# Electronic Supplementary Information

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

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## Supporting Figures

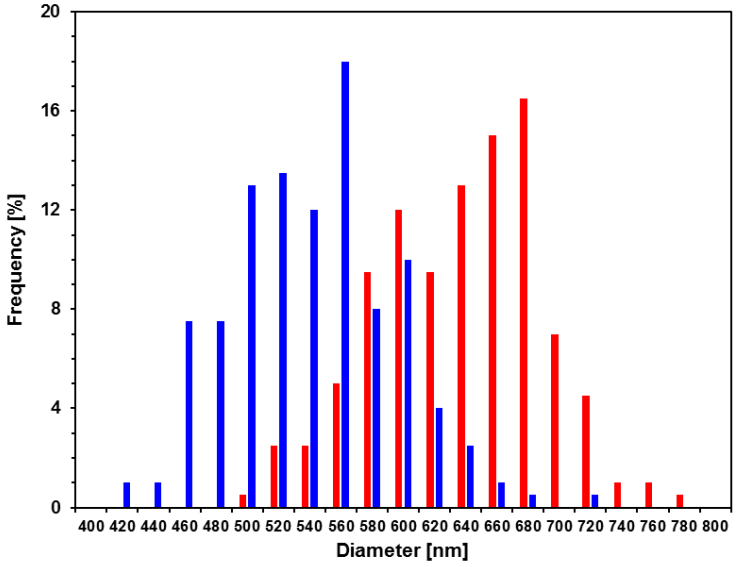


**Figure S1.** Size distribution histogram of $Nb_2O_5$ MARIMOs obtained by 10 min heating (red) in synthesis and by 30 min heating (blue) in synthesis. The size distribution was evaluated by statistical analyses ($N$ = 200) using selected SEM images.

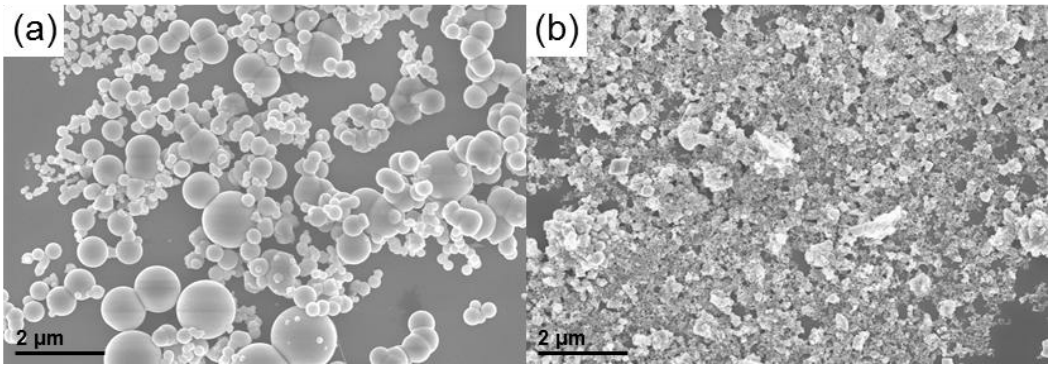


**Figure S2.** SEM images of the $Nb_2O_5$ obtained from precursor solutions of (a) $Nb(OEt)_5$ and methanol and (b) $Nb(OEt)_5$, formic acid, and water.

