr 3d\(_{5/2}\) of Sr\(^{2+}\)-modified TiO\(_2\) surface.\(^{29}\) Fig. 4B shows the deconvoluted peaks of Rh 3d XPS spectra in hollow Sr/Rh-TiO\(_2\)-900 (a) and Rh-TiO\(_2\)-900 (b). It should be noted that isolated observation of Rh\(^{3+}\) and Rh\(^{4+}\) is ambiguous by XPS analysis. However, it is essential to consider the shifting of their binding energies because it would help to evaluate the electron density of Rh atoms contributing to confirm the chemical states in each sample. For the Rh-TiO\(_2\)-900, the Rh 3d XPS spectrum shows two peaks centered at 309.3 eV and 314.2 eV, which could be attributed to 3d\(_{3/2}\) and 3d\(_{5/2}\) of Rh\(^{3+}\) and Rh\(^{4+}\) chemical states, respectively.\(^{31,32}\) Interestingly, these peaks were shifted −0.3 eV and appeared at 390.0 and 313.9 eV for the hollow Sr/Rh-TiO\(_2\)-900, which could be attributed to the higher electron density of Rh cations. In other words, the chemical states of Rh in the hollow Sr/Rh-TiO\(_2\)-900 is lower than that in Rh-TiO\(_2\)-900. This is associated with UV-vis analysis, which confirms mainly presence of Rh\(^{3+}\) chemical state in the hollow Sr/Rh-TiO\(_2\)-900. Fig. 4C shows the Ti 2p XPS spectra of the hollow Sr/Rh-TiO\(_2\)-900 (line a) and Rh-TiO\(_2\)-900 (line b). The Rh-TiO\(_2\)-900 exhibited two peaks at binding energies of 458.2 and 464.1 eV, which could be assigned to Ti 2p\(_{3/2}\) and Ti 2p\(_{1/2}\) of Ti\(^{4+}\) in the rutile phase.\(^{33}\) These peaks are −0.1 eV shifted compared to those of r-TiO\(_2\), suggesting the replacement of Ti\(^{4+}\) by both Rh\(^{3+}\) and Rh\(^{4+}\), which induced a higher electron density around Ti\(^{4+}\) atoms in hollow Sr/Rh-TiO\(_2\)-900 compared to that in Rh-TiO\(_2\)-900 which further confirm the replacement of Ti\(^{4+}\) by Rh\(^{3+}\) in the hollow Sr/Rh-TiO\(_2\)-900. These results, in combination with the data obtained from UV-vis, suggest that Rh is presented in the hollow Sr/Rh-TiO\(_2\)-900 primarily in the form of Rh\(^{3+}\). Fig. 4D presents the O 1s XP spectra of the hollow Sr/Rh-TiO\(_2\)-900 (line a) and Rh-TiO\(_2\)-900 (line b). Two peaks with binding energies of 529.3 and 530.1 eV were observed in the deconvoluted peaks of O 1s in Rh-TiO\(_2\)-900 (line b). The peak centered at 529.3 eV could be ascribed to the lattice oxygen in TiO\(_2\), while other one at 530.1 eV could be attributed to strongly bound Ti–OH. Using the O 1s of rutile-TiO\(_2\) alone as a reference (Table S1†), the O 1s peak (at 529.3 eV) of Rh-TiO\(_2\)-900 exhibited a negative shift in comparison to that of pristine rutile-TiO\(_2\) (at 529.6 eV), which originated from the introduction of partially filled Rh\(^{4+}\) states within the band gap.\(^{33}\) This may cause the downward shifting of Fermi level towards the valence band, which may decrease energy bands along with the reduction potential of photo-generated electrons and induce a negative impact on the photocatalytic activity.\(^{13,34,35}\) In contrast, a strong positive shift in O\(_{1s}\) peak was observed (at 529.9 eV) for hollow Sr/Rh-TiO\(_2\)-900 in comparison to rutile-TiO\(_2\) alone and Rh-TiO\(_2\)-900, for which the O\(_{1s}\) peaks were centered at 529.9 and 530.5 eV. The increased binding energy of O\(_{1s}\) in hollow Sr/Rh-TiO\(_2\)-900 could be assigned to the filling of Rh\(^{3+}\) states within the band gap, which caused the upward shifting of Fermi level towards the conduction band, which increase the energy bands along with the reduction potential of photo-generated electrons and has a positive impact on the photocatalytic activity.\(^{36,37}\) These differences could explain the disadvantages of Rh\(^{4+}\) and the critical role of Rh\(^{3+}\) in doped photocatalysts. Therefore, the introduction of Sr\(^{2+}\) to Rh-doped TiO\(_2\) favors the formation of Rh\(^{3+}\) in the doped TiO\(_2\). In the absence of Sr\(^{2+}\), Rh\(^{3+}\) oxidizes to Rh\(^{4+}\) to re-establish the charge balance, resulting in the formation of Rh\(^{4+}\)-doped TiO\(_2\). In contrast, the presence of Sr\(^{2+}\) which could function as the critical factor limiting this oxidation process and leading to the formation of Rh\(^{3+}\)-doped TiO\(_2\).

