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ARTICLE

Cite this: DOI: 10.1039/x0xx00000x

Received ooth January 2012, Accepted ooth January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

In-situ carbonization of soft-template to directly synthesize the crystalline mesoporous metal oxides with high surface area

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High-surface-area crystalline mesoporous d^{\circ} metal oxides such as Ta₂O₅, Nb₂O₅, and TiO₂ were synthesized via a one-pot method using pluronic P-123 triblock copolymer as a structure directing agent. Mesostructure stability during metal oxide crystallization via high temperature calcination remains difficult to maintain in such synthesis. In this study, two heat treatments were proven to play key roles in achieving this goal. The first one is the intermediate heat treatment that preconsolidates the mesostructure and partially decomposes P-123 into carbon rich species. The second heat treatment relies on high temperature calcination under inert atmosphere to simultaneously form carbon wrapping on the metal oxides in situ and achieve crystallization of metal oxides. These two treatments successfully restricted the porous structure collapse and crystal size growth during high temperature crystallization. The as-synthesized crystalline mesoporous metal oxides show disordered mesoporous structures consisting of polycrystals. Notably, the commonly used P-123 surfactant without sp2-hybridized carbon forms much amorphous carbon in situ, which effectively restricts mass transfer during crystallization and thus successfully prevents crystal size growth. The as-synthesized crystalline mesoporous Ta₂O₅, Nb₂O₅, and TiO₂ displayed surface areas of 117.0, 125, and 76.2 m²/g, respectively, and pore sizes of 5.4, 8.1, and 13.9 nm, respectively. Crystal sizes amounted to 19, 28, and 34 nm for the mesoporous Ta $_2O_5$, Nb $_2O_5$, and TiO₂, respectively. Porous and crystal structures of the as-synthesized samples are characterized using Xray diffraction, thermogravimetric-differential thermal analysis, scanning electron microscopy, transmission electron microscopy, X-ray photoelectron spectroscopy, and N_2 sorption techniques. The photocatalytic performance of as-synthesized crystalline mesoporous Ta_2O_5 is also evaluated. Using NiO_x as cocatalyst, the as-prepared crystalline mesoporous Ta_2O_5 showed stable overall water splitting under Xe lamp irradiation (full arc). When the light intensity is fixed 0.17-0.18 W/cm², the highest H_2 evolution rate is 709.1 µmol/g.h.

Introduction

Mesoporous transition metal oxides are particularly attractive because they possess d-shell electrons confined to nanosized walls, redox active internal surfaces, and connected pore frameworks.^{1,2} Thanks to these attributes, many interesting properties in energy conversion and storage, catalysis, sensing, adsorption, separation, and magnetic devices have been found.¹⁻⁸ In particular, mesoporous oxides consisting of d⁰ metal cations (such as Ta⁵⁺, Nb⁵⁺, and Ti⁴⁺) have attracted extensive attention because of their potential applications such as in stable watersplitting photocatalysts that directly convert light energy into clean, storable hydrogen and oxygen.⁹⁻¹⁴ However, maximum performance can only be achieved in a highly crystalline

state,^{12,15} resulting in extensive investigations on synthetic approaches that produce such materials. These approaches mainly include soft and hard templating methods,¹⁵⁻¹⁹ which usually involve evaporation-induced self-assembly (EISA).²⁰ In the soft templating method, Bresesinski and co-workers used the semi-commercial poly(ethylene-co-butylene)-blockpoly(ethylene oxide) diblock polymer (KLE) to synthesize crystalline mesoporous metal oxides.^{5,17,21-23} The formation of these crystalline materials involves three steps: (a) preparation of homogeneous and stable solution containing stoichiometric amounts of KLE and inorganic precursors; (b) progressive concentration of inorganic precursors into a homogeneous, flexible, and poorly condensed network around the surfactant mesophase through EISA; (c) treatment involving preconsolidation, template removal, and network crystallization.

