Template-free solvothermal synthesis of \( \text{WO}_3/\text{WO}_3\cdot \text{H}_2\text{O} \) hollow spheres and their enhanced photocatalytic activity from the mixture phase effect

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Inorganic materials with hollow spherical structures have attracted much research attention due to their specific void interior and consequently unique physical/chemical properties for various applications, such as active-material encapsulation, drug delivery, micro-reactors, filters, piezoelectric transducers, low dielectric constant substrates and so on. Many research efforts have been devoted to the development of synthesis approaches for hollow spherical materials, including both template and template-free processes. In recent years, a template-free process based on Ostwald ripening has been proven to be an effective approach for the creation of hollow spherical inorganic materials without the potential contamination with templates, and a series of hollow spherical inorganic materials has been successfully synthesized through this process, such as \( \text{TiO}_2 \), \( \text{Cu}_2\text{O} \), \( \text{Co}_3\text{O}_4 \), \( \text{ZnS} \), \( \text{MnO}_2 \), \( \text{SnO}_2 \), \( \text{Fe}_2\text{O}_4 \), \( \text{VO}_2 \), \( \text{BaZrO}_3 \), and so on.

As \( n \)-type semiconductors, tungsten oxide (\( \text{WO}_3 \)) and tungsten oxide hydrates (\( \text{WO}_3\cdot n\text{H}_2\text{O} \)) have attracted considerable attention for their applications in gas sensors, electrochromic devices, optical recording devices, and as visible light-responsive photocatalysts. \( \text{WO}_3\cdot n\text{H}_2\text{O} \) is usually synthesized through the liquid-phase synthesis routes, and \( \text{WO}_3 \) is synthesized by annealing the \( \text{WO}_3\cdot n\text{H}_2\text{O} \) to remove crystal water. To create \( \text{WO}_3 \) hollow spheres, \( \text{WO}_3\cdot n\text{H}_2\text{O} \) hollow spheres were synthesized by both the template process with various sacrificial templates and the template-free process via Ostwald ripening. However, at present, the reported approaches to synthesize \( \text{WO}_3\cdot n\text{H}_2\text{O} \) hollow spheres using the template-free process are still quite limited in the literature, although previous reports have demonstrated that various tungsten precursors and specific synthesis conditions could produce products with different morphologies and crystal structures. Hollow spheres as photocatalysts are beneficial to the photocatalytic performance because the multiple reflections (scattering) from their specific hollow structure can result in better light harvesting and the subsequent generation of more photoelectron-hole pairs.

Thus, the synthesis of \( \text{WO}_3\cdot n\text{H}_2\text{O} \) hollow spheres via the template-free Ostwald ripening mechanism should be further investigated. Recently, we developed a template-free process which successfully synthesized well-dispersed hollow \( \text{TiO}_2 \) spheres via Ostwald ripening, in which the use of a \( \text{PrOH}\cdot \text{H}_2\text{O} \) mixture solvent was critical in the creation of \( \text{TiO}_2 \) hollow spheres with uniform size and
good dispersity. It would be of interest to examine if the PrOH–H₂O mixture solvent could be applicable to the synthesis of well-defined WO₃·nH₂O hollow spheres.

For semiconductor photocatalysts, the electron–hole pair recombination problem could cause the loss of a large portion of photogenerated electron–hole pairs, thus reducing their photocatalytic efficiency. Besides noble metal deposition and semiconductor coupling, the formation of photocatalysts with mixture phases has also been reported to be beneficial to the separation of electron–hole pairs if these mixture phases have matched band structures. For example, enhanced photocatalytic performance has been demonstrated in TiO₂ photocatalysts with mixture phases, including anatase/rutile, anatase/brookite, and rutile/brookite. Recently, In₂O₃/In₂O₃·3H₂O mixture phases have also been reported. However, no report is available on the creation of WO₃-based hollow spheres with mixture phases, although the synthesis of WO₃ hollow spheres by the dehydration of WO₃·H₂O hollow spheres could offer the possibility of creating hollow spheres with mixture phases of pure WO₃ and WO₃ with certain amounts of crystal water.

