Electronic Supplementary Material (ESI) for Dalton Transactions.

Supplementary Information

Urchin-like H-Nb_2O_5 hierarchical microspheres: synthesis, formation mechanism and their applications in lithium ion batteries

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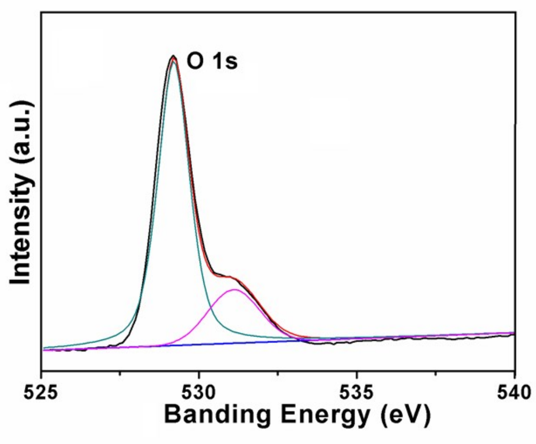

Figure S1 High-resolution XPS O 1s spectrum of urchin-like H-Nb_2O_5 microspheres.

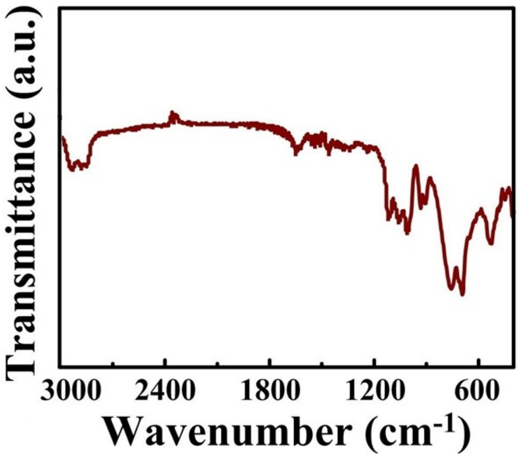

Figure S2 FT-IR spectrum of the $Nb_3(C_3H_5O_3)_5$ precursor.

The FT-IR spectrum of the obtained $Nb_3(C_3H_5O_3)_5$ precursor is investigated to confirm its composition. The absorption peaks at 2927 and 1640 cm^{-1} are assigned to $-CH_2-$ and -OH groups, respectively. The peaks at 1112, 1047, 1010, and 910 cm^{-1} can be attributed to C-C-O and C-O-Nb groups. The peaks at 758 and 690 cm^{-1} are related to Nb-O-Nb angular vibration. The absorption peak at 534 cm^{-1} can be ascribed to the stretching vibration of inorganic Nb-O bond.

