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Porous niobia spheres with large surface area: alcothermal synthesis and controlling of their composition and phase transition behaviour†

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Submicron-sized niobia (Nb₂O₅) porous spheres with a high specific surface area (300 m² g⁻¹) and nano concave–convex surfaces were synthesized *via* a rapid one-pot single-step alcothermal reaction. Prolonged reaction time or high reaction temperatures resulted in a morphology change of Nb₂O₅ from amorphous sphere to rod crystals with hexagonal crystal phase. A similar alcothermal reaction yielded TiO₂–Nb₂O₅ composite porous spheres, whose Ti : Nb molar ratio was controlled by changing the precursor solution component ratios. A simple thermal treatment of amorphous TiO₂–Nb₂O₅ porous spheres consisting of 1 : 2 (molar ratio) Ti : Nb at 600 °C for 2 h induced crystal phase transfer from amorphous to a monoclinic crystal phase of submicron-sized TiNb₂O₇ porous spheres with a specific surface area of 50 m² g⁻¹.

Introduction

Porous materials, including activated carbon, SiO₂, metal oxides, zeolites, and metal–organic frameworks (MOFs), are promising functional materials because of their large surface area that can be used to adsorb several materials and achieve material storage-release for material transfer. These unique properties allow for applications such as gas storage and separation, catalysis, and catalyst supports.¹ In particular, metal oxides are intriguing because of their intrinsic high-temperature stability and durability.²

To obtain porous materials, several methods, including solution combustion,³ dealloying,⁴ electrochemical deposition,⁵ spray pyrolysis,⁶ sol–gel method,⁷ as well as hydrothermal and solvothermal methods,⁸ have been developed. In particular, the solvothermal method using high-temperature non-aqueous solvents as reaction media is a novel approach to prepare size-, morphology-, and stoichiometry-controlled metal oxides. In this context, a unique one-pot and single-step solvothermal method was developed to afford SiO₂, TiO₂, ZnO, ZrO₂, and CeO₂ with porous spherical morphologies, where numerous few nm-sized primary particles aggregate to yield a spherical secondary morphology with a few hundred nm in diameter.⁹

These porous spheres were named meso/macroporously architected roundly integrated metal oxides (MARIMOs). The large surface areas of MARIMOs with micro- and mesopores and nano concave–convex surface structure impart their unique abilities. Both solid and hollow MARIMOs can be obtained with TiO₂. In addition, composite MARIMOs, including CeO₂–ZrO₂,¹⁰ Al₂O₃–TiO₂,¹¹ ZnO–TiO₂,¹¹ SiO₂–TiO₂,¹² Co/Mn oxide,¹³ Ni/Mn oxide,¹³ and Co/Mn/Fe oxide¹³ have been prepared *via* the solvothermal method with tightly controllable stoichiometry. Thus, solvothermal method is a versatile approach for obtaining metal oxides with a porous spherical structure, large surface area, and nano concave–convex surface structure.

Nb₂O₅ has been used as a photocatalyst,^{14,15} solid acid,¹⁶ catalyst support,^{17,18} and anode material for lithium and sodium ion batteries.¹⁹ Several preparation methods are available for these materials.²⁰ For example, Li *et al.* prepared monodisperse glycolated niobium oxide spheres *via* a simple antisolvent precipitation approach. Mesoporous niobium oxide spheres with a high specific surface area of 312 m² g⁻¹ were obtained by hydrothermal treatment.²¹ Li *et al.* synthesized Nb₂O₅ hollow nanospheres by heating a water solution of niobium oxalate and sodium dihydrogen phosphate dihydrate at 220 °C for 48 h.²² Dai *et al.* prepared monodispersed Nb₂O₅ microspheres *via* a facile one-pot solvothermal route using an isopropyl alcohol solution of niobium pentachloride and tetrabutyl ammonium hydroxide at 200 °C for 24 h.²³ However, simpler preparation methods should be developed for further acceleration of their practical uses. Thus, niobium oxide and variants of MARIMOs with large surface area were prepared herein using a facile synthesis method for Nb₂O₅, TiO₂–Nb₂O₅ composite, and TiNb₂O₇ MARIMOs.