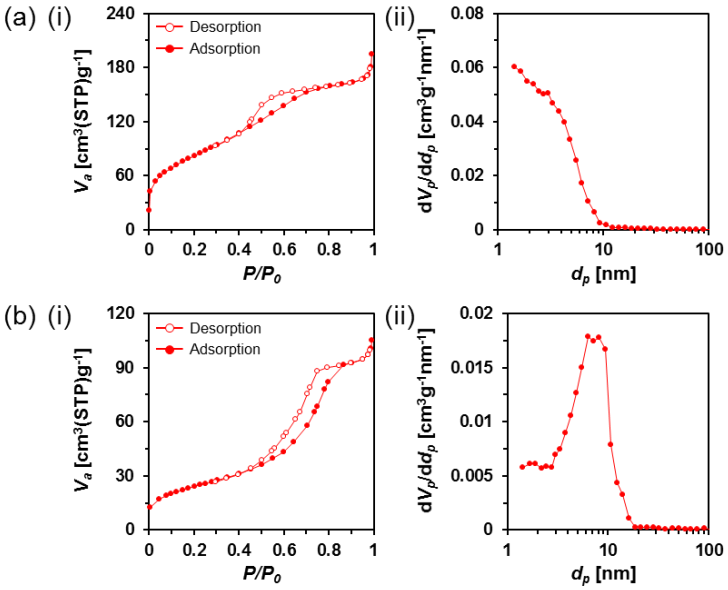


**Figure S3.** Nitrogen adsorption-desorption isotherms (i) and pore size distributions (ii) of (a) $Nb_2O_5$ MARIMO and (b) calcined $Nb_2O_5$ MARIMO at 500 °C.

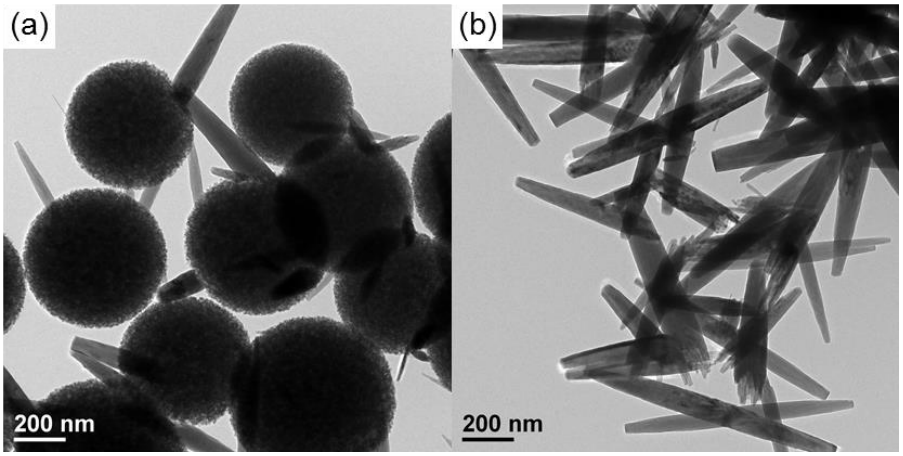


**Figure S4.** TEM images of the $Nb_2O_5$ obtained with different solvothermal-reaction temperature: (a) 325 °C and (b) 350 °C.