Many obtained metal oxide films, including SrTiO₃,²¹ MgTa₂O₆,¹⁷ and NiFe₂O₄,⁶ showed well-defined mesostructures. Mesostructure stability during high-temperature crystallization is usually problematic for amorphous mesoporous metal oxides. To solve this issue, a method that fortifies the mesostructure has been developed using silica or carbon.¹ Domen and co-workers deposited a SiO₂ layer on the pore surface of the amorphous mesoporous Ta_2O_5 using a silicone compound. 11,24 The SiO_2 layers restricted mass transfer during crystallization, thus successfully preventing pore collapse. After SiO₂ removal using NaOH solution, crystalline mesoporous Ta2O5 was obtained with a surface area of 109 m²/g and pore size of 3.7 nm. Wiesner and co-workers prepared crystalline mesoporous TiO_2 and Nb_2O_5 in a one-pot synthesis using block copolymers with sp²-hybridized carbon containing hydrophobic block as structure directing agents (SDA).15 The copolymer was synthesized through anionic polymerization and converted into a sturdy, amorphous carbon in situ on appropriate heating in Ar atmosphere. The formed carbon acted as a sufficiently rigid support keeping the oxide pores intact while crystallizing at a high temperature. Surface areas of 90 and 54 m^2/g and pore sizes of 23 and 35 nm were obtained for the resulting crystalline mesoporous TiO2 and Nb₂O₅.

This study investigated the potential use of the traditional SDAs in the direct synthesis of crystalline mesoporous d^0 metal oxides. A one-pot method was, therefore, developed to produce crystalline Ta₂O₅, Nb₂O₅, and TiO₂ with high surface areas and narrow mesopore size distribution using the triblock copolymer P-123 as an SDA.

Experimental



Preparation of Crystalline Mesoporous Ta₂O₅. All reagents and solvents were commercial available and used without further purification or pre-treatment. Triblock copolymer P-123 (2.5 g) was dissolved in ethanol (25 g) under constant stirring for 30 min and TaCl₅ (m_i) was added to the solution under vigorous stirring for 1.5 h. This sol solution was transferred to Petri dishes for aging at room temperature for 7 days to produce a gel. Thereafter, the crystalline mesoporous Ta₂O₅ samples were synthesized through three different routes. The final samples were named Ta₂O₅-R1-i, R2-i, and R3-i, where R1, R2, and R3 represent synthetic routes 1, 2, and 3, respectively (Figure 1), and i denotes the added TaCl₅ amounts (m_i). The i values 1, 2, 3, and 4 correspond to the m_i values of

5.37, 2.81, 2.00, and 1.50 g, respectively. For example, Ta_2O_5 -R3-1 means that mesoporous Ta_2O_5 was synthesized through route 3 from 5.37 g of TaCl₅.

In route 1, the gel was calcined in an alumina tube furnace at 800 $^{\circ}$ C under N₂ gas flow for 30 min. The resulting black chunks (Ta₂O₅-R1-1-C) were ground into powder and calcined at 600 $^{\circ}$ C for 30 min in air to remove the carbon.

In route 2, the gel was heated to 250 °C for 12 h to partially decompose P-123 and condensate Ta₂O₅ related species. Herein, the above described 250 °C treated powder was named Ta₂O₅-1-250 afterwards. The resulting chunks were ground into powder and calcined at 800 °C for 30 min in air to remove the remaining template and crystallize Ta₂O₅.

In route 3, the gel was treated at 250 $\,^{\circ}$ C for 12h and calcined in a tube furnace at 800 $\,^{\circ}$ C under N₂ gas flow for 30 min to crystallize the Ta₂O₅ species. The obtained black powder was calcined at 600 $\,^{\circ}$ C for 30 min in air to remove the carbon. Ta₂O₅-R3-1 powder was also calcined at 800 $\,^{\circ}$ C for 30 min in air to produce Ta₂O₅-R3-1-HT as a reference sample.