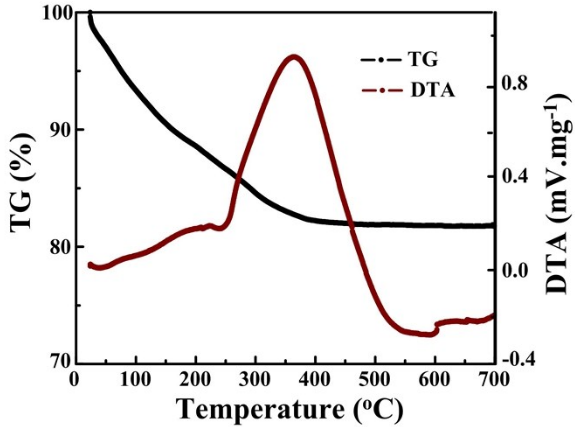

Figure S3 TG-DTA curves of the $Nb_3(C_3H_5O_3)_5$ precursors

To study the conversion process of the $Nb_3(C_3H_5O_3)_5$ precursors, the thermogravimetry - differential thermal analysis (TG-DTA) analyses are carried out from 25 °C to 700 °C with a heating rate of 10 °C min^{-1} in an nitrogen flow of 100 mL min^{-1}, and the TG-DTA curves of the precursors are displayed in Fig. S3. As observed in the TG curve, the initial weight loss at lower temperature (25-100 °C) is ascribed to the release of H_2O or ethanol physically adsorbed on the precursors surfaces [1, 2]. The second mass loss region is in the range of 100 to 500 °C, corresponding to the pyrolysis of $Nb_3(C_3H_5O_3)_5$ [3]; moreover, a huge exothermic peak in the DTA curve indicates an exothermic process in this step [4]. Hence, the calcination temperature should be no less than 500 °C. It is well-known that temperature has an influence on the crystallinity of the sample [5]. Therefore, the precursor is calcined at a temperature of 600 °C to obtain H-Nb_2O_5 with good crystallinity.

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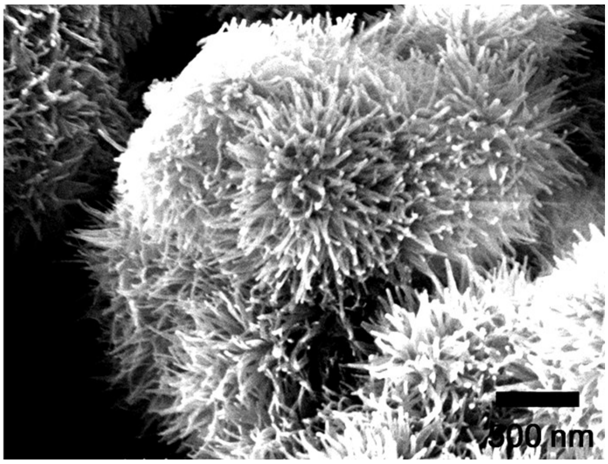

Figure S4 SEM image of the $Nb_3(C_3H_5O_3)_5$ precursor.

The morphology of the obtained $Nb_3(C_3H_5O_3)_5$ precursors is investigated by FESEM and the result is shown in Fig. S4. It is clear that the precursors possess urchin-like morphology and these microspheres are composed of densely packed nanorods.