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Results & discussion

Synthesis and morphology changes of Nb₂O₅ MARIMO

Nb₂O₅ MARIMO was prepared according to a similar method reported previously (entry 1 in Table 1).⁹ Simple heating of a methanol solution of Nb(OEt)₅ and formic acid at 300 °C for 10 min afforded Nb₂O₅ MARIMO in high yield (>90%). The scanning electron microscopy (SEM) images revealed that the obtained Nb₂O₅ MARIMO was perfectly monodispersed (Fig. 1a(i)), and their shape was approximately spherical with a diameter of 630 ± 50 nm (Fig. 1a(ii), 1b(i) and S1,† red line). Also, the obtained Nb₂O₅ MARIMO was composed of many amounts of a few nm sized primary particles (Fig. 1b(ii)). The formation mechanism of Nb₂O₅ MARIMO was expected to be similar to a proposed mechanism in our previous report.⁹ In the initial steps of the reaction, primitive niobium alkoxide oligomers are formed in high-temperature methanol and interconnected *via* surface interactions with carboxyl groups. As the further heating reaction of precursor mixture proceeds, niobium alkoxide oligomers react with the water, which generated by esterification of formic acid and methanol and/or dehydration condensation of methanol, to form Nb₂O₅. The pore structures are formed by gaseous products, such as CO₂ and hydrocarbons generated by decomposition of alkoxide and formic acid, trapped inside the sphere. The Nb₂O₅ MARIMO obtained without formic acid was polydisperse and obtained in low yield (<40%; Fig. S2a†). In addition, when the solvent was changed to water, spherical shapes were not formed (Fig. S2b†). From the results of the control experiment, the combination of Nb(OEt)₅, formic acid, and methanol is essential for the formation of a spherical morphology and high yield.

The direct evidence of the formation of a pore in Nb₂O₅ spheres was confirmed by nitrogen adsorption–desorption measurements (Fig. S3a(i)†). If the obtained Nb₂O₅ MARIMO has no pores, the specific surface area should be a few m² g⁻¹ estimated from the diameter (*ca.* 630 nm) and specific density ($d = 4.6 \text{ g cm}^{-3}$). Contrary to this expectation, the obtained Nb₂O₅ MARIMO showed a high specific surface area (302 m² g⁻¹) and porous structure less than 10 nm-sized (Fig. S3a(ii)†). This fact strongly supports the presence of the penetrated pore inside the spherical particles.

To further characterization of the obtained Nb₂O₅ MARIMO, powder X-ray diffraction (XRD) and electron microscopic

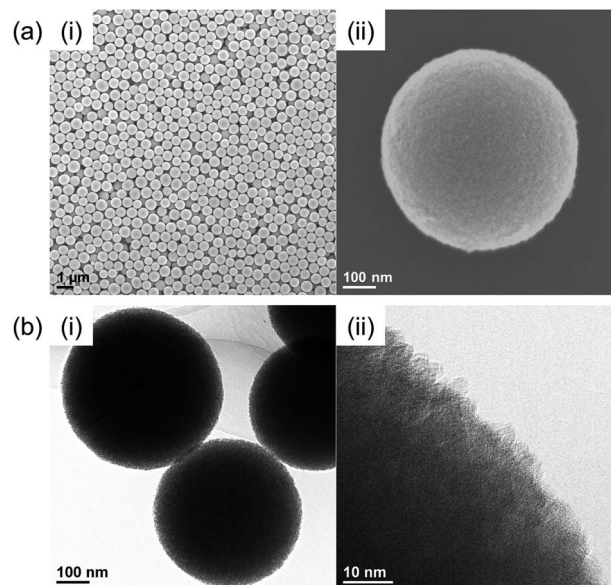


Fig. 1 (a) SEM and (b) TEM images of the prepared Nb₂O₅ MARIMO at (i) low magnification and (ii) high magnification.

measurements were performed. No peaks were observed in the corresponding XRD pattern (Fig. 2c, red line), and no fringe structure in the Nb₂O₅ MARIMO primary particle was observed in the high-resolution transmission electron microscopy (HR-TEM) image (Fig. 1b(ii)). This indicated that the obtained Nb₂O₅ MARIMO was not crystalline but amorphous.

To date, almost 15 polymorphic forms of Nb₂O₅ have been reported; however, hexagonal, orthorhombic, and monoclinic phases are relatively common.²⁰ The crystal phases significantly affect the activity of the photocatalyst²⁴ and solid acid.²⁵ Thus, it is important to control of the crystal phase formation in the obtained Nb₂O₅ MARIMO. The easiest method to improve the crystallinity is further heating. When the heating time of the precursor solution was prolonged to 60 min, the crystal phase dramatically changed from amorphous to the hexagonal phase of Nb₂O₅ (Fig. 2c). This was concomitant with a drastic morphology change from spherical to rod-shaped (Fig. 2a(ii)). The corresponding HR-TEM image (Fig. 2b) showed that the crystal lattice distances were 0.39 nm. In addition, the fast Fourier transform (FFT) pattern in the HR-TEM image indicated