Characterization methods. Powder X-ray diffraction (XRD) patterns of as-synthesized samples were recorded using an RINT2500HLR⁺ XRD (Rigaku) operating at a scanning rate of 5 %min with a CuKα radiation at 40 kV and 80 mA. Scanning electron microscopy (SEM) images were acquired using a FEI Versa 3D Dual Beam field emission electron microscope. The powder samples were fixed on the carbon tape and directly used for observation. Transmission electron microscopy (TEM) images were taken using a JEM-ARM200F instrument equipped with a spherical aberration corrector at an accelerating voltage of 200 kV. Samples for TEM observation were prepared by the following procedures: the as-synthesized mesoporous metal oxide powders were directly dispersed on a carbon covered copper grid. The resulting sample thickness prevented the electron beam from penetrating the particle. Therefore, only the porous and crystalline structure of the small particle's thin edged areas could be clearly examined. Thermogravimetricdifferential thermal analysis (TG-DTA) results were obtained using a Thermo Plus TG8120 apparatus (Rigaku) under an air flow of 50 cm³/min at a heating rate of 10 °C/min. Nitrogen adsorption-desorption measurements were conducted at -196 ℃ using a BELSORP-Mini II instrument. Before measuring, samples were degased at 150 °C for at least 8 h under N₂ flow. Specific surface areas and pore size distributions were calculated according to the Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) models using adsorption branch, respectively. X-ray photoelectron spectroscopy results were obtained using an ESCA-3400 electron spectrometer and the assynthesized Ta₂O₅ samples were analyzed without any pretreatment. The binding energy was normalized by adjusting the C1s peak to 284.6 eV. Raman spectrum results were obtained using RENISHAW inVia Raman Microscope and the samples were analysed without any pretreatment.

Photocatalytic Experiments. Photocatalytic water splitting was performed using a conventional closed circulating system (supporting information (SI), Figure 1). The catalyst (50 mg) was suspended in Ar-saturated water (30 mL). The mixture was

adjusted to pH 11 using a 1 M KOH solution and placed in a quartz reaction cell, which was irradiated using 300W Xe lamp (full arc) as an external light source. During photocatalytic water splitting, the suspension was mixed using a magnetic stirring bar under Ar flow (10.67 kPa). Before the reaction, the system was evacuated to remove any residual air, and the absence of gas leakage was confirmed by a one-hour test reaction without light irradiation. Amounts of formed H₂ and O₂ were determined using a GC-8A gas chromatography apparatus equipped with a thermal conductivity detector (Shimadzu Corp.) and a gas sampler (ca., 10 cm³ in volume). The sampler was directly connected to the reaction system to avoid air contamination. The Xe lamp light intensity was measured using a 30A-P power meter (Ophir Optronics Ltd.) and maintained around 0.17–0.18 W/cm² by adjusting the current value.

Nickel oxide (NiO_x) was loaded onto Ta₂O₅ through impregnation¹¹ and used as a cocatalyst to promote H₂ evolution. During impregnation, a precursor Ni(NO₃)₂ 6H₂O solution was added to Ta₂O₅ powder, dried, and calcined at 300 °C for 1 h. The NiO loaded Ta₂O₅ powder was treated under H₂ flow at 400 °C for 2 h and gently oxidized under O₂ flow at 200 °C for 1 h to finally produce NiO_x loaded Ta₂O₅. The loading amounts were calculated using the molecular weight of NiO.

Results and discussion

Preparation of Crystalline Mesoporous Ta2O5. The production of mesoporous Ta₂O₅ with high crystallinity pore walls and high surface areas requires high temperature calcination-induced crystallization and limited mass transfer to avoid mesostructure collapse. Figure 1 shows the procedures used to synthesize crystalline mesoporous Ta₂O₅. First, a homogeneous P-123-Ta hybrid gel was synthesized through EISA at the mesoscale, as previously reported by Yang and coworkers¹⁵ for synthesis of semicrystalline mesoporous metal oxides. Thereafter, three different synthesis routes were assessed, but only route 3 provided crystalline mesoporous Ta₂O₅ with a high surface area. In route 1, the hybrid gel was calcined at 800 °C under N₂ atmosphere for Ta₂O₅ crystallization concomitant with P-123 carbonization, and then at 600 °C in air for carbon removal. In route 2, the hybrid gel it was heated at 250 °C for 12 h to preconsolidate or condensate Ta species. This intermediate heat treatment also produced a black gel, suggesting a partially carbonized P-123. Next, the ground sample was calcined at 800 °C in air for simultaneous Ta₂O₅ crystallization and SDA removal. In route 3, the hybrid gel was subjected to an intermediate heat treatment. On the other hand, the ground sample was calcined at 800 °C in N2 atmosphere for crystallization before further calcination at 600 °C in air to remove the carbon formed from SDA carbonization.