The photocatalytic activity of a catalyst is strongly dependent on the number of active sites on its surface. Thus, surface and porosity properties are the important parameters governing the performance of a photocatalyst because high specific surface area and large pore volume facilitate mass transfer and effectively promote the kinetics of the photocatalytic reaction. Therefore, the photocatalytic activity is significantly
enhanced.39,40 The specific surface areas of various samples were determined by N2 physical adsorption measurements at 77 K. As shown in Fig. S1A,† hollow Sr/Rh–TiO2-900 exhibits a high adsorption capacity in high relative pressure (P/P0; from 0.8 to 1), suggesting a large porous structure.40 The (Barrett–Joyner–Halenda) BJH pore size distribution obtained from the adsorption branch also reveals that the majority of pores are mainly from 2 to 10 nm, as depicted in Fig. S1B.† As shown in Table 1, the specific surface area of hollow Sr/Rh–TiO2-900 reached 140 m2 g−1, which was ~50 times higher than that of Rh–TiO2-900 (3 m2 g−1). Also, the specific surface area of hollow Sr/Rh–TiO2-900 was significantly higher than those of r-TiO2 (10 m2 g−1) and commercial anatase TiO2 (P25) (50 m2 g−1), and ~13 times that of bulk Sr/Rh–TiO2-900 (Table 1). To the best of our knowledge, this hollow Sr/Rh–TiO2-900 photocatalyst has one of the highest surface areas among doped rutile TiO2 materials reported to date.22,41,42 The above analyses afforded two important findings about the roles of Sr2+: (i) the presence of Sr2+ functioned as a stabilizer to maintain the hollow structure leading to a high surface area photocatalyst; (ii) the chemical oxidation state of Rh3+ could be controlled in the doped TiO2 with the co-presence of Sr2+, which limited the oxidation of Rh3+ to Rh4+. We believe that these two unique properties have a close relation in the resulted photocatalyst.

The photocatalytic activity of hollow Sr/Rh–TiO2-900 was evaluated in the photodecomposition of isopropanol in water. So far, the isopropanol photodegradation is used as a model reaction for photo-oxidation of organic compounds.44 Notably, Pt has been demonstrated to significantly improve the photocatalytic activity of TiO2-based photocatalysts.44 For free-Pt photocatalysts, only small amount of CO2 was evolved from the decomposition of isopropanol for the hollow Sr/Rh–TiO2-900 and no CO2 was detected for the rest of samples, as shown in Fig. S10.† This indicates the critical role of Pt particles as cocatalyst. Therefore, the evolution of CO2 from the decomposition of isopropanol under visible light (λ ≥ 420 nm) and solar light irradiation (see Experimental section) was monitored and compared with those observed using Sr/Rh–TiO2-B, Rh–TiO2-900 and r–TiO2 with the optimized amounts of Pt loading, which were found to be ~1% Pt for the hollow Sr/Rh–TiO2-900, ~0.3% for Sr/Rh–TiO2-B and r–TiO2 and ~0.1% for Rh–TiO2-900, respectively. As shown in Fig. 5A, the photocatalytic activity of hollow Sr/Rh–TiO2-900 was superior to those of Sr/Rh–TiO2-B and Rh–TiO2-900, as indicated by the higher CO2 generation.

