


 Cite this: *RSC Adv.*, 2020, 10, 15360

# Synthesis of nano-sized tungsten oxide particles encapsulated in a hollow silica sphere and their photocatalytic properties for decomposition of acetic acid using Pt as a co-catalyst†

 Takashi Harada, <sup>\*a</sup> En Yagi<sup>a</sup> and Shigeru Ikeda <sup>b</sup>

Nano-sized tungsten oxide (WO<sub>3</sub>) particles, each of which was encapsulated as a core in a hollow silica sphere (WO<sub>3</sub>@SiO<sub>2</sub>), were synthesized using calcium tungstate particles as the starting material. The calcium tungstate particles, each of which was covered with a silica shell, were converted to tungstic acid by nitric acid treatment and then to WO<sub>3</sub> by heat treatment to obtain WO<sub>3</sub>@SiO<sub>2</sub>. A hollow space was formed in WO<sub>3</sub>@SiO<sub>2</sub> between the WO<sub>3</sub> core and the SiO<sub>2</sub> shell as a result of shrinkage of WO<sub>3</sub> during the heat treatment. The thus-obtained WO<sub>3</sub>@SiO<sub>2</sub> was 40 nm in diameter, the WO<sub>3</sub> core was 10 nm in diameter, and the silica shell, which was permeable to gas and liquid, was 10 nm in thickness. WO<sub>3</sub>@SiO<sub>2</sub> absorbed visible light to the wavelength of 454 nm, which enabled photocatalytic reaction under visible light; Pt was loaded on the WO<sub>3</sub> cores in the photocatalytic reactions. In contrast to Pt-loaded bulk WO<sub>3</sub> photocatalysts without an SiO<sub>2</sub> shell, Pt-loaded WO<sub>3</sub>@SiO<sub>2</sub> showed continuous and complete decomposition of gaseous acetic acid in air under visible as well as UV irradiation.

Received 2nd March 2020

Accepted 3rd April 2020

DOI: 10.1039/d0ra01988g

[rsc.li/rsc-advances](http://rsc.li/rsc-advances)

## Introduction

Titanium dioxide (TiO<sub>2</sub>) is well known as the most efficient photocatalyst and has been used in various applications, such as production of renewable energy, decomposition of environmental pollutants and synthesis of useful organic compounds, because electrons and holes photogenerated in TiO<sub>2</sub> have strong reduction and oxidation properties, respectively.<sup>1–3</sup> However, due to its strong oxidation property, TiO<sub>2</sub> indiscriminately decomposes organic compounds, which sometimes leads to problems of decomposition of the support of TiO<sub>2</sub> photocatalysts. To solve this problem, a core-shell structure in which TiO<sub>2</sub> particles are covered with robust inorganic materials has been proposed.<sup>4</sup> The shell is permeable to gas and liquid, while it prevents contact between TiO<sub>2</sub> particles, leading to suppression of degradation of supports made of organic materials. However, the structure had the disadvantage of lowered photocatalytic activity because a large part of the TiO<sub>2</sub> surface, which is important for the photocatalyst, was covered with the shell material. To solve the problem, we have recently

developed a TiO<sub>2</sub> photocatalyst encapsulated in a hollow silica shell (TiO<sub>2</sub>@SiO<sub>2</sub>), in which a gap space is formed between the core and the shell. As a result, the TiO<sub>2</sub>@SiO<sub>2</sub> showed photocatalytic activity as high as that of an intrinsic TiO<sub>2</sub> photocatalyst, and showed size-selectivity for materials to be decomposed, depending on the pore size of the permeable shell.<sup>5–8</sup> In addition, other features of core-hollow shell structure, such as improvement adsorption properties, high temperature stability of core material and application for cascade reaction, have been reported.<sup>9–11</sup>

There have been many efforts to modify TiO<sub>2</sub> so as to enable absorption of visible light; an intrinsic TiO<sub>2</sub> photocatalyst shows low photocatalytic activity in normal environments because it shows photocatalytic activity only under UV light due to its large band gap (3.2 eV). Approaches to solve this problem include doping of TiO<sub>2</sub> with transition metals<sup>12–15</sup> and replacement of oxygen in TiO<sub>2</sub> with sulfur or nitrogen.<sup>16–21</sup> Another approach is to use low band gap materials instead of TiO<sub>2</sub>. Tungsten oxide (WO<sub>3</sub>) is a good candidate of these materials because of its narrow band gap (2.8 eV), high oxidation property, nontoxicity, and chemical stability.<sup>22</sup> However, a pure WO<sub>3</sub> photocatalyst shows low photocatalytic activity for decomposition of organic compounds because of the low energy level of its conduction band (CB) edge, which is not high enough for the electrons in the CB to reduce O<sub>2</sub> or H<sub>2</sub>O. Sayama *et al.* reported that loading co-catalysts, such as CuO, Pd and Pt, on the surface of WO<sub>3</sub> was effective for improving its photocatalytic activity.<sup>23,24</sup> Although the co-catalysts do not affect the energy level of the CB

<sup>a</sup>Research Center for Solar Energy Chemistry, Osaka University, 1-3 Machikaneyama, Toyonaka 560-8531, Japan. E-mail: harada@chem.es.osaka-u.ac.jp