Fig. 2 XRD patterns of mesoporous Ta_2O_5 samples synthesized through three different routes. Bar markers correspond to peaks for crystalline Ta_2O_5 . (JCPDS No. 71-0639).



Fig. 3 N_2 adsorption–desorption isotherms (a) and pore size distributions (b) of mesoporous Ta_2O_5 samples synthesized through different routes.



Fig. 4 SEM images of mesoporous Ta_2O_5 samples (a) Ta_2O_5 -R2-1 and (b) Ta_2O_5 -R3-1. Scale bars correspond to 500 nm.

Figure 2 shows XRD patterns of Ta₂O₅ samples synthesized through routes 1–3. All three patterns showed well-resolved, smooth diffraction peaks on a flat baseline, suggesting the formation of highly crystalline oxides. Comparing peak positions with crystallographic databases identifies the materials as Ta₂O₅ crystals (JCPDS No. 71-0639). Ta₂O₅-R₃-1 showed wider peaks and lower diffraction intensity than Ta₂O₅-R₁-1 and Ta₂O₅-R₂-1, suggesting that route 3 leads to the formation of the smallest crystallites. Crystallite sizes were calculated from (001) diffraction peaks using Scherrer's equation and amounted to 39, 50, and 28 nm for Ta₂O₅-R₁-1, Ta₂O₅-R₂-1, and Ta₂O₅-R₃-1, respectively (Table 1).

Figure 3 shows nitrogen sorption isotherms (a) and pore size distribution (b) for Ta₂O₅-R1-1, Ta₂O₅-R2-1, and Ta₂O₅-R3-1 and the associated physical properties are summarized in Table 1. All isotherms exhibited type-IV patterns, which is typical of mesoporous materials. They also indicated that Ta₂O₅-R1-1 adsorbed much less N₂ than the other two samples, resulting in a pore volume of 0.08 cm³/g for Ta₂O₅-R1-1 and 0.13 cm³/g for Ta₂O₅-R2-1 and Ta₂O₅-R3-1. In addition, Ta₂O₅-R2-1 displayed a significantly greater N₂ uptake leap within a partial pressure (p/p₀) range of 0.82–0.95 than Ta₂O₅-R1-1 and Ta₂O₅-R3-1, which explains larger pores for Ta₂O₅-R2-1 (24.5 nm) than for Ta₂O₅-R1-1 and Ta₂O₅-R3-1 (9.2 nm). The low pore volume of Ta₂O₅-R1-1 may be attributed to a partial mesostructure collapse, demonstrating that Ta network preconsolidation through the intermediate heat treatment played an important role in fortifying the entire porous structure. The large Ta₂O₅-R2-1 pores may be attributed to crystal size growth consistent with the crystal size calculated from the XRD patterns. These results revealed that route 3 preserved the stability of the entire mesostructure and at

the same time effectively prevented the grain size growth during crystallization. Moreover, Ta₂O₅-R3-1 exhibited a drastically higher surface area (56.6 m²/g) than Ta₂O₅-R1-1 (37.7 m²/g) and Ta₂O₅-R2-1 (24.0 m²/g).



Fig. 5 TEM images of (a) Ta_2O_5 -R3-1-C and (b) Ta_2O_5 -R3-1.

