Supplementary material (ESI) for Journal of Materials Chemistry

Template-free Synthesis of VOx Hierarchical Hollow Spheres

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Electronic Supplementary Information

ESI 1. Synthesis procedure and FTIR, TG results of vanadium acetylacetone

Vanadium pentoxide (V_2O_5) and acetylacetone (analysis grade) were used as received without further purification. 2.7282g (0.015mol) V_2O_5 was dissolved into 30mL acetylacetone and refluxed at 80℃ for 24 hours. The resulted glaucous product was filtered and washed with ethanol for several times and dried at ambient atmosphere. The structural formula, IR spectrum and TGA result are shown as figure S1a, b and c, respectively.

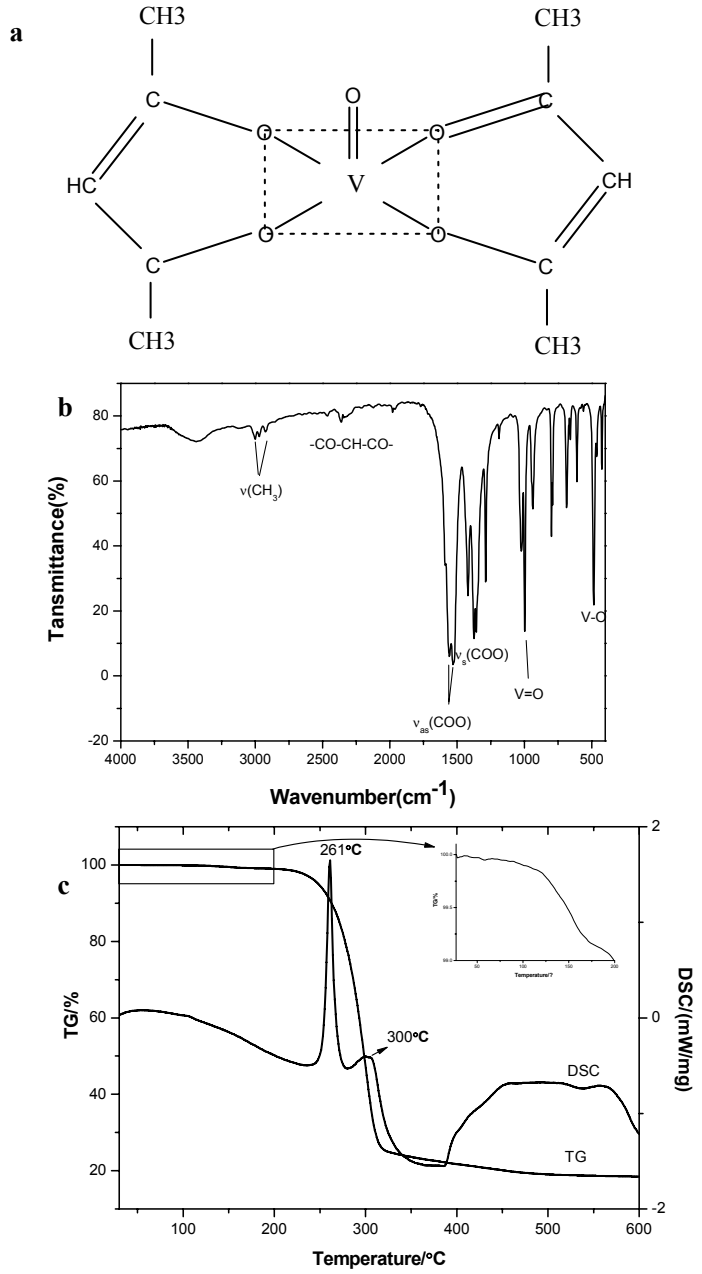

Figure S1. The structural formula (a), FTIR spectrum (b), TGA and DSC results (c) of vanadium acetylacetone. The FTIR spectrum is well in agreement with the commercial product of vanadium acetylacetone. In the inset of Fig.S1c, weight loss of about 1% at 150℃ can be assigned to the evaporation of absorbed water in vanadium acetylacetone. It is known that vanadium acetylacetone has some tendency to sublimate (Reference: Galembecka, A.; Alves, O.L. Thin Solid Films 2000, 365, 90-93), and two endothermic peaks centered on 261℃ and 300℃ are observed in the DSC curve, which can be attributed to the sublimate and decomposition processes, respectively. So the weight loss from 200℃ to 500℃ shown in TG curve is more than the decomposition loss of vanadium acetylacetone.