Table 1 Molar ratios of Ti and Nb, specific surface area, pore size, and TiO₂ crystalline size of the prepared MARIMOs

Entry	Sample name of MARIMO ^a	Molar ratio of Ti and Nb		Specific surface area ^c [m ² g ⁻¹]	Pore size ^d [nm]	TiO ₂ crystalline size ^e [nm]
		Precursor solution	Product ^b			
1	Nb ₂ O ₅	0 : 100	—	302	3.3	—
2	TiO ₂ -Nb ₂ O ₅ -75	25 : 75	21.7 : 78.3	274	5.9	34.7
3	TiO ₂ -Nb ₂ O ₅ -50	50 : 50	50.1 : 49.9	200	8.9	13.6
4	TiO ₂ -Nb ₂ O ₅ -25	75 : 25	74.3 : 25.7	250	3.4	10.0
5	TiO ₂	100 : 0	—	234	3.6	9.6

^a Denotes the atomic% of Nb to total number of Nb and Ti atoms. ^b Evaluated by STEM/EDX analysis. ^c BET method. ^d BJH plot. ^e Estimated using the Scherrer equation.



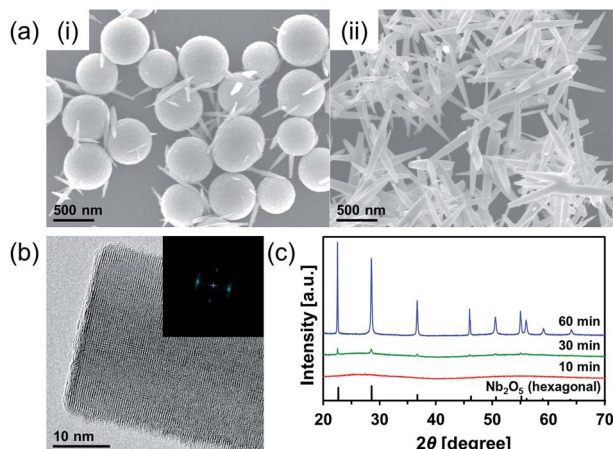


Fig. 2 (a) SEM images of the Nb_2O_5 obtained at 300 °C with different solvothermal-reaction times (i) 30 min and (ii) 60 min. (b) HR-TEM image of the rod-like Nb_2O_5 ; corresponding FFT image is inset. (c) XRD patterns of the powdery products obtained using different solvothermal-reaction times (blue, 60 min; green, 30 min; red, 10 min). Reference peaks of hexagonal Nb_2O_5 (JCPDS 00-007-0061) are represented by the black line.

that the direction of rod growth was along the [001] facet. When a 30 min heating procedure was used, spheres and rods coexisted. Compared to 10 min heating, a volume reduction of approximately 40% was observed for the 30 min heating process, where the diameter of the obtained Nb_2O_5 MARIMO decreased to 530 ± 50 nm (Fig. 2a(i) and S1,† blue line). Ostwald ripening was likely responsible for this shrinkage.^{26,27} Similarly, higher reaction temperatures (325 and 350 °C) with a fixed reaction time (10 min) resulted in rod-like hexagonal phase nanocrystals (Fig. S4†). Although the crystallinity was successfully improved by extending the reaction time or using a high reaction temperature, the porosity was lost due to the morphology change, and the specific surface area was greatly reduced.

Calcination of the as-synthesized amorphous Nb_2O_5 MARIMO was used as an alternative method to change the crystal phase. Generally, amorphous Nb_2O_5 crystallizes at 500 °C into hexagonal or orthorhombic phase, tetragonal phase at 800 °C, and monoclinic phase at >1000 °C.²⁸ An exothermic phenomenon was observed at approximately 240 and 560 °C in the thermogravimetric-differential thermal analysis (TG-DTA, Fig. 3a). The exothermic peak at approximately 240 °C originated from the combustion of organic residues included in MARIMO. In addition, the exothermic peak with negligible weight loss at approximately 560 °C was assigned to a crystalline phase transfer.²⁹ Calcination of the as-synthesized amorphous Nb_2O_5 MARIMO yielded a hexagonal phase at 500 °C and an orthorhombic phase at >600 °C, as determined from their XRD patterns (Fig. 3b). The spherical morphology was maintained at ≤ 600 °C, but collapsed at 700 °C (Fig. 3c(i) and S5†). Thus, Nb_2O_5 MARIMO with improved crystallinity was successfully obtained *via* calcination at 500 or 600 °C for 2 h (Fig. 3b, c and S5a†). The specific surface area of Nb_2O_5 MARIMO calcined at