<sup>b</sup>Department of Chemistry, Faculty of Science and Engineering, Konan University, Okamoto, Higashinada, Kobe 658-8501, Japan

 † Electronic supplementary information (ESI) available: XRD patterns of reference samples. TG-DTA curves time courses for CO<sub>2</sub> evolution and acetic acid decomposition and methanol production during photocatalytic reaction. See DOI: 10.1039/d0ra01988g


of  $\text{WO}_3$ , they kinetically enhance the electron transfer from  $\text{WO}_3$  to  $\text{O}_2$  or  $\text{H}_2\text{O}$  and, as a result, increase photocatalytic activity of  $\text{WO}_3$ . We expect that  $\text{WO}_3$  particles encapsulated in a hollow silica sphere ( $\text{WO}_3@\text{SiO}_2$ ) would be suitable as a photocatalyst used under visible light.

A number of synthesis procedures have been developed to produce the core–hollow shell structure using, for example, the Kirkendall effect,<sup>25</sup> a hard template,<sup>26</sup> and an etching process.<sup>27</sup> We previously reported the synthesis of  $\text{TiO}_2@\text{SiO}_2$  using a carbon material as a hard template.<sup>5–8</sup> The hard template method is useful for obtaining well-defined core–hollow shell structures.<sup>5–8,26</sup> However, this method requires the formation and removal of solid templates, which are troublesome procedures, especially for practical use. Moreover, core–hollow shell structures thus-obtained are often large in size and irregular in shape. Because these structures show low mechanical stability due to the large hollow space, the structure needs to be small and, ideally, spherical.

We recently developed a simple procedure for making nickel nanoparticles encapsulated in a hollow silica sphere.<sup>28</sup> In this procedure, small crystals of a nickel hydrazine complex were prepared in a reverse microemulsion system and were directly covered with a silica layer. The nickel hydrazine crystals were converted to nickel nanoparticles by heat treatment. Because the nickel nanoparticles were smaller than nickel hydrazine crystals, a core–hollow shell structure was automatically obtained during the heat treatment. Here, we applied this strategy to the synthesis of  $\text{WO}_3@\text{SiO}_2$  and evaluated its photocatalytic activity for decomposition of acetic acid in gas phase, which was used as a model reaction.

## Experimental

### Synthesis of tungsten oxide photocatalysts

Tungsten oxide encapsulated in a hollow silica sphere ( $\text{WO}_3@\text{SiO}_2$ ) was synthesized as follows. To 34 g polyoxyethylene cetyl ether ( $n = 15$ ) (30 mmol) dissolved in 75  $\text{cm}^3$  of cyclohexane were added 4.5  $\text{cm}^3$  of 0.1 M aqueous  $\text{Ca}(\text{NO}_3)_2$  (0.45 mmol) and 4.5  $\text{cm}^3$  of 0.1 M aqueous  $\text{Na}_2\text{WO}_4$  (0.45 mmol). After the mixture had been stirred at 55 °C for 1 h, 1.5  $\text{cm}^3$  of hydrazine monohydrate (30 mmol) was added and the mixture was stirred at 55 °C for 1 h. Then 3  $\text{cm}^3$  of tetraethylorthosilicate (TEOS: 13.4 mmol) was added to the suspension, which was stirred at 55 °C for 2 h. After addition of 240  $\text{cm}^3$  of 2-propanol to the suspension, the mixture was centrifuged (3000 rpm, 4 min) to recover the precipitate, which was washed with 2-propanol three times. The precipitate was added to 2.5 M aqueous  $\text{HNO}_3$  at 80 °C for 6 h and then washed with distilled water until the effluent showed neutral pH. After drying at 80 °C, the powder was calcined at 700 °C for 2 h in air to produce  $\text{WO}_3@\text{SiO}_2$ .

As a reference photocatalyst, we synthesized bulk  $\text{WO}_3$  ( $\text{WO}_3(\text{B})$ ) powder by the same procedure but without the use of the reverse micelle system and silica source.  $\text{WO}_3(\text{B})$  physically mixed with  $\text{SiO}_2$  ( $\text{WO}_3(\text{B})/\text{SiO}_2$ ) was also used as a reference photocatalyst. This reference photocatalyst was prepared using  $\text{H}_2\text{WO}_4$ , which is a precursor of  $\text{WO}_3(\text{B})$ , and about 30 nm of

$\text{SiO}_2$  powder, which is synthesized by a slightly modified Stöber method.<sup>29</sup> They were mechanically mixed and calcined at 700 °C. The  $\text{WO}_3$  content of  $\text{WO}_3(\text{B})/\text{SiO}_2$  was adjusted to be the same as that of  $\text{WO}_3@\text{SiO}_2$ .

### Characterization

TEM images were taken on a Hitachi H-9000NAR instrument operated at 300 kV. Powder X-ray diffraction (XRD) patterns were recorded using a Rigaku MiniFlex X-ray diffractometer ( $\text{CuK}\alpha$ , Ni filter). Analyses of the surface area and pore structure were carried out using a Quantachrome AUTOSORB-1 automated gas-sorption system with  $\text{N}_2$  as the adsorbate, after pretreatment of the sample at 200 °C for 2 h under reduced pressure. The BET surface area was calculated from the adsorption branch of the isotherm. Ultraviolet and visible-light diffuse reflection (UV-vis DR) spectra were obtained with a Hitachi U-4100 UV-vis-NIR spectrometer equipped with an integrating sphere using  $\text{BaSO}_4$  as a reference. The reflectance spectra were converted to absorbance spectra by the Kubelka–Munk method.