High magnification SEM images (Figure 4) clearly showed that Ta₂O₅-R2-1 and Ta₂O₅-R3-1 presented clear mesoporous structures and Ta₂O₅-R2-1 consisted of much larger pores than Ta₂O₅-R3-1, in agreement with N₂ sorption results. High resolution TEM images showed that Ta₂O₅-R3-1-C and Ta₂O₅-R3-1 adopted a crystalline porous structure (Figure 5) and amorphous carbon layers wrapped around the crystalline Ta₂O₅-R3-1-C and Ta₂O₅ of Ta₂O₅-R3-1-C. The Raman spectrum of Ta₂O₅-R3-1-C and Ta₂O₅-R3-1-C, only the bands corresponding to carbon can be observed. For Ta₂O₅-R3-1, only the bands corresponding to the Ta₂O₅ can be

observed. The results demonstrated not only the carbon has been completely removed in sample Ta₂O₅-R3-1 but also Ta₂O₅ in the sample Ta₂O₅-R3-1-C was completely wrapped by the in-situ formed carbon. In addition, the corresponding N2 sorption of Ta₂O₅-R3-1-C was also measured (SI Figure 3), which showed higher surface area (95.9 m²/g) and lower pore volume (0.06 cm³/g) comparing with those of Ta₂O₅-R3-1. Overall, these results indicated that the carbon layer formed in situ limited Ta₂O₅ crystal growth in Ta₂O₅-R3-1 leading to its much higher surface area and smaller pore size compared with Ta₂O₅-R2-1. This carbon layer was easily removed by calcination in air, which provided a well-defined crystalline mesoporous Ta₂O₅ (Figure 5b) with high surface area. TG-DTA measurements provided carbon mass contents of 3.94 and 7.16 wt% for Ta₂O₅-R1-1-C and Ta₂O₅-R3-1-C, respectively (SI, Figures 4a and 4c). The partially decomposed or carbonized P-123 during heat treatment at 250 °C contributed to an increase in carbon yield, which predominantly originates from SDA carbonization during the calcination.



Fig. 6 XRD patterns of mesoporous Ta_2O_5 samples synthesized through route 3. Bar markers correspond to peaks for crystalline Ta_2O_5 . (JCPDS No. 71-0639).





Fig. 7 $N_{\rm 2}$ sorption isotherms (a) and pore size distributions (b) of mesoporous Ta_2O_5 samples synthesized using route 3.





Fig. 8 TEM images of (a) Ta₂O₅-R3-2, (b) Ta₂O₅-R3-3, (c) Ta₂O₅-R3-4, and (d) Ta₂O₅-R3-4-C. (Insets) Corresponding diffraction patterns.

The role of the in situ formed carbon was further investigated by varying its final concentration in mesoporous Ta₂O₅. A gradual decrease in the amount of TaCl₅ added to the precursor solution increased the final content of the in situ formed carbon in mesoporous Ta₂O₅ compared to Ta₂O₅-R3-1-C. More carbon wrapped around Ta₂O₅ pores would restrict mass transfer more effectively during crystallization and limit the crystal size. Three additional samples (Ta₂O₅-R3-2, Ta₂O₅-R3-3, and Ta₂O₅-R3-4) were synthesized through route 3. XRD patterns (Figure 6) showed well-resolved peaks for all samples; evidence for the formation of crystalline Ta₂O₅. Diffraction intensities decreased and the peaks widened when the added amount of TaCl₅ decreased. Crystal sizes calculated from (001) diffraction peaks using Scherrer's equation equalled 25, 21, and 19 nm for Ta₂O₅-R3-2, Ta₂O₅-R3-3, and Ta₂O₅-R3-4, respectively. Figure 7 shows N₂ sorption isotherms (a) and pore size distributions (b) for the three samples. All isotherms displayed type-IV patterns and revealed that Ta₂O₅-R3-2, Ta₂O₅-R3-3, and Ta₂O₅-R3-4 exhibited much higher N₂ adsorbed volumes and their N₂ uptake leap point gradually moved to lower p/p_0 range compared to Ta₂O₅-R3-1, indicative of their higher surface area and smaller pores. Pore volumes of 88.8, 110.0, and 117 m²/g and pore sizes of 10.6, 7.1, and 5.4 nm were obtained for Ta₂O₅-R3-2, Ta₂O₅-R3-3, and Ta₂O₅-R3-4, respectively (Table 1). To the best of our knowledge, the crystalline mesoporous Ta₂O₅-R3-4 has the highest surface area reported.