Herein, well-defined WO₃·H₂O hollow spheres composed of nanoflakes were successfully synthesized by a solvothermal process with i-PrOH–H₂O mixture solvent. The hollowing process was investigated, the results of which demonstrated clearly that their formation followed the Ostwald ripening mechanism. Hollow spheres with WO₃ (major) and WO₃·H₂O (minor) mixture phases created by calcination with appropriate temperature demonstrated a largely enhanced photocatalytic activity for RhB degradation under visible light irradiation compared with either pure WO₃·H₂O hollow spheres or pure WO₃ hollow spheres. The WO₃·H₂O and WO₃ phases had matched band structures. Thus, an effective charge carrier separation can occur between the WO₃ phase and the WO₃·H₂O phase under visible light irradiation, contributing to their largely enhanced photocatalytic performance.

**Experimental**

**Chemicals and materials**

Sodium tungstate dehydrate (Na₂WO₄·2H₂O, 99.5%), oxalic acid (H₂C₂O₄·2H₂O, 99.8%), hydrochloric acid (HCl, 36%), and isopropyl alcohol (i-PrOH, 99.7%) were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, P.R. China). Deionized (DI) water was prepared using a lab ultra-pure water purifier. Rhodamine B (RhB, AR) was purchased from Shenyang No. 3 Chemical Reagent Factory (Shenyang, P.R. China).

**Template-free synthesis of WO₃·H₂O hollow spheres and their dehydration**

WO₃·H₂O hollow spheres were synthesized through a solvothermal process. Under vigorous stirring, 0.5 mmol Na₂WO₄·2H₂O and 1 mmol H₂C₂O₄·2H₂O were added to 30 mL of DI water. After they were dissolved completely, 36 mL of i-PrOH and 2 mL of HCl were added to this aqueous solution in sequence to change the solvent from pure water to an i-PrOH–H₂O mixture. The solution was then transferred to a Teflon-lined autoclave with a capacity of 90 mL which was then sealed, kept in an oven at 80 °C for 12 h, and then air cooled to room temperature. To obtain samples at various solvothermal reaction times, the autoclave was kept at 80 °C for a desired time and then water-cooled to better preserve the morphology and structure of these samples. The obtained precipitate was centrifuged, washed with water and ethanol several times, and then dried at 70 °C to obtain WO₃·H₂O hollow spheres. WO₃·H₂O hollow spheres were further calcinated at the desired temperatures (200 °C, 350 °C, and 500 °C) for 2 h in a muffle furnace with a heating rate of 2 °C min⁻¹.

**Characterization of hollow spheres**

SEM images were obtained using a Leo-Supra-55 scanning electron microscope (Carl Zeiss, Oberkochen, Germany). TEM images and SAED patterns were taken using a JEOL-2100 transmission electron microscope (JEOL, Tokyo, Japan). XRD analysis was conducted using a D/Max-2004 X-ray powder diffractometer (Rigaku, Tokyo, Japan) with Ni-filtered Cu Kα radiation (0.15418 nm) at 56 kV and 182 mA. TG-DSC curves were measured using a STA 449 Jupiter simultaneous thermal analyzer (Netzsch, Selb, Germany) from room temperature to 550 °C with a heating rate of 10 °C min⁻¹. The Brunauer–Emmett–Teller (BET) data were measured by nitrogen adsorption–desorption isotherms using Autosorb-1 surface area and pore size analyzers (Quantachrome, Boynton Beach, USA). The total pore volume and the average pore size were calculated using the Barrett–Joyner–Halenda (BJH) model. The optical absorbance was determined from the diffuse reflectance spectra (DRS) measurements with a UV-2550 UV-vis spectrophotometer (Shimadzu, Kyoto, Japan) using BaSO₄ as the reference.

**Photocatalytic degradation of Rhodamine B under visible light irradiation**

The photocatalytic performance of both uncalcined and calcined samples was evaluated by examining their photocatalytic degradation of RhB under visible light irradiation. 50 mg of the photocatalyst was added to 50 mL of RhB solution (20 mg L⁻¹) in a 250 mL glass reactor with a quartz top cover. The solution was stirred for 30 min in the dark and then exposed to visible light irradiation. The light source was a 300 W Xe arc lamp (PLS-SXE300, Beijing Trusttech Co. Ltd) with a UV cutoff filter (λ > 400 nm). The light intensity was ~100 mW cm⁻². 2 mL of the solution was sampled at each time and the concentration of RhB was determined using a UV-vis spectrophotometer (UV-2550, Shimadzu, Kyoto, Japan).