### Photocatalytic decomposition of acetic acid in gaseous phase

Photocatalytic decomposition of acetic acid was carried out over Pt-loaded  $\text{WO}_3$  photocatalysts ( $\text{Pt}/\text{WO}_3$ ) in gaseous phase. Pt-loading on  $\text{WO}_3$  photocatalysts was carried out by the photo-deposition method sequentially from an aqueous methanol (10 vol%) solution of  $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ .<sup>30</sup> The loading amount of Pt was fixed at 0.5 wt% of  $\text{WO}_3$  for all of the photocatalysts.

Photocatalytic decomposition of acetic acid was performed in a 225  $\text{cm}^3$  Pyrex cylindrical reaction vessel (64 mm in diameter) with a quartz top window. The photocatalyst, containing 30 mg of  $\text{WO}_3$ , was spread on the slide glass (38 mm  $\times$  26 mm) and set in the vessel. After closing the vessel, 1  $\mu\text{l}$  of acetic acid (17.5  $\mu\text{mol}$ ) was introduced into the vessel. After acetic acid had been fully vaporized and had reached an absorption equilibrium in the vessel, the sample was photoirradiated with a 300 W Xe lamp through the quartz top window.  $\text{CO}_2$  was analyzed with a Shimadzu GC-8A gas chromatograph equipped with a TCD detector and an activated carbon column, and organic compounds were analyzed with a Shimadzu GC-2014 gas chromatograph equipped with a BID detector and a TC-FFAP column. For the analyses, a portion of the gas phase was sampled with an air-tight syringe at appropriate intervals.

## Results and discussion

### Synthesis and characterizations of tungsten oxide nanoparticles encapsulated in a hollow silica sphere

Synthesis of nano-sized  $\text{WO}_3@\text{SiO}_2$  was performed in a water in oil (W/O) microemulsion system. In the first step, an aqueous  $\text{Ca}(\text{NO}_3)_2$  solution was added to a cyclohexane solution containing polyoxyethylene cetyl ether ( $n = 15$ ) to form a W/O microemulsion. Addition of an aqueous  $\text{Na}_2\text{WO}_4$  solution into the W/O microemulsion solution induced a color change from transparent to white; it became turbid after a while, indicating formation of solid components. By adding a hydrazine



monohydrate solution and TEOS to this solution, polycondensation of the siliceous component was continuously carried out. After 2 h agitation of the mixture, the solid part was collected. Fig. 1a shows an XRD pattern of the thus-obtained white powder. All of the peaks were assigned to  $\text{CaWO}_4$  as referred from the JCPDS card (no. 41-1431). A TEM image of the white powder showed spherical core-shell structure (Fig. 2a). These results indicate that  $\text{CaWO}_4$  particles were directly covered with a silica shell ( $\text{CaWO}_4@\text{SiO}_2$ ). The diameter of the  $\text{CaWO}_4$  core was 10–20 nm and the thickness of the silica shell was about 10 nm.

The thus-obtained  $\text{CaWO}_4@\text{SiO}_2$  powder was treated with aqueous  $\text{HNO}_3$  solution at 80 °C for 6 h. During  $\text{HNO}_3$  treatment, the white color of the turbid solution gradually changed to yellow. The corresponding XRD pattern of the thus-obtained yellow powder was assigned to  $\text{H}_2\text{WO}_4$  as referred from the JCPDS card (no. 43-0679) (Fig. 1b). The TEM image showed that the core-shell structure was not changed by the  $\text{HNO}_3$  treatment, as shown in Fig. 2b. These results indicate that the  $\text{CaWO}_4$  core particle of  $\text{CaWO}_4@\text{SiO}_2$  was converted to  $\text{H}_2\text{WO}_4$  by the  $\text{HNO}_3$  treatment and that a core-shell material having an  $\text{H}_2\text{WO}_4$  core and a silica shell ( $\text{H}_2\text{WO}_4@\text{SiO}_2$ ) was obtained.

After calcination of  $\text{H}_2\text{WO}_4@\text{SiO}_2$  at 700 °C, the color changed to light green. The XRD pattern of this sample showed the formation of monoclinic  $\text{WO}_3$  (JCPDS card no. 43-1035) (Fig. 1c), which was obtained by dehydration of  $\text{H}_2\text{WO}_4$ . To confirm dehydration of  $\text{H}_2\text{WO}_4$ , thermogravimetric-differential thermal analysis (TG-DTA) was carried out. The TG-DTA curves of  $\text{H}_2\text{WO}_4@\text{SiO}_2$  were shown in Fig. S2.† A weight loss with endothermic peak was observed at around 100 °C and 200 °C. These are due to desorption of physically adsorbed water molecule on  $\text{H}_2\text{WO}_4@\text{SiO}_2$  particles and coordinated water molecules of  $\text{H}_2\text{WO}_4$ , respectively. A weight loss of exothermic peak was observed at 250–700 °C, due to combustion of surfactant and siliceous compounds including removal of residual coordinated water.<sup>31</sup> A TEM image and high resolution TEM (HRTEM) image of this sample are shown in Fig. 2c and inset of Fig. 2c, respectively. In contrast to the TEM image of