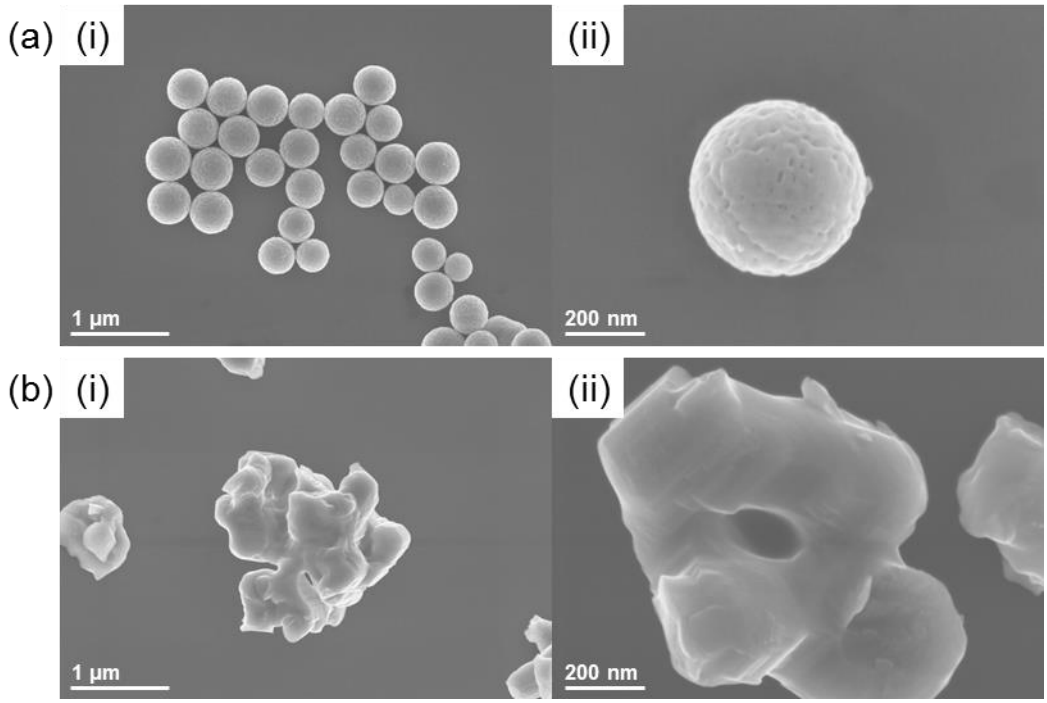


**Figure S5.** SEM images of the $Nb_2O_5$ obtained with different calcined temperature: (a) 600 °C and (b) 700 °C.

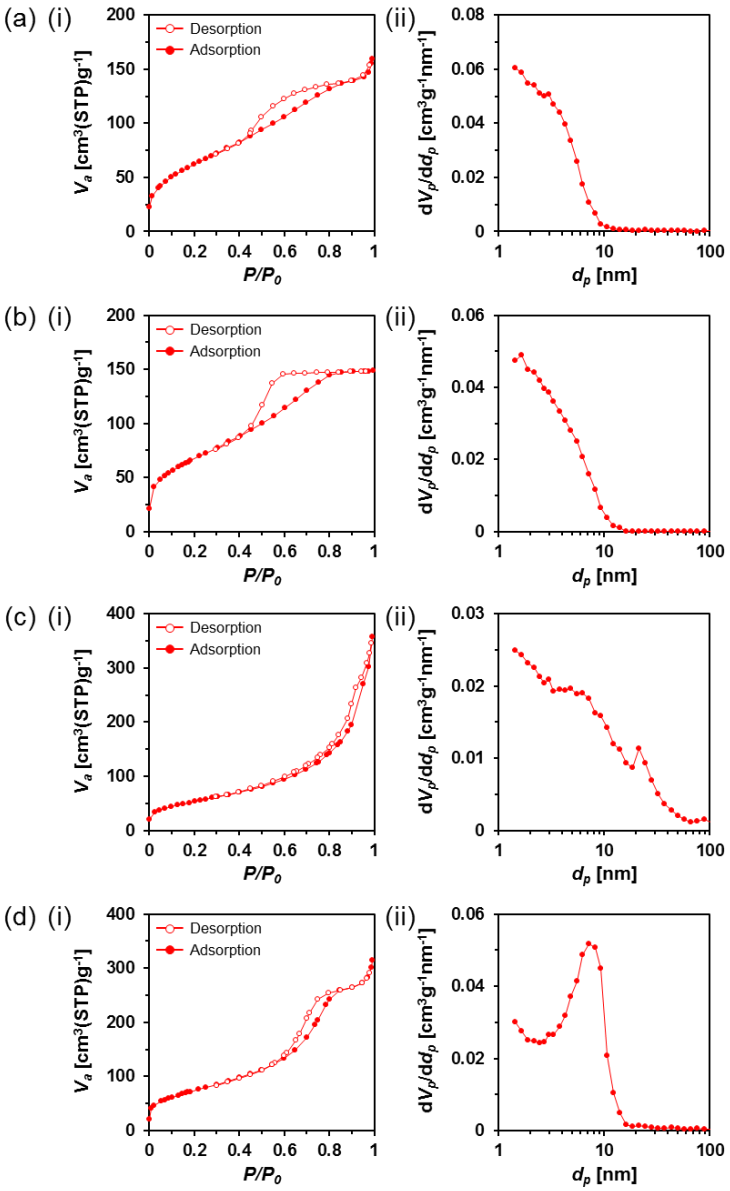


**Figure S6.** Nitrogen adsorption-desorption isotherms (i) and pore size distributions (ii) of (a) $TiO_2$, (b) $TiO_2$–$Nb_2O_5$-25, (c) $TiO_2$–$Nb_2O_5$-50, and (d) $TiO_2$–$Nb_2O_5$-75.