The amount of CO2 produced over the hollow Sr/Rh–TiO2-900 under visible light was 27.5 μmol g−1 h−1, which was more than 23 times higher than that of Sr/Rh–TiO2-B (1.2 μmol g−1 h−1). Under similar reaction conditions, CO2 was not detected for the Rh–TiO2-900 and r–TiO2 samples, indicating their negligible photoactivities under visible light. As shown in Fig. 5B, hollow Sr/Rh–TiO2-900 also exhibited a higher photoactivity than bulk Sr/Rh–TiO2-B and r–TiO2 under simulated solar irradiation. The amount of CO2 evolved for hollow Sr/Rh–TiO2-900 was 146 μmol g−1 h−1, which was ~25 times higher than that of Sr/Rh–TiO2-900 (5.68 μmol g−1 h−1), whereas r–TiO2 and Rh–TiO2-900 showed very low photoactivities. Compared to hollow Sr/Rh–TiO2-550, hollow Sr/Rh–TiO2-900 exhibited ~2.5 times higher CO2 generation (Fig. S11†), despite the higher surface area of hollow Sr/Rh–TiO2-550 (see Table 1). Moreover, the amount of CO2 produced with the hollow Sr/Rh–TiO2-900 catalyst was 6.6 times higher than that of commercial TiO2 (P25). Therefore, the superior activity of hollow Sr/Rh–TiO2-900 could be attributed to the synergistic effect of doping Rh3+ into the TiO2 structure in the presence of Sr2+, which causes strong solar light absorption, and a hollow structure with a high surface area. These features significantly enhanced the generation of electron–hole pairs and improved the charge separation during photocatalysis.

The photocatalytic efficiency (PE) for the photocatalytic decomposition of isopropanol under solar irradiation was calculated using the following equation:

\[
PE = \frac{N_{\text{consumed photons for CO2}}}{N_{\text{incident photons}}} 
\]

Table 1 Physicochemical properties of various samples

<table>
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<th>Photocatalyst</th>
<th>TiO2 phase</th>
<th>Morphology</th>
<th>% dopants (Rh3+, Sr2+)</th>
<th>Band gap energy (eV)</th>
<th>Specific surface area (m2 g−1)</th>
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<td>Hollow spheres</td>
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Fig. 5 CO2 formation from the photodegradation of isopropanol of different types of photocatalysts with 1% Pt: (A) under visible light, (B) under solar simulator irradiation (AM 1.5 G, intensity 100 mW cm−2). (a) hollow Sr/Rh–TiO2-900; (b) bulk Sr/Rh–TiO2-B; (c) rutile TiO2; (d) Rh–TiO2-900. ND: not detected.
where $N_{\text{consumed}}$ is the number of photons consumed for CO$_2$ generation and $N_{\text{incident}}$ is the total number of incident photons of simulated solar light. The details of this calculation were described previously. The PE for CO$_2$ generation using hollow Sr/Rh–TiO$_2$-900 under simulated solar light was 0.242%, which is significantly higher than that using bulk Sr/Rh–TiO$_2$-900-B (~0.01%) and TiO$_2$ (P25, 0.03%), confirming the promising application for solar-driven photodecomposition of organic pollutants.

The stability of the hollow Sr/Rh–TiO$_2$-900 was also studied by performing multi-reusing experiments under the same conditions, as shown in Fig. SI 12.† No significant change in the production of CO$_2$ was observed after 5 cycles. Also, the morphology was retained after the fifth cycle indicating the stability of the hollow Sr/Rh–TiO$_2$-900, as shown in Fig. SI 13.†

It has been demonstrated that rutile-TiO$_2$ contains a large amount of adsorbed oxygen on its surface. Therefore, the photodecomposition of organic pollutants should be mainly directed toward the electron usage route, which produces strong oxidants (O$_2$\textsuperscript{-}) toward the electron usage route, which produces strong oxidants (O$_2$\textsuperscript{-}) directed toward the electron usage route, which produces strong oxidants (O$_2$\textsuperscript{-}) for CO$_2$ generation with Sr/Rh-doped TiO$_2$ is proposed in Fig. 6. Hollow Sr/Rh–TiO$_2$-900 exhibited high photoactivity, which could be due to the synergistic contribution of strong solar light absorption and high surface area. Therefore, our hollow material has significant potential for applications in water purification under natural solar illumination. Furthermore, this synthetic strategy can be extended to other hollow systems for a wide range of applications in catalysis and energy conversion. Work into gaining further insight into the mechanistic aspects of this process is in progress.