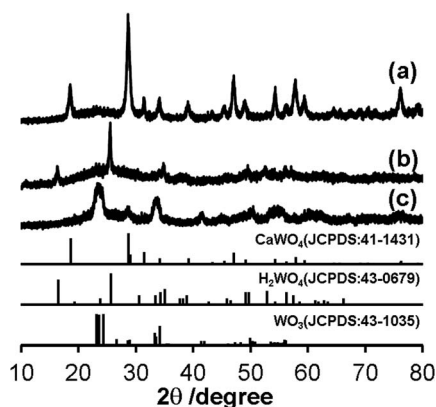


Fig. 1 XRD patterns of (a)  $\text{CaWO}_4@\text{SiO}_2$ , (b)  $\text{H}_2\text{WO}_4@\text{SiO}_2$  and (c)  $\text{WO}_3@\text{SiO}_2$ . The standard data of  $\text{CaWO}_4$  (JCPDS: 41-1431),  $\text{H}_2\text{WO}_4$  (JCPDS: 43-0679) and  $\text{WO}_3$  (JCPDS: 43-1035) are shown as a reference.

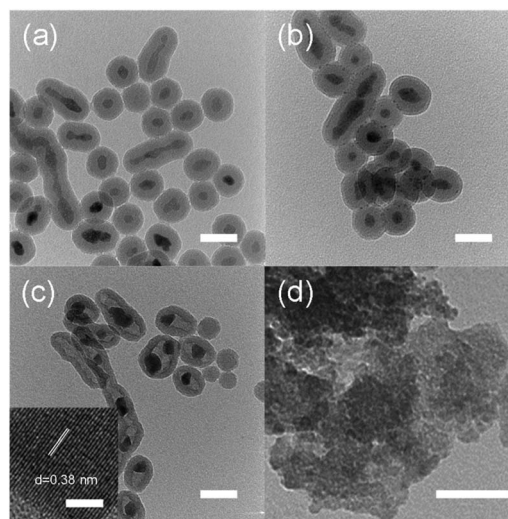


Fig. 2 TEM images of (a)  $\text{CaWO}_4@\text{SiO}_2$ , (b)  $\text{H}_2\text{WO}_4@\text{SiO}_2$ , (c)  $\text{WO}_3@\text{SiO}_2$  and (d)  $\text{WO}_3(\text{B})$ . Scale bars are corresponding to 40 nm. Inset of (c) is HRTEM image of  $\text{WO}_3@\text{SiO}_2$  and scale bar is corresponding to 5 nm.

$\text{H}_2\text{WO}_4@\text{SiO}_2$ , a hollow space was observed in this sample, indicating the formation of  $\text{WO}_3$  encapsulated in a hollow silica sphere ( $\text{WO}_3@\text{SiO}_2$ ). The hollow space was caused by shrinkage of the volume as  $\text{H}_2\text{WO}_4$  was converted to  $\text{WO}_3$ . The size of the  $\text{WO}_3$  particles was about 10 nm in diameter, which is smaller than that of the  $\text{H}_2\text{WO}_4$  core in  $\text{H}_2\text{WO}_4@\text{SiO}_2$ . The lattice fringes of HRTEM image of  $\text{WO}_3$  particle are assigned to the (100) plane of monoclinic  $\text{WO}_3$ . This is agreement with the XRD result. The silica shell thickness seems to be slightly decreased after the heat treatment. A TEM image of  $\text{WO}_3(\text{B})$  powder that was prepared without using the reverse microemulsion system and silica source showed that the particle size was large and inhomogeneous (40–100 nm) as can be seen in Fig. 2d, although  $\text{WO}_3(\text{B})$  was obtained by the same route as  $\text{WO}_3@\text{SiO}_2$  (Fig. S1†). These results suggest that the use of the reverse microemulsion system and the silica shell structure are effective for suppressing the growth of  $\text{WO}_3$  particles during calcination.

Fig. 3 shows  $\text{N}_2$  adsorption-desorption isotherms of  $\text{WO}_3(\text{B})$ ,  $\text{CaWO}_4@\text{SiO}_2$  and  $\text{WO}_3@\text{SiO}_2$  samples. The isotherm of  $\text{WO}_3(\text{B})$  is classified as characteristic type III according to the IUPAC nomenclature and the BET surface area is 13  $\text{m}^2 \text{g}^{-1}$ , indicating a nonporous structure. The isotherm of  $\text{CaWO}_4@\text{SiO}_2$  is classified as characteristic type II and showed a slight increase in  $\text{N}_2$  uptake at a relative pressure ( $P/P_0$ ) below 0.1, indicating the existence of micropores in the silica shell. The BET surface area of  $\text{CaWO}_4@\text{SiO}_2$  was found to be 65  $\text{m}^2 \text{g}^{-1}$ . The isotherm of  $\text{WO}_3@\text{SiO}_2$  showed a characteristic type IV with a hysteresis loop and the BET surface area was 175  $\text{m}^2 \text{g}^{-1}$ . Compared with  $\text{CaWO}_4@\text{SiO}_2$ ,  $\text{WO}_3@\text{SiO}_2$  showed a steep increase in  $\text{N}_2$  uptake at  $P/P_0$  below 0.1, indicating the formation of a well-developed micropore system probably due to removal of the surfactant in the silica shell during high temperature calcination. Moreover, a hysteresis loop enclosed at a  $P/P_0$  of ca. 0.4–0.9 was observed. These phenomena are attributed to the tensile