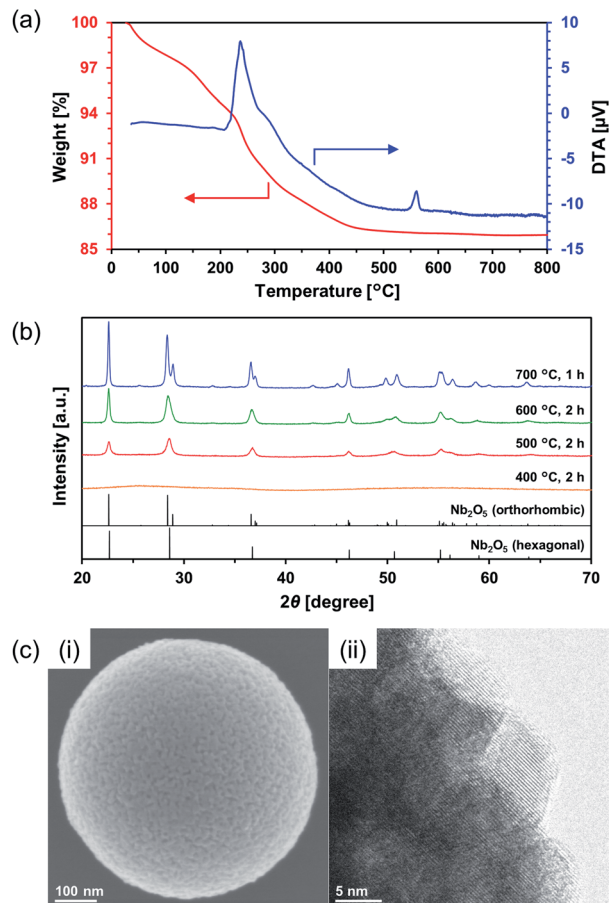


Fig. 3 (a) TG-DTA profiles of the as-synthesized Nb_2O_5 MARIMO measured in air at a heating rate of 2 °C min^{-1} . (b) XRD patterns of calcined Nb_2O_5 MARIMO at 400–700 °C (blue, 700 °C; green, 600 °C; red, 500 °C; orange, 400 °C). Reference peaks of orthorhombic Nb_2O_5 (JCPDS 01-071-0336) and hexagonal Nb_2O_5 (JCPDS 00-007-0061) are represented by black lines. (c) SEM (i) and HR-TEM (ii) images of the Nb_2O_5 MARIMO calcined at 500 °C for 2 h. The crystal lattice distances were 0.31 nm.

500 °C was 88 $\text{m}^2 \text{g}^{-1}$ and average pore size expanded from 3.3 to 6.4 nm upon calcination (Fig. S3b†).

Synthesis of TiO_2 - Nb_2O_5 composite MARIMO

Ti-Nb binary oxides have attracted significant attention since their discovery as they exhibit reduced electrical resistance,³⁰ high photocatalytic activity under visible light irradiation,³¹ and controlled Brønsted/Lewis acidity.³² In particular, using Ti-Nb binary oxides in lithium and sodium ion batteries^{19,33,34} has attracted great attention because of its improved electronic conductivity,³⁵ ion diffusion path expansion,³⁵ and high theoretical capacity.³⁶ As mentioned in the introduction, composite MARIMOs consisting of plural metal oxides have been successfully synthesized.^{10–13} Herein, a one-pot and single-step technique was used to obtain TiO_2 - Nb_2O_5 composite MARIMOs.

A methanol solution of $\text{Ti}(\text{O}^i\text{Pr})_4$ and $\text{Nb}(\text{OEt})_5$ with formic acid was heated at 300 °C for 10 min. The molar ratio of Ti to Nb



in the product MARIMO was easily controlled by changing the ratio in the corresponding precursor solution (entries 2–4 in Table 1). Nearly equivalent Ti/Nb ratios between the precursor solutions and products were obtained. As shown in Fig. 4a(i–iii), Ti and Nb atoms were equally distributed at the nano-level in the $\text{TiO}_2\text{-Nb}_2\text{O}_5\text{-75}$, $\text{TiO}_2\text{-Nb}_2\text{O}_5\text{-50}$, and $\text{TiO}_2\text{-Nb}_2\text{O}_5\text{-25}$ samples, where the numbers denote the atomic percentage of Nb among the total number of Nb and Ti atoms. In addition, the $\text{TiO}_2\text{-Nb}_2\text{O}_5$ composite MARIMOs were highly porous with specific surface areas of $>200\text{ m}^2\text{ g}^{-1}$ (Table 1 and Fig. S6†).