**Results and discussion**

The structure and morphology of WO₃·H₂O hollow spheres

Fig. 1 shows the XRD pattern of the samples synthesized by a solvothermal process at 80 °C for 12 h in an i-PrOH–H₂O
mixture solvent. All of the diffraction peaks could be indexed as the orthorhombic structure of the WO₃·H₂O phase (JCPDS no. 84-0886, space group: Pmn nb (62), RIR: 12.81), suggesting that the synthesis process we developed could produce a single-phase WO₃·H₂O product. Fig. 2 shows the SEM images, TEM images and corresponding SAED patterns of these WO₃·H₂O hollow spheres. It could be observed from the lower magnification SEM image in Fig. 2a that well-defined WO₃·H₂O hollow spheres were successfully created using our approach. Their sizes are highly uniform with an outer diameter of approximately 2 μm. Fig. 2b shows the higher magnification SEM image of a single hollow sphere enlarged from the center area in Fig. 2a. From its broken shell, the hollow interiors of these spheres could be clearly identified. The shell thickness is ca. 200 nm, and the shell is composed of nanoflakes having a side length ranging from tens to hundreds of nanometers and a thickness ranging from several to tens of nanometers. Furthermore, nanoflakes of a smaller size are located at the inner area (marked as A) of the shell, while nanoflakes of a larger size are located at the outer area (as B marked) of the shell. This observation indicates a typical Ostwald ripening process, in which smaller crystallites dissolve and are transferred to the outer part for the growth of larger crystallites located at the outer part. Fig. 2c shows the TEM image of a single WO₃·H₂O hollow sphere; its hollow nature could be easily identified from the contrast difference. It could also be observed that these nanoflakes were grown crosswise and large interstices exist between them, resulting in good permeability of the shells. The permeable nature of the shells could allow easy access of water, other molecules, and part of the incident photons to the shells and the interior voids. Thus, photocatalytic reactions could happen either at the outer/inner surfaces or the shells of these hollow spheres. Fig. 2d shows the corresponding SAED pattern which indicates that these hollow spheres have a polycrystalline orthorhombic WO₃·H₂O phase. Fig. 2e shows the TEM image of a single nanoflake, which has a nearly square shape, approximately 280 × 200 nm² in size. Its corresponding SAED pattern (Fig. 2f) suggests that these nanoflakes are single-crystalline. The diffraction spots could be indexed as (002) and (200) with the electron beam parallel to the [020] direction. The SAED patterns are in accordance with the XRD analysis result.

![Fig. 1 XRD pattern of the as-prepared WO₃·H₂O hollow spheres.](image1)

![Fig. 2 SEM images of the as-prepared WO₃·H₂O hollow spheres at (a) a lower magnification and (b) a higher magnification. (c) The TEM image of a single WO₃·H₂O hollow sphere. (d) The corresponding SAED pattern of the single WO₃·H₂O hollow sphere in (c). (e) The TEM image of a single nanoflake. (f) The corresponding SAED pattern of the single nanoflake in (e).](image2)
The formation process and mechanism of WO$_3$·H$_2$O hollow spheres

To investigate the formation process and mechanism of these hollow WO$_3$·H$_2$O spheres, time-dependent experiments were conducted at 80 °C for different reaction times. Water cooling was adopted to stop the reaction immediately at the desired time to better preserve the morphology and structure of these samples. Fig. 3a–d show the TEM images of the time-dependent samples obtained at reaction times of 90, 120, 150, and 180 min, respectively. Fig. 3 demonstrates that the hollow spheres evolved from the hollowing of solid spheres. Small voids firstly formed at the center of the solid spheres, gradually enlarging to finally form hollow interiors. Fig. 4 shows the XRD patterns of these time-dependent samples. Different from the pure WO$_3$·H$_2$O phase of the sample obtained after 12 h of reaction (Fig. 1), these time-dependent samples (reaction time up to 6 h) were all composed of both the WO$_3$·H$_2$O phase (JCPDS no. 84-0886) and the WO$_3$·2H$_2$O phase (JCPDS no. 18-1420), wherein the WO$_3$·H$_2$O phase was the major one. As the reaction time increased from 30 min to 360 min, the diffraction peak strength of the samples increased, indicating the enhanced crystallinity. Meanwhile, for each sample, the relative diffraction peak strength of the WO$_3$·2H$_2$O phase became weaker and weaker compared with that of the WO$_3$·H$_2$O phase, indicating a phase transition from WO$_3$·2H$_2$O to WO$_3$·H$_2$O with increasing reaction time. After 6 h of reaction, only a very small fraction of WO$_3$·2H$_2$O remained. After 12 h of reaction, the sample had a pure WO$_3$·H$_2$O phase.