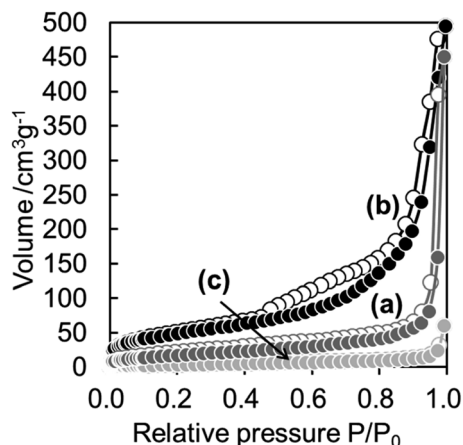


Fig. 3 N<sub>2</sub> sorption isotherms of (a) CaWO<sub>4</sub>@SiO<sub>2</sub>, (b) WO<sub>3</sub>@SiO<sub>2</sub> and (c) WO<sub>3</sub>(B). Filled and open circles denote adsorption and desorption isotherms, respectively.

strength effect observed in materials having a hollow structure encapsulated by a pore system of relatively small pore size.<sup>32</sup> These results are in agreement with the TEM images and indicate the formation of a hollow structure with a well-developed pore system in the silica shell.

The content of the WO<sub>3</sub> component in WO<sub>3</sub>@SiO<sub>2</sub> was estimated by the gravimetric method. The weight of the WO<sub>3</sub> component in WO<sub>3</sub>@SiO<sub>2</sub> was measured after etching the SiO<sub>2</sub> component by diluted HF aqueous solution; we confirmed in advance that WO<sub>3</sub> was not dissolved in the dilute HF aqueous solution. From the measurement, the WO<sub>3</sub> content was found to be 60 wt% of WO<sub>3</sub>@SiO<sub>2</sub>.

UV/Vis diffuse reflectance spectra of WO<sub>3</sub>@SiO<sub>2</sub> and WO<sub>3</sub>(B) powders are shown in Fig. 4. Reflectance is converted to absorbance by the Kubelka–Munk equation:

$$F(R) = (1 - R)^2/2R, \quad (1)$$

where  $F(R)$  denotes Kubelka–Munk function and  $R$  denotes reflectance of the sample relative to that of a non-absorbing

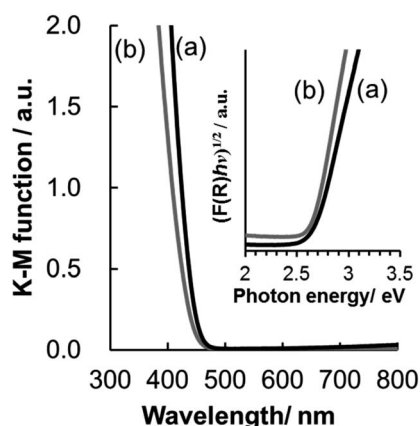


Fig. 4 UV-visible diffuse reflectance spectrum of (a) WO<sub>3</sub>@SiO<sub>2</sub> and (b) WO<sub>3</sub>(B).

standard (BaSO<sub>4</sub>). The spectra indicate that the on-set values of the absorption bands are located at 454 and 486 nm for WO<sub>3</sub>@SiO<sub>2</sub> and WO<sub>3</sub>(B), respectively. Considering that WO<sub>3</sub> is an indirect n-type semiconductor, its energy band gap ( $E_g$ ) can be determined by optical absorption measurements using the following relationship:<sup>33</sup>

$$(F(R)hv)^{1/2} = K(hv - E_g), \quad (2)$$

where  $hv$  the incident photon energy and  $K$  is a constant. The inset in Fig. 4 shows plots of  $(F(R)hv)^{1/2}$  versus  $hv$ . By extrapolating the plots linearly, the energy band gaps of WO<sub>3</sub>@SiO<sub>2</sub> and WO<sub>3</sub>(B) are estimated to be 2.65 and 2.63 eV, respectively. The estimated energy band gaps are in good agreement with the values (2.5–2.8 eV) reported in the literature.<sup>34</sup> The reflectance spectrum of the WO<sub>3</sub>@SiO<sub>2</sub> powder showed a slight blue shift compared with that of the bulk WO<sub>3</sub>(B) powder, probably due to the differences of WO<sub>3</sub> particle size and/or crystallinity.<sup>35,36</sup>

### Photocatalytic decomposition of acetic acid

Photocatalytic decomposition of acetic acid in gaseous phase was used as a measure of photocatalytic activity of WO<sub>3</sub> having different morphologies. Since WO<sub>3</sub> photocatalysts show poor catalytic activity for decomposition of organic compounds due to their low reduction property, we loaded a Pt co-catalyst on WO<sub>3</sub> particles of all of the photocatalysts we examined; these particles are denoted by Pt/WO<sub>3</sub>.