Only the tetragonal (anatase-type) TiO_2 peaks were observed in the XRD profiles when Nb atoms were included in the product MARIMOs (Fig. 4b(i)). Lower angle shifts of the diffraction peaks were also observed in the XRD profiles (Fig. 4b(ii)), indicating that the composite MARIMOs consisted of solid solutions and the crystal lattice was enlarged by the doped Nb atoms with larger ionic radii ($\text{Nb}^{5+} = 0.64\text{ \AA}$, $\text{Ti}^{4+} = 0.61\text{ \AA}$).³⁷ Additionally, precursor solutions containing larger amounts of $\text{Nb}(\text{OEt})_5$ resulted in the larger primary particle sizes of TiO_2 in the resulting MARIMOs (Table 1). However, this crystalline growth of TiO_2 was not observed for the $\text{Al}_2\text{O}_3\text{-TiO}_2$,

ZnO-TiO_2 , and $\text{SiO}_2\text{-TiO}_2$ composites.^{11,12} Thus, the observed crystalline growth of TiO_2 can be ascribed to the catalytic effect of solid Nb_2O_5 as a solid acid that promoted crystalline growth.

Interestingly, hollow MARIMO were formed at a 50 : 50 Ti/Nb molar ratio (Fig. 4a(ii) and S7†). However, solid $\text{TiO}_2\text{-Nb}_2\text{O}_5\text{-50}$ MARIMO was obtained (Fig. S8†) when the reaction was immediately quenched at 0 min (the reaction temperature was $300\text{ }^\circ\text{C}$). From the XRD patterns, the longer reaction time yielded better crystallinity (Fig. S9†). Ostwald ripening was likely the cause of the hollow MARIMO formation.³⁸ These unique hollow structures imparted large surface area, low density, and high loading capacity. Therefore, the prepared materials offer promising potential for use in advanced micro-/nanoreactors, catalysis, energy storage/conversion, biomedicine, sensors, and environmental remediation applications.^{39–41}

Formation of TiNb_2O_7 MARIMO by crystallization of amorphous $\text{TiO}_2\text{-Nb}_2\text{O}_5$ composite MARIMO

TiNb_2O_7 as an anode material for lithium ion batteries has a high theoretical capacity of 387.6 mA h g^{-1} derived from its 5-electron transfer mechanism ($\text{Ti}^{4+}/\text{Ti}^{3+}$, $\text{Nb}^{5+}/\text{Nb}^{4+}$, and $\text{Nb}^{4+}/\text{Nb}^{3+}$). This value is approximately two times higher than that of the commonly used $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (175 mA h g^{-1}).³⁶ Thus, TiNb_2O_7 has attracted significant attention is promising for application in electric vehicles.^{19,33,34} However, TiNb_2O_7 suffers from low ionic and electric conductivity. Tailoring special nanostructures of TiNb_2O_7 can be used to harness the advantages of nano-materials, including high electrode/electrolyte contact area and short ion diffusion distances. In particular, microscale spherical materials with hierarchical nanoscale structure are promising for solving the drawbacks of pure nanoscale porous materials with low tap densities and poor coulombic efficiency. Although, the syntheses of TiNb_2O_7 porous spheres have been previously reported, those with larger surface areas remain elusive (Table S1†). Thus, to obtain TiNb_2O_7 porous spheres with large surface area, the synthetic conditions of the precursor composite $\text{TiO}_2\text{-Nb}_2\text{O}_5$ as well as the calcination conditions were closely examined.

First, a similar alcohothermal treatment of a 1 : 2 (mol ratio) $\text{Ti}(\text{O}^i\text{Pr})_4$ and $\text{Nb}(\text{OEt})_5$ mixed methanol solution including formic acid at $300\text{ }^\circ\text{C}$ afforded a precursor composite MARIMO with tetragonal (anatase-type) TiO_2 and amorphous Nb_2O_5 as determined from its XRD pattern (Fig. S10,† blue line). The corresponding SEM images revealed characteristically large primary particles on the MARIMO surface (Fig. S11a(i)†). The second step involved calcination of the precursor MARIMO at $700\text{ }^\circ\text{C}$ for 2 h and yielded monoclinic TiNb_2O_7 MARIMO (Fig. S11a(ii) and S12a†, blue line). However, the XRD patterns showed that the calcined MARIMO contained mainly monoclinic TiNb_2O_7 with a small amount of tetragonal (anatase-type) TiO_2 and orthorhombic Nb_2O_5 (Fig. S12b†, blue line). This indicates that a pure TiNb_2O_7 MARIMO was not afforded by the calcination of the as-synthesized $\text{TiO}_2\text{-Nb}_2\text{O}_5$ MARIMO obtained at $300\text{ }^\circ\text{C}$.