**Experimental section**

**Chemicals**

D-(+) Glucose, hexachloroplatinic acid hexahydrate, strontium chloride, rhodium(III)nitrato, and tetrabutyl titanate butoxide were purchased from Sigma-Aldrich. All reagents were used as received without further purification.

**Material syntheses**

**Synthesis of carbon colloidal spheres@Sr/Rh (C@Sr/Rh).** D-(+) Glucose (17 g) was first dissolved in deionized water (160 mL). SrCl$_2$ (3.2 g) and an aqueous solution of Rh(NO$_3$)$_3$ (2 g, 1 mg mL$^{-1}$) were then added to the obtained solution. The resulting mixture was heated in a Teflon-lined autoclave at 180 °C for 18 h. Subsequently, the solid product was collected by centrifugation at 6000 ppm for 10 min, and was washed several times with water and ethanol before being dried overnight at 80 °C.

**Synthesis of hollow Sr/Rh-doped TiO$_2$.** The obtained carbon colloidal spheres C@Sr/Rh were loaded with a titanium alkoxide precursor as follows: C@Sr/Rh (2 g) was dispersed in anhydrous ethanol (30 mL) and then stirred for 1 h, followed by sonication for 15 min to ensure good dispersion. A solution of tetraethyl titanate butoxide in ethanol (15 mL, 50 mg mL$^{-1}$) was then added dropwise to the above solution with stirring for 1 h. Subsequently, a solution of water in ethanol (3.5 mg mL$^{-1}$ water) was slowly added dropwise to the above solution to accelerate the hydrolysis of the titanium precursor. After stirring for 6 h, the resulting material was recovered by centrifugation, washed with anhydrous ethanol, and dried overnight at 80 °C in a vacuum oven to yield carbon colloidal spheres@Sr/Rh–TiO$_2$ (C@Sr/Rh–TiO$_2$). The as-prepared C@Sr/Rh–TiO$_2$ was loaded in an aluminum crucible and subjected to two-step calcination at different temperatures. The first step was carried out at 550 °C for 5 h (heating rate of 1 °C min$^{-1}$) to obtain anatase TiO$_2$ (denoted as hollow Rh/Sr–TiO$_2$-550). The second step was carried out at 900 °C for 10 h (heating rate of 3 °C min$^{-1}$) to achieve the rutile phase (denoted as hollow Sr/Rh–TiO$_2$-900).

**Synthesis of Rh-doped TiO$_2$-900 and TiO$_2$-900.** Rh-doped TiO$_2$-900 (denoted as Rh–TiO$_2$-900) and TiO$_2$-900 were synthesized using the same procedure as described above except that only Rh$^{III}$ was added to the mixture of colloidal spheres for the Rh–TiO$_2$-900 and neither Sr$^{II}$ or Rh$^{III}$ was used for undoped TiO$_2$-900 samples.

**Synthesis of bulk Sr/Rh–TiO$_2$-900.** Bulk Sr/Rh-doped TiO$_2$-900 (Sr/Rh–TiO$_2$-900-B) was prepared via a solid-state reaction for comparison. The starting materials (SrCl$_2$, Rh(NO$_3$)$_3$, and TiO$_2$) were mixed in the same atomic ratio as for hollow Sr/Rh–TiO$_2$-900. The mixture was calcined at 1000 °C for 10 h.
Characterization
Transmission electron microscopy (TEM) images of the samples were obtained using a JOEL JEM 1230 operated at 120 kV. Scanning electron microscopy (SEM) images were obtained using a JEOL 6360 operated at 15 kV. Powder X-ray diffraction (XRD) patterns of the samples were obtained using a Bruker SMART APEXII X-ray diffractometer equipped with a Cu Kα radiation source ($\lambda = 1.5418$ Å). X-ray photoelectron spectroscopy (XPS) measurements were carried out on the samples in the ion-pumped chamber (evacuated to $10^{-9}$ Torr) of a photoelectron spectrometer (Kratos Axis-Ultra) equipped with a focused X-ray source (Al Kα, $hv = 1486.6$ eV). UV-vis spectra were recorded on a Cary 300 Bio UV-visible spectrophotometer. N$_2$ adsorption–desorption isotherms of the samples were obtained at 77 K using a Quantachrome Autosorb-1 MP analyzer. Prior to the measurements, the samples were outgassed under vacuum for 6 h at 150 °C.