A comparison of time courses of CO<sub>2</sub> evolution during decomposition of acetic acid under full-arc irradiation from a 300 W Xe lamp with various Pt-loaded WO<sub>3</sub> photocatalysts and TiO<sub>2</sub> photocatalyst made of commercially available TiO<sub>2</sub> (ST-01, Ishihara Sangyo Co. Ltd.) is shown in Fig. 5. In 100 min, the TiO<sub>2</sub> and Pt/WO<sub>3</sub>@SiO<sub>2</sub> photocatalysts produced CO<sub>2</sub> continuously to the level of 35 μmol, which corresponds to the stoichiometric amount of the introduced acetic acid (17.5 μmol), indicating complete decomposition of acetic acid. The initial high rate of CO<sub>2</sub> evolution with the TiO<sub>2</sub> photocatalyst seems to be due to its intrinsically high photocatalytic activity. However,

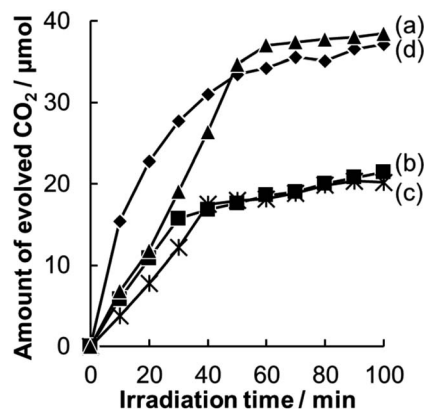


Fig. 5 Time courses for CO<sub>2</sub> evolution during photocatalytic decomposition of acetic acid over (a) Pt/WO<sub>3</sub>@SiO<sub>2</sub>, (b) Pt/WO<sub>3</sub>(B), (c) Pt/WO<sub>3</sub>(B)/SiO<sub>2</sub> and (d) TiO<sub>2</sub> (ST-01) under full-arc light irradiation from a 300 W Xe lamp.



the  $\text{WO}_3$  photocatalysts ( $\text{Pt}/\text{WO}_3@/\text{SiO}_2$  and  $\text{Pt}/\text{WO}_3(\text{B})$ ) showed much higher activity than that of the  $\text{TiO}_2$  photocatalyst, as shown in Fig. 6, suggesting the usefulness of  $\text{WO}_3$  photocatalysts under visible light conditions. Of the  $\text{WO}_3$  photocatalysts,  $\text{Pt}/\text{WO}_3@/\text{SiO}_2$  was effective for complete decomposition of acetic acid, as shown in Fig. 5 and 6.

In Fig. 5,  $\text{Pt}/\text{WO}_3@/\text{SiO}_2$  and  $\text{Pt}/\text{WO}_3(\text{B})/\text{SiO}_2$  show concave slopes for  $\text{CO}_2$  evolution in the initial period. This unique property of the photocatalysts seems to be related to the hollow shell structure. We consider that the release of  $\text{CO}_2$  from the hollow space of the photocatalysts to the outer space is hindered to some extent by the porous  $\text{SiO}_2$  shell, leading to the concave slope until the concentration of  $\text{CO}_2$  reaches a certain level. For the same reason, we can expect that reactive products produced in the hollow space have as higher chance of reaction on the photocatalyst because their escape from the hollow space and supply of acetic acid to the hollow space are hindered by the silica shell. The concentration of the intermediate in the hollow shell of  $\text{Pt}/\text{WO}_3@/\text{SiO}_2$  can be lower than that of  $\text{Pt}/\text{WO}_3(\text{B})$  in the gas phase because the intermediate competes with acetic acid for the reaction sites (or photogenerated holes) on  $\text{WO}_3$ . Such a function of the hollow shell (or hollow shell effect) will affect the activity of the photocatalysts as mentioned later.

$\text{Pt}/\text{WO}_3@/\text{SiO}_2$  and  $\text{Pt}/\text{WO}_3(\text{B})$  showed almost the same reaction rates for  $\text{CO}_2$  evolution during the initial reaction period, as shown in Fig. 5. However, the evolution rate of  $\text{CO}_2$  with  $\text{Pt}/\text{WO}_3(\text{B})$  decreased drastically when the amount of  $\text{CO}_2$  reached half of the stoichiometric level, suggesting that methanol or formaldehyde, both of which are the chief intermediates for decomposition of acetic acid, accumulates in the system. To confirm this assumption, we added acetic acid to the system with  $\text{Pt}/\text{WO}_3(\text{B})$  after the  $\text{CO}_2$  evolution rate had decreased and we found that the  $\text{CO}_2$  evolution rate almost recovered to the initial rate (Fig. S3†). This result strongly suggests that the decrease in the  $\text{CO}_2$  evolution rate with  $\text{Pt}/\text{WO}_3(\text{B})$  is not due to poisoning of the active sites of  $\text{WO}_3$  but is due to the slow decomposition rate of the intermediate. This is also consistent

with the fact that  $\text{CO}_2$  evolution continued even after the  $\text{CO}_2$  evolution rate had decreased over  $\text{Pt}/\text{WO}_3(\text{B})$ .