Therefore, amorphous $\text{TiO}_2\text{-Nb}_2\text{O}_5$ composite MARIMO was selected as an alternative precursor (Fig. S10, red line and

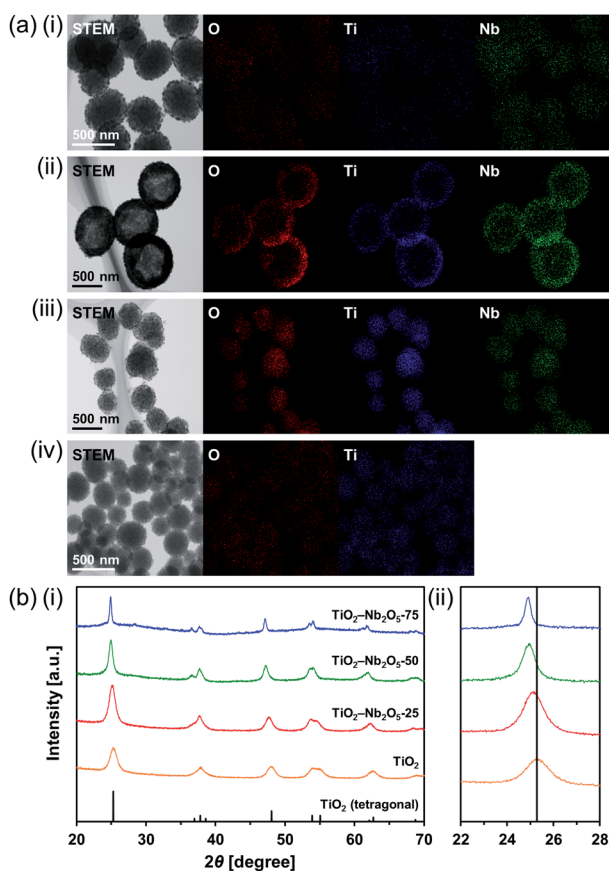


Fig. 4 (a) STEM/EDX analysis of the prepared $\text{TiO}_2\text{-Nb}_2\text{O}_5$ composite MARIMOs; (i) $\text{TiO}_2\text{-Nb}_2\text{O}_5\text{-75}$, (ii) $\text{TiO}_2\text{-Nb}_2\text{O}_5\text{-50}$, (iii) $\text{TiO}_2\text{-Nb}_2\text{O}_5\text{-25}$, and (iv) TiO_2 . (b) XRD patterns of the obtained powdery products prepared with different molar ratios of Ti/Nb (blue, $\text{TiO}_2\text{-Nb}_2\text{O}_5\text{-75}$; green, $\text{TiO}_2\text{-Nb}_2\text{O}_5\text{-50}$; red, $\text{TiO}_2\text{-Nb}_2\text{O}_5\text{-25}$; orange, TiO_2). Reference peaks corresponding to tetragonal TiO_2 (JCPDS 00-021-1272) are represented by the black line. The 2θ range: (i) $20\text{--}70^\circ$, (ii) $22\text{--}28^\circ$.



S11b(i)†). The material was prepared using a lower temperature (200 °C) alcohothermal reaction. As shown in Fig. 5a, calcination of the amorphous $\text{TiO}_2\text{-Nb}_2\text{O}_5$ composite MARIMO at >600 °C for 2 h produced the desired TiNb_2O_7 MARIMO with a pure monoclinic phase. In addition, tetragonal (anatase-type) TiO_2 and orthorhombic Nb_2O_5 peaks were not observed even in case of the obtained sample at 700 °C (Fig. S12b†, red line). Fringe structures were observed in the HR-TEM image (Fig. 5b(i)) of the primary particles, clearly showing that the MARIMO was composed of single crystals of TiNb_2O_7 . The TiNb_2O_7 porous morphology was clearly demonstrated by high angle annular dark-field scanning transmission electron microscopy (HAADF-STEM; Fig. 5b(ii)). The specific surface area of the obtained monoclinic TiNb_2O_7 MARIMO was smaller ($50\text{ m}^2\text{ g}^{-1}$) than that before calcination (Fig. S13†, $497\text{ m}^2\text{ g}^{-1}$), but $50\text{ m}^2\text{ g}^{-1}$ is the highest value reported for this type of material to the best of our knowledge (Fig. 5c(i) and Table S1†). As expected, the average pore size was enlarged from 2.5 to 8.8 nm (Fig. 5c(ii)), which is favourable for guest materials to access deep into the porous

spheres. In addition, the pore space between the TiNb_2O_7 MARIMO can buffer volume changes derived from the phase transitions occurring during lithiation/delithiation, which may result in good cycling performance *via* enhanced structural stability.⁴² Thus, TiNb_2O_7 porous spheres were successfully prepared with a monoclinic crystal phase and wide pores by calcination of the amorphous $\text{TiO}_2\text{-Nb}_2\text{O}_5$ composite MARIMO precursor.