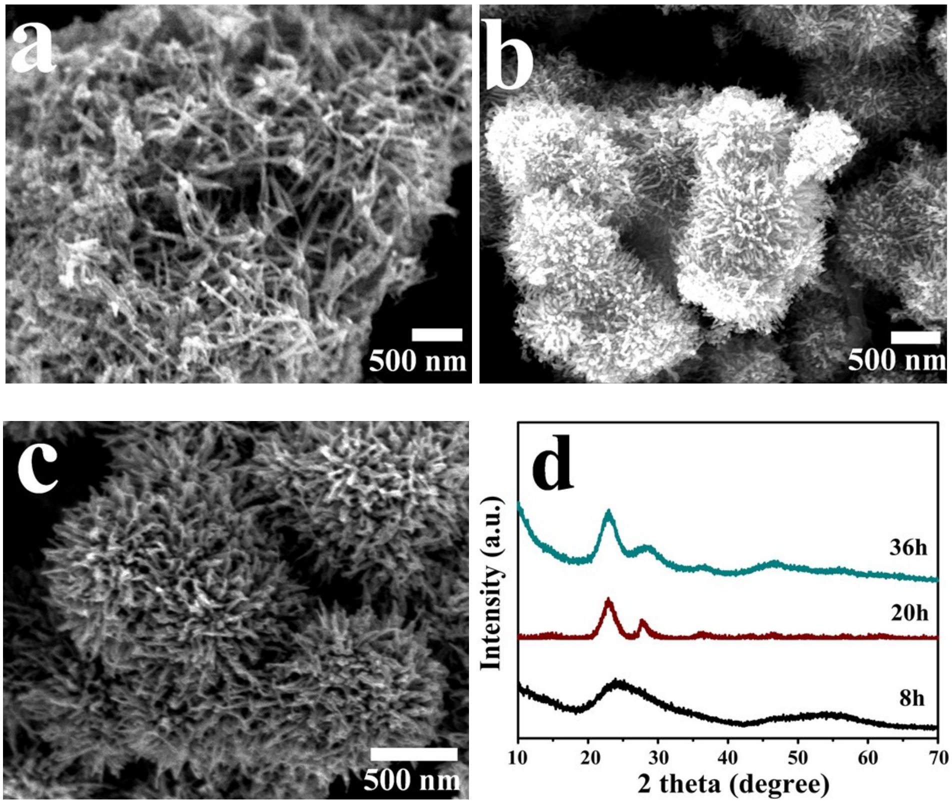

Figure S5 SEM images of the precursors formed at different reaction times with the other reaction parameters uncharged: (a) 8 h; (b) 20 h; and (c) 36 h; (d) XRD patterns of the precursors formed at different reaction times.

To understand the formation mechanism of the urchin-like precursors, it is necessary to investigate the crystal structure and morphology evolution of the intermediates involved in the growth process, and the XRD and SEM results are shown in Fig. S4. Under the present synthetic conditions, nanoparticles and nanorods coexist in the product after solvothermal treatment for 8 h (Fig. S5a). As the reaction time is prolonged to 20 h, sphere-like congeries appears as a result of self-assembly (Fig. S5b). With a longer reaction time, from 20 to 36 h, urchin-like microspheres composed of nanorods are synthesized (Fig. S5c). Finally, as shown in Fig. S4, hierarchical urchin-like microspheres are formed after 48 h and these microspheres are assembled by nanorods, thicker than those of the sample synthesized for 36. Thus, it can be deduced that the formation mechanism of the urchin-like precursors can be attributed to a self-assembled process of metastable nanorods. In addition, Fig. S5d shows the XRD patterns of the precursors formed at different reaction times. It can be seen that the intensities of the peaks are gradually enhanced with the increasing of reaction time.

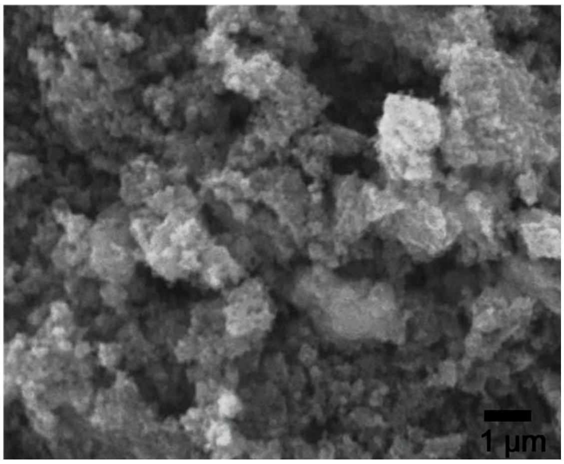

Figure S6 SEM image of H-Nb_2O_5 nanoparticles as isopropanol is replaced by 30 mL distilled water with other reaction parameters unchanged.

Table S1. Electrochemical properties of Nb_2O_5 nano/micromaterials as anodes for LIBs

Morphology	Discharge capacity in first cycle (mAh g^{-1})	Reversible capacity after n cycles (mAh g^{-1})	Current density	Ref.
Nb_2O_5 nanosheets	184.0	117.0 (100)	1.0 C	[1]
Nb_2O_5 nanoparticles	145.0	143.0 (800)	2.5 C	[2]
Nb_2O_5 hollow nanospheres	197.0	178.0 (100)	0.5 C	[3]
Macroporous nanostructured Nb_2O_5	190.0	-	0.5 C	[4]
Nb_2O_5 nanosheets	355.0	185.0 (40)	0.1 A g^{-1}	[5]
Nb_2O_5 nanobelts	250.0	180.0 (50)	0.1 A g^{-1}	[6]
Nb_2O_5 microspheres	-	131.0 (1000)	1.0 A g^{-1}	[7]
H-Nb_2O_5 microspheres	201.7	180.2 (70)	0.5 C	in this work

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