To confirm the effect of the intermediates, products in the gas phase were analyzed during the photocatalytic reaction. As a result, methanol was observed in the gas phase together with very small amounts of methyl formate and methyl acetate. However, formaldehyde was not observed. It is well known that formaldehyde is the major oxidation product from methanol.<sup>37</sup> Formaldehyde was not detected in this system probably because formaldehyde was strongly adsorbed on the photocatalysts or decomposed rapidly. The amount of methanol over  $\text{Pt}/\text{WO}_3@/\text{SiO}_2$  was smaller than that over  $\text{Pt}/\text{WO}_3(\text{B})$  (Fig. S4†). This result is consistent with the hollow shell effect mentioned above.

In the case of  $\text{Pt}/\text{WO}_3(\text{B})$ , even after methanol and other intermediates had been completely decomposed, the amount of  $\text{CO}_2$  was insufficient for a stoichiometric amount, indicating that the formaldehyde produced is strongly adsorbed on  $\text{Pt}/\text{WO}_3(\text{B})$ . Formaldehyde is easily polymerized to a stable paraformaldehyde at a high concentration as reported in the literature.<sup>38,39</sup> Since paraformaldehydes are relatively difficult to decompose, the  $\text{CO}_2$  evolution rate is drastically reduced if they accumulate on the photocatalyst.

In the case of the hollow space of  $\text{Pt}/\text{WO}_3@/\text{SiO}_2$ , however, the sequential photo decomposition reaction of intermediates proceeds efficiently due to the hollow shell effect, which maintains the concentration of formaldehyde at a low level. As a result, formation of paraformaldehyde was probably suppressed and continuous complete decomposition of acetic acid was achieved. The catalytic activity of  $\text{Pt}/\text{WO}_3(\text{B})/\text{SiO}_2$ , which is physically mixed  $\text{WO}_3(\text{B})$  with  $\text{SiO}_2$ , was almost the same as that of  $\text{Pt}/\text{WO}_3(\text{B})$ . These results indicate that the hollow structure, not the  $\text{SiO}_2$  content, is important for the complete decomposition of acetic acid. Although further studies are needed to understand the detailed reaction mechanisms, the hollow structure is expected to be effective for the photodecomposition of organic compounds through stable intermediates.

## Conclusions

We developed a procedure for the synthesis of  $\text{WO}_3$  nanoparticles encapsulated in a hollow silica sphere by effectively using a reverse micelle system and volume change of tungsten compounds. The obtained core–hollow shell structure was composed of  $\text{WO}_3$  nanoparticles of 10 nm in diameter and a porous  $\text{SiO}_2$  shell of 10 nm in thickness with highly developed micropores. The core–hollow shell structure of Pt-loaded  $\text{WO}_3@/\text{SiO}_2$  has great advantages in photocatalytic applications, as exemplified by the continuous and complete decomposition of acetic acid, compared to other bulk  $\text{WO}_3$  photocatalysts. The findings will lead to further improvement in the catalytic activity of  $\text{WO}_3@/\text{SiO}_2$  by an optimized core–hollow shell structure.

## Conflicts of interest

There are no conflicts to declare.

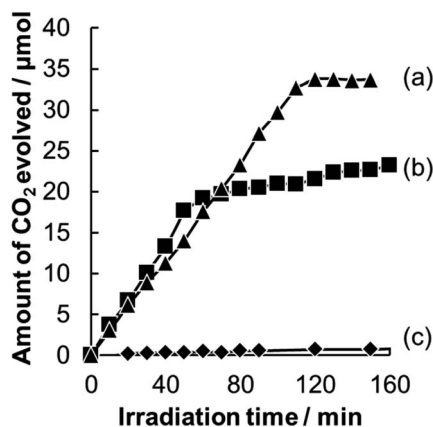


Fig. 6 Time courses for  $\text{CO}_2$  evolution during photocatalytic decomposition of acetic acid over (a)  $\text{Pt}/\text{WO}_3@/\text{SiO}_2$ , (b)  $\text{Pt}/\text{WO}_3(\text{B})$  and (c)  $\text{TiO}_2$  (ST-01) under visible light irradiation ( $\lambda > 400$  nm).



## Acknowledgements

TEM measurement was carried out by using a facility in the Research Center for Ultra-High Voltage Electron Microscopy, Osaka University and TEM observation was supported by Dr Takao Sakata. This research was partially supported by Kansai Research Foundation for Technology Promotion and JSPS KAKENHI Grant Numbers JP15K14127 and JP18K05273.