Conclusions

Monodispersed Nb_2O_5 porous spheres (Nb_2O_5 MARIMO) with 630 nm in diameter were prepared *via* the simple alcohothermal reaction of a methanol solution of $\text{Nb}(\text{OEt})_5$ with formic acid. The crystallinity and pore size of the prepared Nb_2O_5 MARIMO were improved by prolonging the reaction time or simple calcination of the product. $\text{TiO}_2\text{-Nb}_2\text{O}_5$ composite MARIMO was obtained using a similar alcohothermal reaction of $\text{Ti}(\text{O}^i\text{Pr})_4$, $\text{Nb}(\text{OEt})_5$, and formic acid in methanol, with a product Ti : Nb atomic ratio that was controlled by changing molar ratio of $\text{Ti}(\text{O}^i\text{Pr})_4$ and $\text{Nb}(\text{OEt})_5$ in the precursor solution. A two-step synthetic approach for the generation of TiNb_2O_7 porous spheres was developed *via* an alcohothermal treatment of a 1 : 2 (molar ratio) mixed solution of $\text{Ti}(\text{O}^i\text{Pr})_4$ and $\text{Nb}(\text{OEt})_5$ in methanol followed by simple calcination. Considering the fact that the obtained submicron-sized porous spheres of niobia and their composites have a large surface area, high performance can be expected in the field of catalysts and batteries. To evaluate catalyst and battery performance, the research for a practical application is undergoing.

Experimental section

Materials

Methanol, formic acid, niobium(v) ethoxide [$\text{Nb}(\text{OEt})_5$], and titanium tetraisopropoxide [$\text{Ti}(\text{O}^i\text{Pr})_4$] were obtained from FUJIFILM Wako Pure Chemical Corporation. All reagents were used as received unless otherwise noted.

Synthetic procedure

Synthesis of Nb_2O_5 MARIMO. First, $\text{Nb}(\text{OEt})_5$ (0.35 mmol) was added to a solution of formic acid (1.75 mmol) in methanol (3.5 mL) under vigorous stirring. The resultant precursor solution was transferred to an SUS-316 stainless steel tubular reactor with a 10 mL inner volume and the reactor was then sealed with an SUS-316 screw cap. The sealed reactor was heated to 300 °C at a rate of $5.4\text{ }^\circ\text{C min}^{-1}$ and the temperature was maintained at 300 °C for 10 min. The reaction was quenched by placing the reactor in an ice-water bath. The obtained precipitates were centrifuged, washed several times with methanol, and dried under vacuum to afford a powdery product.

Synthesis of $\text{TiO}_2\text{-Nb}_2\text{O}_5$ composite MARIMOs. Aliquots of $\text{Ti}(\text{O}^i\text{Pr})_4$ and $\text{Nb}(\text{OEt})_5$ were added to a solution of formic acid (1.75 mmol) in methanol (3.5 mL) under vigorous stirring. Similar treatments of the solution as the above mentioned