Thus, the synthesis of WO$_3$·H$_2$O hollow spheres followed the Ostwald ripening mechanism. In this process, H$_2$C$_2$O$_4$ and WO$_4^{2−}$ firstly formed the complex ion [WO$_2$(C$_2$O$_4$)$_2$]$^{2−}$ following eqn (1):

$$\text{WO}_4^{2−} + 2\text{H}_2\text{C}_2\text{O}_4 \rightarrow [\text{WO}_2(\text{C}_2\text{O}_4)_2]^{2−} + 2\text{H}_2\text{O} \quad (1)$$

It is rather stable and wouldn’t react with HCl at room temperature. This step is critical to the creation of the hollow spherical structure. When no H$_2$C$_2$O$_4$ is present, precipitates will form immediately when HCl is added to the sodium tungstate solution; the final product after solvothermal treatment is composed of irregularly shaped micrometer-sized crystals.

At elevated temperature under solvothermal conditions, [WO$_2$(C$_2$O$_4$)$_2$]$^{2−}$ reacts with HCl to form precipitates of both WO$_3$·2H$_2$O and WO$_3$·H$_2$O at a much slower hydrolysis rate following eqn (2) and (3), respectively:

$$[\text{WO}_2(\text{C}_2\text{O}_4)_2]^{2−} + 2\text{H}^+ + 3\text{H}_2\text{O} \rightarrow \text{WO}_3\cdot2\text{H}_2\text{O} + 2\text{H}_2\text{C}_2\text{O}_4 \quad (2)$$

$$[\text{WO}_2(\text{C}_2\text{O}_4)_2]^{2−} + 2\text{H}^+ + 2\text{H}_2\text{O} \rightarrow \text{WO}_3\cdot\text{H}_2\text{O} + 2\text{H}_2\text{C}_2\text{O}_4 \quad (3)$$

These primary crystallites first aggregate into solid spheres as demonstrated in Fig. 3a. Then, these solid spheres undergo Ostwald ripening to finally form the hollow spherical structure. In addition, the phase transition from WO$_3$·2H$_2$O to WO$_3$·H$_2$O occur following eqn (4):

$$\text{WO}_3\cdot2\text{H}_2\text{O} \rightarrow \text{WO}_3\cdot\text{H}_2\text{O} + \text{H}_2\text{O} \quad (4)$$

Thus, the amount of WO$_3$·2H$_2$O gradually decreased as the reaction time increased, finally disappearing after 12 h of reaction due to this dehydration reaction.

In this approach, another critical factor in the formation of well-defined hollow WO$_3$·H$_2$O spheres is the use of i-PrOH–H$_2$O mixture solvent. When only water was used as the solvent, the obtained product was composed of both individual nanoflakes and hollow spherical aggregates of

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Fig. 3 TEM images of the time-dependent samples synthesized at 80 °C for (a) 90 min, (b) 120 min, (c) 150 min, and (d) 180 min.

Fig. 4 XRD patterns of the time-dependent samples synthesized at 80 °C for 30 min, 90 min, 180 min, and 360 min.
nanoflakes with different sizes and shapes (see Fig. S1 in the ESI†). As we found for n-PrOH in the creation of well-dispersed hollow TiO₂ spheres in our previous work,²² the introduction of i-PrOH to H₂O could reduce the hydrolysis rate of the tungsten precursor, which is beneficial to the aggregation of primary crystallites into well-defined solid spheres.

The creation of hollow spheres with WO₃·H₂O and WO₃ mixture phases

Thermal analysis was conducted on the WO₃·H₂O hollow sphere sample by measuring its TG and DSC curves as demonstrated in Fig. 5a. The sample was heated from room temperature to 550 °C at a heating rate of 10 °C min⁻¹ and then cooled to room temperature. From room temperature to ~170 °C, the TG curve showed a slight decrease of ca. 0.7% and a broad weak endothermic peak appeared on the corresponding DSC curve. This part of mass loss mainly resulted from the evaporation of surface-adsorbed water. From ~170 °C to ~280 °C, the TG curve had a large decrease of ca. 6.7%, and a large endothermic peak appeared on the corresponding DSC curve with the peak position at ~218 °C. From ~280 °C to ~500 °C, the TG curve had a slight decrease of ca. 0.3%, and the DSC curve showed a continuous endothermic process. Thus, the sum of these two parts of mass loss of ca. 7% resulted from the phase transition from WO₃·H₂O to WO₃. The theoretical mass loss in the process is 7.2%, very close to the experimental data. Thermal analysis suggested that the phase transition from WO₃·H₂O to WO₃ began at ~170 °C and mostly finished at ~280 °C. With further temperature increase, the residual crystal water was removed and the crystallinity of WO₃ enhanced.