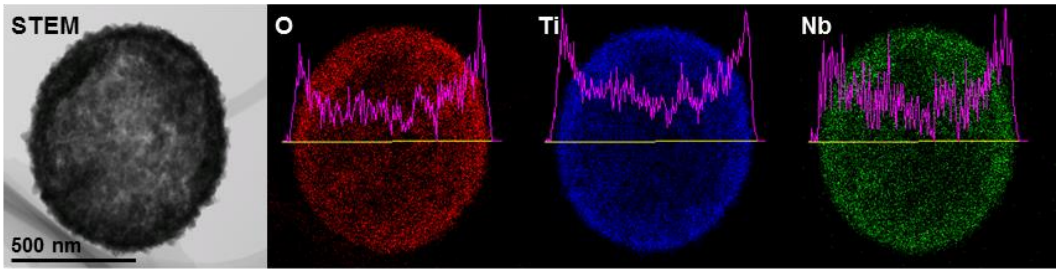


**Figure S7.** EDX mapping and line-scan of the prepared $TiO_2$–$Nb_2O_5$-50 MARIMO.

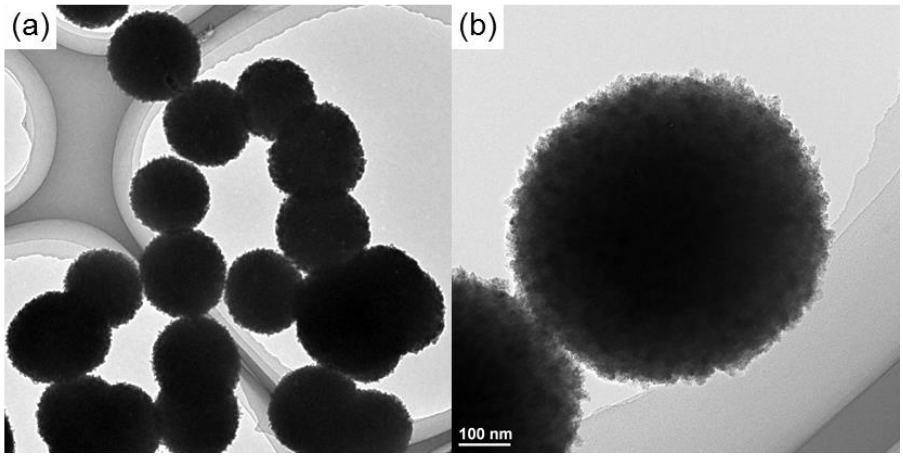


**Figure S8.** TEM images of the prepared solid $TiO_2$–$Nb_2O_5$-50 MARIMO.

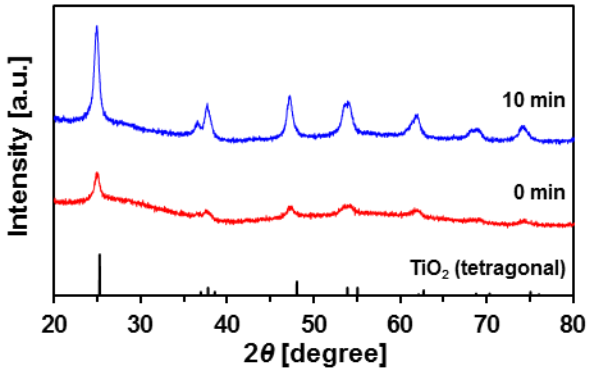


**Figure S9.** XRD patterns of the powdery products with different solvothermal-reaction time (blue, 10 min; red, 0 min). Reference peaks of tetragonal $TiO_2$ (anatase-type, JCPDS 00-021-1272) are represented by the black line.