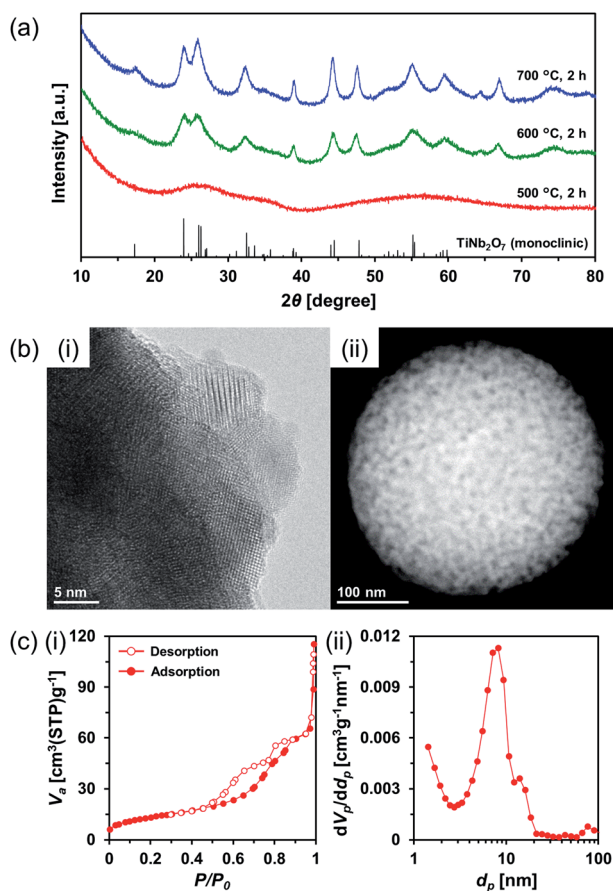


Fig. 5 (a) XRD patterns of the calcined amorphous $\text{TiO}_2\text{-Nb}_2\text{O}_5$ composite MARIMO at 500–700 °C (blue, 700 °C; green, 600 °C; red, 500 °C). Reference peaks of monoclinic TiNb_2O_7 (JCPDS 00-039-1407) are indicated by the black line. (b) HR-TEM (i) and HAADF-STEM (ii) images of the amorphous $\text{TiO}_2\text{-Nb}_2\text{O}_5$ composite MARIMO calcined at 600 °C. (c) Nitrogen adsorption–desorption isotherms (i) and pore size distributions (ii) of the amorphous $\text{TiO}_2\text{-Nb}_2\text{O}_5$ composite MARIMO calcined at 600 °C.



Nb₂O₅ MARIMO synthesis yielded the TiO₂-Nb₂O₅ composite MARIMO powdery products.

Formation of TiNb₂O₇ MARIMO via crystallization of the amorphous TiO₂-Nb₂O₅ composite MARIMO. First, Ti(OⁱPr)₄ (0.58 mmol) and Nb(OEt)₅ (1.17 mmol) was added to a solution of formic acid (8.75 mmol) in methanol (17.5 mL) under vigorous stirring. The resultant precursor solution was sealed in a Teflon-lined autoclave with a 50 mL inner volume. The sealed autoclave was heated to 200 °C at a rate of 5.4 °C min⁻¹ and the temperature was maintained at 200 °C for 3 h. After cooling at room temperature, the precipitates were centrifuged, washed several times with methanol, and dried under vacuum to afford a powdery amorphous TiO₂-Nb₂O₅ composite MARIMO. The obtained product was calcined in air at 600 °C for 2 h at 2 °C min⁻¹ heating rate to yield the final product.

Characterization methods

Transmission electron microscopy. The transmission electron microscopy (TEM) images were obtained using a JEOL JEM-2100F microscope. The specimens were prepared as follows: samples were dispersed in methanol; 10 μL of the resultant dispersion was drop-casted onto a carbon-coated copper micro grid (Okenshoji, Japan); and the solvent was evaporated under atmospheric pressure. Energy-dispersive X-ray (EDX) mapping and line-scan plots for the STEM images were obtained using an Oxford INCA X-max 80 EDX spectrometer.

Scanning electron microscopy. Scanning electron microscopy (SEM) was performed using a Hitachi SU8020 FE-SEM microscope. The specimens were prepared by drop-casting the sample dispersion on a silicon wafer.

X-ray diffraction measurements. X-ray diffraction (XRD) patterns were recorded using a Rigaku SmartLab diffractometer with graphite-monochromatized Cu K α radiation (X-ray wavelength: 1.5418 Å) in steps of 0.02° over the 2 θ range of 10–80°. The powdery samples were placed on a non-refractive silicon holder (Overseas X-ray Service, Japan). The average TiO₂ crystalline sizes were estimated from the obtained (101) peaks using the Scherrer equation.

Thermogravimetric-differential thermal analysis. Thermogravimetric-differential thermal analysis (TG-DTA) was performed using a HITACHI STA7200RV instrument. The samples were placed on an open platinum sample pan and the experiments were conducted in air at a 2 °C min⁻¹ heating rate.

Nitrogen adsorption-desorption isotherm measurements. Nitrogen adsorption-desorption isotherms were obtained using a Belsorp Mini II instrument (MicrotracBEL Corp.). The specific surface areas were determined using the Brunauer-Emmett-Teller (BET) multipoint method with BELMaster7 software. The average pore size distributions were calculated using the Barrette-Joyner-Halenda (BJH) method from the nitrogen adsorption isotherm data.

Conflicts of interest

There are no conflicts to declare.

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