From the thermal analysis result, three temperatures of 200, 350 and 500 °C were chosen for the calcination of the as-prepared WO₃·H₂O hollow spheres to create final products with different phases. Fig. 5b shows the XRD patterns of these three samples calcined at different temperatures. The as-prepared WO₃·H₂O hollow spheres had a pure orthorhombic WO₃·H₂O phase. After calcination at 500 °C for 2 h, the sample completely transformed to the well-crystallized, pure WO₃ phase (JCPDS no. 43-1035, space group: P₂₁/n (14), RIR: 5.04) with three distinct strong diffraction peaks of (002), (020), and (200). The sample calcined at 350 °C also only had a pure WO₃ phase; however the intensity of its diffraction peaks was weaker. In the XRD pattern of the sample calcined at 200 °C, however, two sets of diffraction peaks could be identified. Besides the major phase of WO₃, the (111) and (020) diffraction peaks of WO₃·H₂O could also be observed, suggesting that it was composed of a mixture of WO₃ and WO₃·H₂O. The
WO$_3$/WO$_3$·H$_2$O weight ratio ($\omega_1$/\omega$_2$) of the sample calcined at 200 °C could be estimated by the reference intensity method using eqn (5):

$$I_1 = \frac{RIR_1 \omega_1}{I_2 = \frac{RIR_2 \omega_2}{}$$ (5)

where $I_1$ and $I_2$ are the intensities of the WO$_3$ (200) and WO$_3$·H$_2$O (111) peaks, respectively, measured from the XRD pattern. RIR$_1$ and RIR$_2$ are the reference intensities of the WO$_3$ and WO$_3$·H$_2$O phases compared to the $\alpha$-Al$_2$O$_3$ standard, respectively, taken from the JCPDS cards. The boundary condition is that the sum of $\omega_1$ and $\omega_2$ is 1. From the XRD data, it could be roughly estimated that $\omega_1/\omega_2$ is ~0.91/0.09. Thus, the chosen calcination temperature of 200 °C based on the thermal analysis result created the final product with the WO$_3$–WO$_3$·H$_2$O mixture phases.

Fig. 5c shows the SEM image of the sample calcined at 200 °C; the SEM images of samples calcined at 350 °C and 500 °C could be found in Fig. S2 in the ESL†. After calcination, all samples kept their hollow sphere morphology, which indicates that the mechanical strength of these hollow spheres was pretty good during the calcination to sustain their structure. Similar observations have been reported for WO$_3$·nH$_2$O hollow structures$^{17,18,21}$ and TiO$_2$ hollow structures$^{22,23}$ in which the hollow structures were well-maintained during the calcination process.

Table 1 summarizes the BET specific surface area, pore volume, and pore size data for these samples. The sample calcinated at 200 °C had BET specific surface area, pore volume, and pore size very close to those of the as-prepared WO$_3$·H$_2$O hollow spheres. When the calcination temperature increased to 350 °C and 500 °C, the obtained samples’ BET specific surface area decreased by ~20% and ~58%, respectively, and their pore volume and pore size also decreased. These results were in accordance with the XRD and DSC analysis results. With a higher calcination temperature, the sample’s crystallinity increases, resulting in a lower BET specific surface area and a smaller pore size/volume. Similar results have been reported for the calcination of WO$_3$·H$_2$O hollow spheres.$^{18}$