## References

- M. R. Hoffmann, S. T. Martin, W. Choi and D. W. Bahnemann, *Chem. Rev.*, 1995, **95**, 69.
- A. Fujishima, K. Hashimoto and T. Watanabe, *TiO<sub>2</sub> Photocatalysis Fundamentals and Applications*, BKC, Tokyo, 1999, p. 176.
- A. Fujishima, T. N. Rao and D. A. Tryk, *J. Photochem. Photobiol., C*, 2000, **1**, 1.
- H. S. Lee, S. M. Koo and J. W. Yoo, *J. Ceram. Process. Res.*, 2012, **13**, s300.
- S. Ikeda, Y. Ikoma, H. Kobayashi, T. Harada, B. Ohtani, T. Torimoto and M. Matsumura, *Chem. Commun.*, 2007, 3753.
- S. Ikeda, H. Kobayashi, Y. Ikoma, T. Harada, T. Torimoto, B. Ohtani and M. Matsumura, *Phys. Chem. Chem. Phys.*, 2007, **9**, 6319.
- S. Ikeda, H. Kobayashi, T. Sugita, Y. Ikoma, T. Harada and M. Matsumura, *Appl. Catal., A*, 2009, **363**, 216.
- S. Ikeda, H. Kobayashi, Y. Ikoma, T. Harada, S. Yamazaki and M. Matsumura, *Appl. Catal., A*, 2009, **369**, 113.
- W. Zhang, X.-J. Lin, Y.-G. Sun, D.-S. Bin, A.-M. Cao and L.-J. Wan, *ACS Appl. Mater. Interfaces*, 2015, **7**, 27031–27034.
- Y. Kuwahara, Y. Sumida, K. Fujiwara and H. Yamashita, *ChemCatChem*, 2016, **8**, 2781–2788.
- Y. Yang, X. Liu, X. Li, J. Zhao, S. Bai, J. Liu and Q. Yang, *Angew. Chem., Int. Ed.*, 2012, **51**, 9164–9168.
- T. Umebayashi, T. Yamaki, H. Itoh and K. Asai, *J. Phys. Chem. Solids*, 2002, **63**, 1909–1920.
- N. Murakami, T. Chiyoya, T. Tsubota and T. Ohno, *Appl. Catal., A*, 2008, **348**, 148.
- C. Wang, Z. Chen, H. Jin, C. Cao, J. Lia and Z. Mib, *J. Mater. Chem. A*, 2014, **2**, 17820.
- V. Moradi, M. B. G. Jun, A. Blackburn and R. A. Herring, *Appl. Surf. Sci.*, 2018, **427**, 791.
- R. Asahi, T. Morikawa, T. Ohwaki, K. Aoki and Y. Taga, *Science*, 2001, **293**, 269.
- G. R. Torres, T. Lindgren, J. Lu, C.-G. Granqvist and S.-E. Lindquist, *J. Phys. Chem. B*, 2004, **108**, 5995.
- H. Irie, Y. Watanabe and K. Hashimoto, *J. Phys. Chem. B*, 2003, **107**, 5483.
- H. Irie, Y. Watanabe and K. Hashimoto, *Chem. Lett.*, 2003, **32**, 772.
- T. Ohno, T. Tsubota, K. Nakajima and Z. Miyamoto, *Chem. Lett.*, 2004, **33**, 750.
- T. Umebayashi, T. Yamaki, S. Tanaka and K. Asai, *Chem. Lett.*, 2003, **32**, 330.
- G. Xin, W. Guo and T. Ma, *Appl. Surf. Sci.*, 2009, **256**, 165.
- T. Arai, M. Yanagida, Y. Konishi, Y. Iwasaki, H. Sugihara and K. Sayama, *Catal. Commun.*, 2008, **9**, 1254.
- T. Arai, M. Horiguchi, M. Yanagida, T. Gunji, H. Sugihara and K. Sayama, *Chem. Commun.*, 2008, 5565.
- Y. Yin, R. M. Rioux, C. K. Erdonmez, S. Hughes, G. A. Somorjai and A. P. Alivisatos, *Science*, 2004, **304**, 711.
- T. Harada, S. Ikeda, Y. H. Ng, T. Sakata, H. Mori, T. Torimoto and M. Matsumura, *Adv. Funct. Mater.*, 2008, **18**, 2190.
- J. Lee, J. C. Park and H. Song, *Adv. Mater.*, 2008, **20**, 1523; J. C. Park, J. U. Bang, J. Lee, C. H. Ko and H. Song, *J. Mater. Chem.*, 2010, **20**, 1239.
- T. Harada, T. Misaka, T. Sakata, S. Ikeda and M. Matsumura, *Appl. Mech. Mater.*, 2013, **372**, 132.
- W. Stöber, A. Fink and E. J. Bohn, *J. Colloid Interface Sci.*, 1968, **26**, 62.
- R. Abe, H. Takami, N. Murakami and B. Ohtani, *J. Am. Chem. Soc.*, 2008, **130**, 7780.
- J. Cao, B. Luo, H. Lin, B. Xu and S. Chen, *Appl. Catal., B*, 2012, **111–112**, 288.
- J. C. Groen, L. A. A. Peffer and J. P. Trez-RamRez, *Microporous Mesoporous Mater.*, 2003, **60**, 1.
- A. Chithambararaj and A. C. Bose, *Beilstein J. Nanotechnol.*, 2011, **2**, 585.
- M. A. Butler, *J. Appl. Phys.*, 1997, **48**, 1914.
- H. Kominami, K. Yabutani, T. Yamamoto, Y. Keraa and B. Ohtani, *J. Mater. Chem.*, 2001, **11**, 3222.
- G. W. Ho, K. J. Chua and D. R. Siow, *Chem. Eng. J.*, 2012, **181–182**, 661.
- M. Kawai, T. Kawai, S. Naito and K. Tamaru, *Chem. Phys. Lett.*, 1984, **110**, 58.
- J. L. Davis and M. A. Barteau, *J. Am. Chem. Soc.*, 1989, **111**, 1782.
- A. K. Chakraborty, S. Y. Chai and W. I. Lee, *Bull. Korean Chem. Soc.*, 2008, **2**, 494.