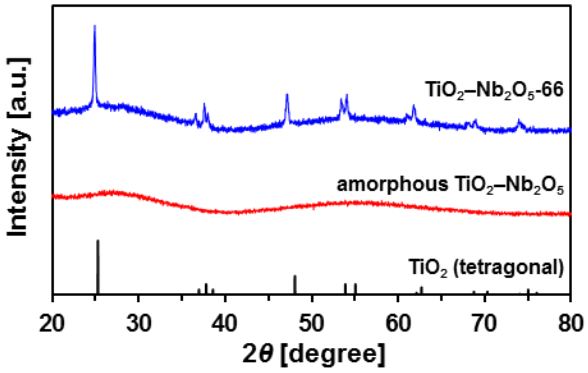


**Figure S10.** XRD patterns of the obtained powdery products prepared with different solvothermal-reaction temperature and time (blue, 300 °C 10 min; red, 200 °C 3 h). Reference peaks of tetragonal $TiO_2$ (anatase-type, JCPDS 00-021-1272) are represented by the black line.

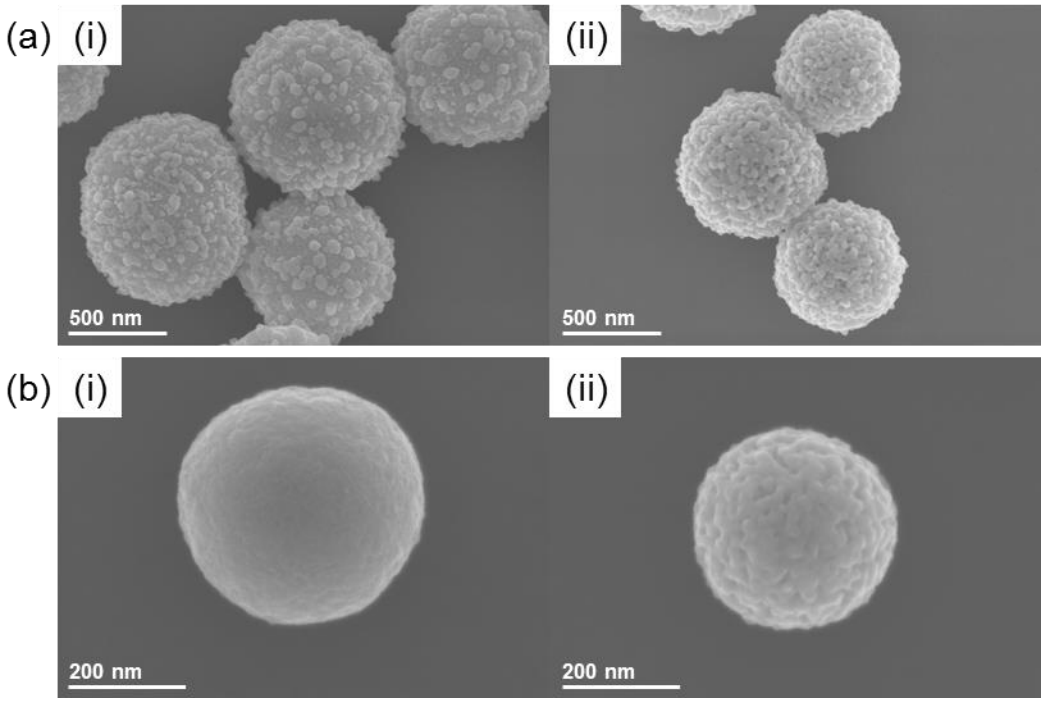


**Figure S11.** SEM images of the $TiNb_2O_7$ MARIMO (a) obtained by the synthesis at 300 °C and (b) at 200 °C in the synthesis process; (i) as-synthesized and (ii) after calcination at 700 °C for 2 h.