### Optical properties of hollow sphere samples

The optical absorbance of these samples was investigated by UV-vis diffuse reflectance spectroscopy (DRS) measurement, as shown in Fig. 6a. From the reflectance data, optical absorbance could be approximated by the Kubelka–Munk function given by eqn (6):

$$F(R) = \frac{(1-R)^2}{2R}$$ (6)

where $R$ is the diffuse reflectance.$^{39}$ The as-prepared WO$_3$·H$_2$O hollow spheres had an absorption edge at ~525 nm, indicating a good visible light absorption capability. After calcination, the absorption stopping edges of all samples blue-shifted. Samples calcined at 350 °C and 500 °C had very close light absorption curves with a stopping edge at ~455 nm, while the sample calcined at 200 °C had better visible light absorption with a stopping edge at ~510 nm. The samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Specific surface area (m$^2$ g$^{-1}$)</th>
<th>Total pore volume (cm$^3$ g$^{-1}$)</th>
<th>Average pore size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>WO$_3$·H$_2$O</td>
<td>22.0</td>
<td>0.077</td>
<td>15.4</td>
</tr>
<tr>
<td>200 °C</td>
<td>22.2</td>
<td>0.079</td>
<td>14.2</td>
</tr>
<tr>
<td>350 °C</td>
<td>17.6</td>
<td>0.062</td>
<td>13.8</td>
</tr>
<tr>
<td>500 °C</td>
<td>9.3</td>
<td>0.022</td>
<td>9.6</td>
</tr>
</tbody>
</table>

Fig. 6 (a) Optical absorbance curves of the as-prepared WO$_3$·H$_2$O hollow spheres and samples calcinated at 200 °C, 350 °C, and 500 °C. (b) Tauc plots of the as-prepared WO$_3$·H$_2$O spheres and the sample calcinated at 500 °C (pure WO$_3$ phase) constructed from (a).
calcined at 350 °C and 500 °C were composed of a pure WO₃ phase, therefore they had almost identical light absorption curves. The sample calcinated at 200 °C, however, was composed of a mixture of both WO₃ (major) and WO₃·H₂O (minor) phases. Thus, its light absorption curve was between those of WO₃ and WO₃·H₂O and closer to that of WO₃.

For semiconductors, the optical absorption near the band edge follows eqn (7):\(^{39}\)

\[
\alpha h\nu = A(h\nu - E_g)^n
\]

where \(\alpha\), \(h\nu\), \(A\), and \(E_g\) are the absorption coefficient, light frequency, proportionality constant, and band gap, respectively, and \(n\) is equal to either 0.5 for allowed direct transition or 2 for allowed indirect transition. The optical band gap of tungsten oxide (hydrate) is between the oxygen 2p orbitals and the tungsten 5d orbitals, which are indirect band transitions.\(^{40,41}\) Hence the value of \(n\) was determined to be 2. Fig. 6b shows the Tauc plots ((\(\alpha h\nu\))\(^{1/2}\) vs. \(h\nu\)) of the as-prepared WO₃·H₂O hollow spheres and the sample calcinated at 500 °C (pure WO₃ phase) constructed from Fig. 6a, demonstrating the linear Tauc region just above the optical absorption edge to determine the semiconductor band gap. Extrapolation of this line to the photon energy axis yields the semiconductor band gap. Thus, the \(E_g\) of WO₃·H₂O was determined to be ~2.35 eV, and the \(E_g\) of WO₃ was determined to be ~2.72 eV.

**Photocatalytic degradation of RhB under visible light irradiation by hollow sphere samples**

The photocatalytic activities of these hollow sphere samples were demonstrated by their degradation effect on RhB under visible light irradiation, as shown in Fig. 7. A control experiment with only visible light irradiation was also conducted, and no RhB concentration change was observed, suggesting that visible light irradiation itself could not degrade RhB (not shown in Fig. 7). Before the photocatalytic degradation experiment, all samples were mixed with the RhB solution in the dark to reach the adsorption–desorption equilibrium. It was found that 0.5 h was enough for the adsorption–desorption equilibrium to be established in these samples. For example, the adsorption kinetic curve of the sample calcinated at 200 °C shown in Fig. 7 demonstrated that the residual RhB concentration reached a plateau after 0.5 h of adsorption. Dark adsorption could remove ~18%, ~18%, ~13%, and ~8% RhB from the RhB solution for the as-prepared WO₃·H₂O hollow spheres and samples calcinated at 200 °C, 350 °C, and 500 °C, respectively. The difference observed may be attributed to their BET specific surface area differences. Under visible light irradiation, all samples demonstrated photocatalytic RhB degradation activities, which could be attributed to their visible light absorption as demonstrated in Fig. 6a. After 5 h of visible light irradiation, ~24%, ~60%, ~23%, and ~22% RhB in the RhB solution was further removed by photocatalytic degradation using the as-prepared WO₃·H₂O hollow spheres and the samples calcinated at 200 °C, 350 °C, and 500 °C, respectively. Thus, the sample calcinated at 200 °C demonstrated the best photocatalytic RhB degradation effect under visible light irradiation among the four hollow sphere samples.