TEM images clearly showed that Ta₂O₅-R3-2 (Figure 8a), Ta₂O₅-R3-3 (Figure 8b) and Ta₂O₅-R3-4 (Figure 8c) adopted clear mesoporous structures, and their diffraction patterns (insets) suggested the crystallinity of Ta₂O₅. High resolution TEM images also displayed clear crystalline stripes and mesopores(SI, Figure 5). The TG–DTA measurements provided in situ carbon contents of 8.5, 12.7, and 17.2 wt% for Ta₂O₅-R3-2-C, Ta₂O₅-R3-3-C, and Ta₂O₅-R3-4-C, respectively (SI, Figures 4d–f). Between Ta₂O₅-R3-1-C and Ta₂O₅-R3-4-C, in situ formed carbon contents increased from 7.16 to 17.2 wt% and surface areas increased from 28 to 19 nm, further suggesting that the in situ formed carbon limits mass transfer and crystal size growth during crystallization and finally leads to the formation of crystalline mesoporous Ta₂O₅ with a high surface area.





Fig. 9 (a) N_2 sorption isotherms and pore size distribution (inset) and (b) XRD pattern of $Nb_2O_5\text{-R3}$. Bar markers correspond to peaks for crystalline Nb_2O_5 (JCPDS No. 71-0336).



Fig. 10 (a) N_2 sorption isotherms and pore size distribution (inset) and (b) XRD pattern of TiO₂-R3. Bar markers correspond to peaks for crystalline TiO₂ (JCPDS No. 99-0008).

 Table 1. Physical properties of as-synthesized crystalline mesoporous metal oxide samples

Sample name	$S_{BET}\!/m^2.g^{\text{-}1}$	Pore size/nm	Pore volume/ mL.g ⁻¹	Crystallite size/nm*
Ta ₂ O ₅ -R1-1	37.7	9.2	0.08	39
Ta ₂ O ₅ -R2-1	24.0	24.5	0.13	50
Ta ₂ O ₅ -R3-1	56.6	9.2	0.13	28
Ta ₂ O ₅ -R3-2	88.8	10.6	0.28	25
Ta ₂ O ₅ -R3-3	110.0	7.1	0.23	21
Ta2O5-R3-4	117.0	5.4	0.18	19
Ta ₂ O ₅ -R3-1-HT	23.3	21.3	0.13	44
Nb ₂ O ₅ -R3	125.0	8.1	0.25	28
TiO ₂ -R3	76.2	13.9	0.39	34
[*] Crystallite sizes were calculated using Scherrer's equation. Calculations				

used (001) diffraction peaks for Ta_2O_5 and Nb_2O_5 samples and (101) peaks for TiO_2 samples.

Crystalline mesoporous Nb2O5 and TiO2 synthesis. The route 3 was extended to the synthesis of crystalline mesoporous Nb₂O₅ and TiO₂, and experimental details are enclosed in SI. Nb₂O₅-R3 (Figure 9a) and TiO₂-R3 (Figure 10a) showed type-IV N₂ sorption isotherms and narrow mesopore size distribution. Surface areas of 125.0 and 76.2 m²/g and pore sizes of 8.1 and 13.9 nm were obtained for Nb₂O₅-R3 and TiO₂-R3, respectively. The obtained results were significantly high compared to the reported data.¹⁵ The XRD patterns of Nb₂O₅-R3 (Figure 9b) and TiO₂-R3 (Figure 10b) showed several well-resolved peaks. Comparing peak positions with crystallographic databases identifies the materials as niobium oxide for Nb₂O₅-R3 (PDF no. 71-0336) and anatase phase for TiO₂-R3 (PDF no. 21-1272). Low magnification and high resolution TEM images, along with selected area diffraction patterns, clearly showed that the mesoporous Nb₂O₅-R3 (SI, Figure 6) and TiO₂-R3 structure (SI, Figure 7) consisted of polycrytallites. Since the synthetic conditions of crystalline mesoporous Nb2O5 and TiO2 have not been optimized yet, materials with higher surface areas are still expected.