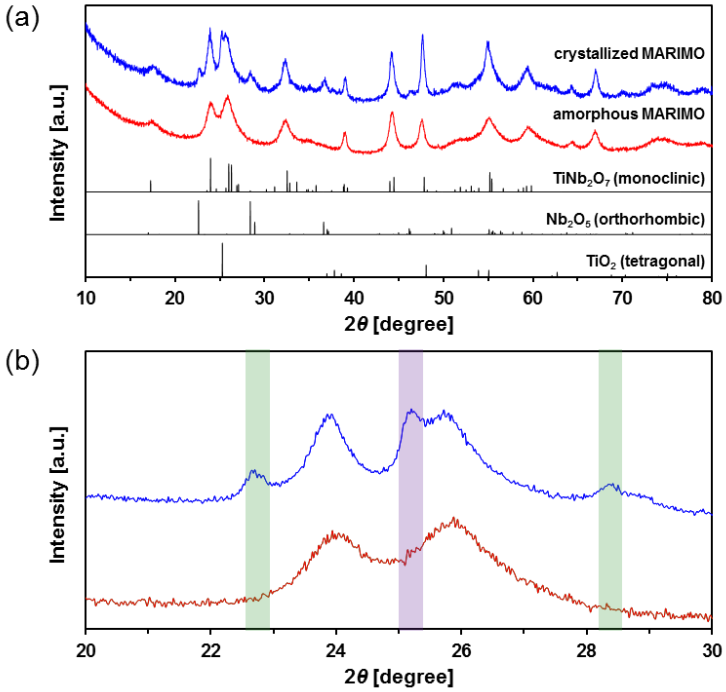


**Figure S12.** XRD patterns of the $TiNb_2O_7$ MARIMO obtained by calcination of different precursor MARIMOs (blue, crystallized MARIMO; red, amorphous MARIMO). Reference peaks of monoclinic $TiNb_2O_7$ (JCPDS 00-039-1407), orthorhombic $Nb_2O_5$ (JCPDS 01-071-0336), and tetragonal $TiO_2$ (anatase-type, JCPDS 00-021-1272) are represented by black lines. The 2θ range: (a) 10−80°, (b) 20−30° (green, orthorhombic $Nb_2O_5$; purple, tetragonal $TiO_2$).

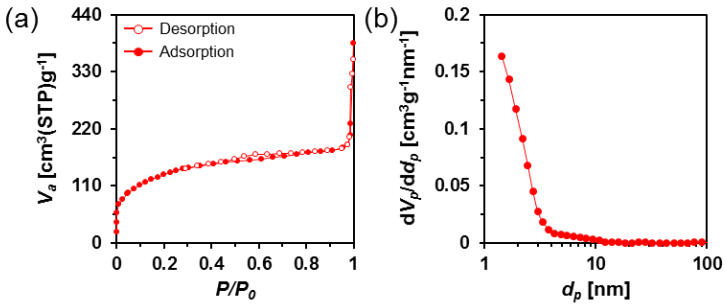


**Figure S13.** Nitrogen adsorption-desorption isotherms (a) and pore size distributions (b) of the amorphous $TiO_2$–$Nb_2O_5$ composite MARIMO.

**Table S1.** Reaction conditions to synthesize $TiNb_2O_7$ and specific surface area of the products.

| Solvent | Ti precursor | Nb precursor | Additive | Solvothermal conditions | Calcination conditions | Specific surface area [$m^2/g$] | Ref. |
|---|---|---|---|---|---|---|---|
| isopropyl alcohol | $Ti(O^nBu)_4$ | $Nb(OEt)_5$ | diethylenetriamine | 200 °C, 12 h | 700 °C, 5 h | 25.2 | 1 |
| ethanol | $Ti(O^iPr)_4$ | $NbCl_5$ | – | 200 °C, 24 h | 700 °C, 2 h | 25.3 | 2 |
| ethanol | $Ti(O^nBu)_4$ | $NbCl_5$ | block copolymer Pluronic P123 | 220 °C, 16 h | 800 °C, 5 h | 23.4 | 3 |
| isopropyl alcohol | $Ti(O^iPr)_4$ | $NbCl_5$ | glycerol | 180 °C, 24 h | 750 °C, 12 h | 22.2 | 4 |
| isopropyl alcohol | $Ti(O^iPr)_4$ | $NbCl_5$ | diethylenetriamine | 200 °C, 24 h | 800 °C, 10 h | 14.3 | 5 |

## Reference


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