The slope of the RhB degradation curves in Fig. 7 represents the RhB degradation rate at certain treatment times. The photocatalytic activity enhancement could be further demonstrated quantitatively by the initial RhB degradation rates over different photocatalysts. The initial RhB degradation rates were determined to be ~1.2, ~4.4, ~1.8, and ~1.4 mg (g h)\(^{-1}\) for the as-prepared WO₃·H₂O hollow spheres and the samples calcinated at 200 °C, 350 °C, and 500 °C, respectively. The initial photocatalytic RhB degradation rate by the sample calcinated at 200 °C was ~3.7, ~2.4, and ~3.1 times greater than those by the as-prepared WO₃·H₂O hollow spheres and the samples calcinated at 350 °C and 500 °C, respectively, clearly demonstrating its largely enhanced photocatalytic activity under visible light irradiation.

**Photocatalytic enhancement mechanism of the WO₃/WO₃·H₂O sample**

Although the visible light absorption of the as-prepared WO₃·H₂O hollow spheres was stronger than that of the sample calcinated at 200 °C and their BET specific surface areas were very close, its photocatalytic RhB degradation performance under visible light illumination was much worse than that of the sample calcinated at 200 °C. The pure WO₃ hollow spheres (samples calcinated at 350 °C and 500 °C) had much better crystallinity than the sample calcinated at 200 °C. However, their initial photocatalytic RhB degradation rates were just ~41% and ~32% compared to that of the sample calcinated at 200 °C, while their BET specific surface areas were ~79% and ~42% compared to that of the sample calcinated at 200 °C, respectively. This observation suggests
that the surface area difference itself could not explain the different photocatalytic activities.

It is well-known that photocatalysts may not demonstrate good photocatalytic activity even with high light absorption capacity because of the loss of charge carriers due to recombination. The effective separation of charge carriers is critical to their photocatalytic performance. The largely enhanced photocatalytic activity of the sample calcinated at 200 °C under visible light irradiation could be attributed to its specific mixture nature of both WO3 and WO3·H2O phases. The Eg values of WO3·H2O and WO3 were determined from the Tauc plots (Fig. 6b) to be ~2.35 eV and ~2.72 eV, respectively. The conduction band (CB) bottom values and valence band (VB) top values of the two semiconductors could be estimated using eqn (8) and (9): \[ E_{CB} \approx X_{comp} - E^e - 1/2E_g \]
\[ E_{VB} = E_{CB} + E_g \]
where E^e is equal to 4.5 eV and X_{comp} is the electronegativity of a compound. Calculation details could be found in the ESI†. The CB and VB edges of WO3 are ~0.73 and ~3.45 eV with respect to the NHE, respectively, and the CB and VB edges of WO3·H2O are ~1.21 and ~3.56 eV with respect to the NHE, respectively. Thus, an effective charge carrier separation can occur between the WO3 and WO3·H2O phases as schematically illustrated in Fig. 8. When the sample calcinated at 200 °C was exposed to visible light irradiation, both WO3 and WO3·H2O phases could be excited, subsequently generating electron–hole pairs. Because the CB of WO3 is more negative than that of WO3·H2O, the photogenerated electrons in the CB of WO3 could flow to the CB of WO3·H2O, while the photogenerated holes in the VB of WO3·H2O could flow to the VB of WO3 because the VB of WO3·H2O is more positive than that of WO3. Thus, the photogenerated electrons and holes could be separated effectively from each other and could further react with electron acceptors and electron donors, respectively, contributing to the largely enhanced photocatalytic performance.

Conclusions

In summary, well-defined WO3·H2O hollow spheres composed of nanoflakes were synthesized through a template-free solvothermal process via Ostwald ripening. Hollow spheres with WO3 (major) and WO3·H2O (minor) mixture phases were created by calcination with appropriate temperature, and a matched band structure was created between the two phases. Thus, an effective charge carrier separation can occur between the WO3 phase and the WO3·H2O phase under visible light irradiation. These hollow spheres with WO3 and WO3·H2O mixture phases demonstrated a largely enhanced photocatalytic activity for RhB degradation under visible light irradiation compared with either pure WO3·H2O hollow spheres or pure WO3 hollow spheres.

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Notes and references

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