From above described results and discussions, one general method is successfully developed to synthesize crystalline mesoporous d⁰ metal oxides with higher surface area and narrow mesopore size distribution. During the synthesis procedure, two treatments play vital roles to finally obtain crystalline mesoporous metal oxides. One is the intermediate heat treatment to reconsolidate the structure and partially decompose the P-123 into carbon rich species; the other treatment is high temperature calcination in inert atmosphere to form the in situ carbon wrapping on metal oxides. By these two treatments, the porous structure collapse and crystal size growth during crystallization at a high temperature have been successfully restricted. Notably, the commonly used surfactant P-123 without sp²-hybridizedcarbon can also form enough in situ carbon, which can effectively restrict mass transfer during crystallization and thus successfully prevent the crystal size growth.

Photocatalytic Performance of As-Synthesized Crystalline Mesoporous Ta₂O₅. Ta₂O₅ using NiO_x as the cocatalyst is well known for its overall water splitting under UV light irradiation.²⁵⁻²⁷ With the attributes of high surface area (more cocatalysts and active sites) and thin crystalline wall (short distance for photoexcited electrons and holes to research reaction surface), the crystalline mesoporous Ta₂O₅ showed enhanced photocatalytic water splitting.^{11,13} Herein, the water splitting activities of the as-synthesized crystalline mesoporous Ta2O5 samples using NiOx as cocatalyst were also evaluated. Figure 11 shows the dependence of the photocatalytic activity of assynthesized crystalline mesoporous Ta2O5 on the loading amount of NiOx. For all the samples, the activity increased with the loading amount increase of NiO_x at first, and then gradually decreased. The highest H₂ evolution rate for Ta₂O₅-R1-1, Ta₂O₅-R2-1, and Ta₂O₅-R3-1 were 124.6, 648.4 and 273.5 μ mol g⁻¹ h⁻¹, respectively. The corresponding results on the time course of gas evolution from water splitting are enclosed in SI. Figure 8. Notably, Ta₂O₅-R3-1 had the highest surface area, but Ta₂O₅-R2-1 showed the best photocatalytic activity, whose results are inconsistent with former reports.^{11,13} The x-ray photoelectron spectroscopy (XPS) was used to investigate the oxidation state of the crystalline mesoporous Ta₂O₅ samples. Figure 12 shows the Ta 4p and Ta 4d orbitals of XPS spectra of Ta₂O₅. Compared with the Ta 4p and Ta 4d peaks of Ta₂O₅-R2-1, the Ta 4p and Ta 4d peaks of Ta₂O₅-R3-1-C shifted to lower binding energy, which showed that some Ta atoms were reduced by carbon during calcination in N2.28 The reduced Ta atoms might have produced defects that functioned as trap sites for photogenerated electron and holes. This was the main reason Ta2O5-R3-1 showed lower activity compared with Ta₂O₅-R2-1. After the heat treatment at 800 °C in air, the photocatalytic activity of Ta₂O₅-R3-1-HT was greatly enhanced (Figure 11d), and the highest H₂ evolution rate of Ta₂O₅-R3-1-HT was 709.1 μ mol g⁻¹ h⁻¹. The Ta 4p and Ta 4d peaks of XPS spectra of Ta₂O₅-R3-1-HT (Figure 12) shifted to higher binding energy compared with those of Ta₂O₅-R3-1 and Ta₂O₅-R2-1. The SEM image and N₂ sorption isotherm (inset is the pore size distribution) of Ta₂O₅-R3-1-HT (SI, Figure 9) showed that the mesopore size increased to 21.3 nm (9.2 nm for Ta₂O₅-R3-1) and the surface area greatly decreased to 23.3 m^2/g (56.6 m^2/g for Ta₂O₅-R3-1). Simultaneously, the crystal size grew up from 19 (Ta₂O₅-R3-1) to 44 nm (Ta₂O₅-R3-1-HT). From the TG-DTA results (SI, Figure 4), the slight weight increase for all the samples with carbon was clearly observed, which is different from the results of Ta₂O₅-1-250 (SI, Figure 4b) and can be ascribed to the oxidization of reduced Ta and some O atoms incorporated into the crystal lattice of Ta₂O₅. The results indirectly demonstrated the existence of some reduced Ta atoms in the samples (Ta2O5-R3-1-C). In fact, already there are some reports²⁹⁻³³ utilizing the reduction property of carbon at increased temperature to in-situ reduced transition metal ions. Then, the transition metal/carbon composite can be obtained.