Photocatalytic tests
The photocatalytic decomposition of isopropanol was carried out in a top-irradiated reactor at ambient temperature and pressure. Prior to the photocatalytic tests, Pt was photodeposited on the catalyst. In a typical photocatalytic experiment, 20 mg of the photocatalyst, the optimum amount of photocatalyst for this photocatalytic reactor system, was dispersed in a 200 ppm solution of isopropanol in water. The reaction cell was then filled with fresh synthetic air (Prax air), stirred for 1 h to get steady-state regime prior to be illuminated with a solar simulator 150 W Xe lamp (AM 1.5 G, 100 mW cm$^{-2}$) for 3 h. To evaluate the photocatalytic activity of the samples under visible light, a UV cut-off filter ($\lambda \geq 420$ nm) was used to produce visible light from the solar simulator. The amount of CO$_2$ gas generated during the reaction was analyzed using a gas chromatograph (Agilent 7820A) equipped with a thermal conductivity detector (TCD) and HP-PLOT U column, using helium as the carrier gas.

Photocatalytic efficiency (PE) calculations
Photocatalytic efficiency can be measured by the ratio of the number of product formed to the number of incident photons on the system and in a wavelength range $\lambda_1$-$\lambda_2$. Under full solar irradiation, the number of incident photons calculated by integrating the intensity at each wavelength was $2.75 \times 10^{17}$ photon per s per cm$^2$. A 4.5 cm$^2$ area of the sample was irradiated for 3 h. Therefore, the number of incident photons was calculated as follows:

$$N_{\text{incident}} \text{photons} = (2.75 \times 10^{17}) \times 3 \times 4.5 \times 3600 = 1.31 \times 10^{22} \text{photons} \tag{2}$$

For CO$_2$ generation, assuming that the conversion of isopropanol (C$_3$H$_6$O) to CO$_2$ takes place on hollow Sr/Rh–TiO$_2$-900 according to the following equation, (six photons are required to produce one CO$_2$ molecule):

$$\text{C}_3\text{H}_6\text{O} + 9\text{O}_2 + 18\text{H}^+ + 18\text{e}^- \rightarrow 3\text{CO}_2 + 13\text{H}_2\text{O} (2\text{e}^- + \text{O}_2 + 2\text{H}^+ \rightarrow \text{H}_2\text{O}_2; \text{C}_3\text{H}_6\text{O} + 9\text{H}_2\text{O}_2 \rightarrow 3\text{CO}_2 + 13\text{H}_2\text{O}); \text{2H}_2\text{O} + 4\text{H}^+ \rightarrow \text{O}_2 + 4\text{H}^+$$

The amount of CO$_2$ generated under simulated solar light was determined to be 8.8 μmol. Therefore, the number of photons consumed to produce CO$_2$ under solar light illumination over 3 h was calculated as follows:

$$N_{\text{consumed}} \text{photons for CO}_2 = 6 \times (8.8 \times 10^{-6}) \times (6.023 \times 10^{23}) = 3.18 \times 10^{19} \tag{3}$$

$$\text{PE} = \frac{N_{\text{consumed}} \text{photons for CO}_2}{N_{\text{incident}} \text{photons}} = \frac{(3.18 \times 10^{19}/1.31 \times 10^{22}) \times 100}{100} = 0.242\% \tag{4}$$

The same procedure was used to determine the PE of commercial TiO$_2$ (P25) and Sr/Rh–TiO$_2$-900-B.

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Notes and references