Fig. 11 Dependence of the photocatalytic activity of as-synthesized crystalline mesoporous Ta_2O_5 on loading amount of NiO_x , (a) Ta_2O_5 -R1-1, (b) Ta_2O_5 -R2-1, (c) Ta_2O_5 -R3-1 and (d) Ta_2O_5 -R3-1-HT.



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Fig. 12 X-ray photoelectron spectroscopy (XPS) spectra of Ta 4p (a) and Ta 4d (b) of mesoporous Ta_2O_5 samples.

Owing to the wide band gap of Ta_2O_5 (4.0 eV), water splitting can be only achieved under UV irradiation.^{13,27} Tantalum (oxy)nitride (TaON) and tantalum nitride (Ta₃N₅) have narrower band gap and the proper conduction and valence band to achieve water splitting under visible light irradiation.³⁴⁻³⁶ Based on the method developed in this study, further research on the crystalline mesoporous TaON and Ta₃N₅ synthesis are under the consideration.

Conclusions

In a summary, crystalline mesoporous Ta₂O₅, Nb₂O₅, and TiO₂ with a high surface area and narrow mesopore size distribution have been successfully synthesized using triblock copolymer (P123) as the mesostructure directing agent. The pretreatment at intermediate temperature on the EISA induced gel made the porous structure stable during the following calcination at higher temperatures. In addition, the pretreatment partially decomposed the P-123 into carbon- rich species, which can yield more in situ formed carbon during the following calcination in N₂ atmosphere. Notably, we successfully demonstrated that the very commonly used SDA P-123 can be also converted into a much amorphous carbon, although no sp²-hybridized-carbon exists in the P-123. The in situ formed carbon wrapping on the metal oxides can restrict the mass transfer and crystal growth during crystallization at high temperature calcination. The surface area and pore size of the typically synthesized crystalline mesoporous Ta₂O₅, Nb₂O₅ and TiO₂ are 117.0 m²/g (5.4 nm), 125 m²/g (8.1 nm) and 76.2 m²/g (13.9 nm), respectively. The as-synthesized crystalline samples such as Ta₂O₅-R3-1-C have some reduced Ta atoms, which produced defects and deteriorated the photocatalytic activity of the corresponding sample after carbon removal. We believe our method offers a very good and flexible choice to synthesize crystalline mesoporous transition metal oxides with high surface areas.

Acknowledgements

This work was supported by the International Institute for Carbon-Neutral Energy Research (WPI-I²CNER), which was established by the World

Premier International Research Centre Initiative (WPI), the Ministry of Education, Culture, Sports, Science and Technology (MEXT) and Grantsin-Aid: 26810125 from MEXT (Japan). Kyushu University offered the financial supporting for English editing.

Notes and references

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 \dagger Electronic Supplementary Information (ESI) available: Experimental, Raman spectrum, SEM image, TEM images, N_2 sorption isotherms, TG-DTA curves, and photocatalytic results. See DOI: 10.1039/b000000x/

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