ESI 2.

Table S1 Effect of solvothermal reaction conditions on the size of VHSs.

sample	vanadium source dosage	reaction temperature	size	TEM images
A	0.05 g	250 □	150-300 nm	Fig.S2a
B	0.1 g	250 □	350-600 nm	Fig.1e
C	0.05 g	230 □	150-250 nm	Fig.S2b
D	0.1 g	230 □	350-600 nm	Fig.S2c
E	0.05 g	210 □	150-200 nm	Fig.1b
F	0.1 g	210 □	150-300 nm	Fig.S2d
G	0.05 g	190 □	150-200 nm	Fig.S2e
H	0.1 g	190 □	300-600 nm	Fig.S2f
I	0.2 g	190 □	150-1200 nm	Fig.S2g
K	0.2 g[a]	190 □	700-1100 nm	Fig.S2h

[a] 0.375 mmol octodecylamine was added.

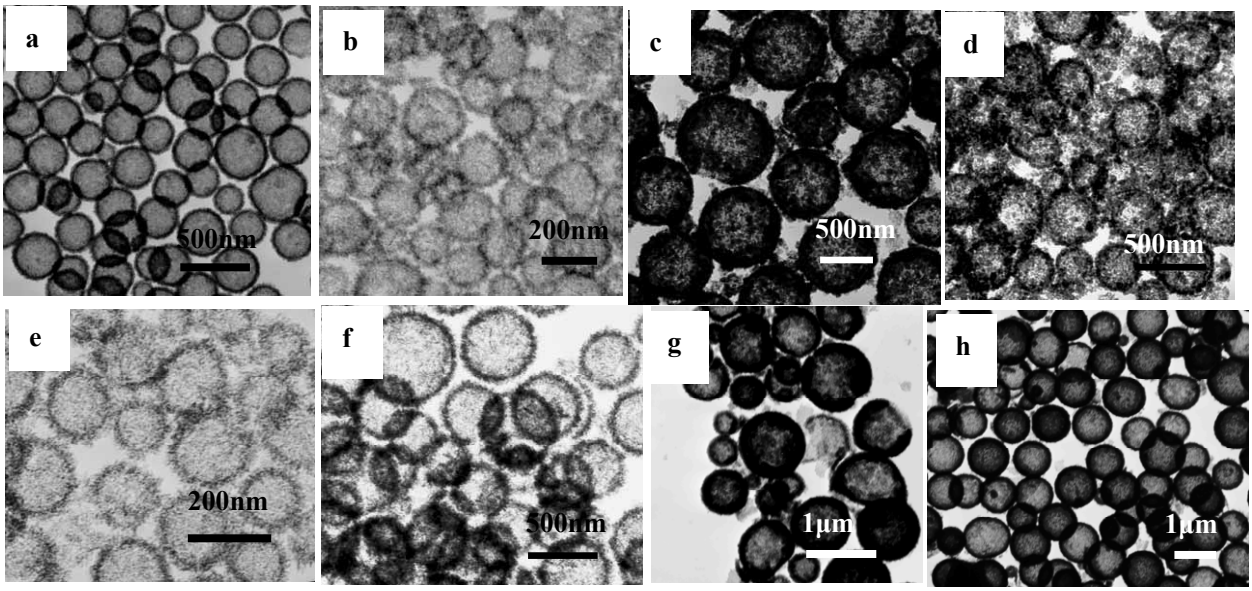

Figure S2. TEM images of sample A(a), C(b), D(c), F(d), G(e), H(f), I(g) and K(h) in Table S1.

ESI 3.

The Effect of water content on the morphology of the product

Sample	Content of water	morphology	TEM image
1	0.5 mL	loose V_2O_3 hollow spheres and nanoparticles	Fig.S3a
2	1 mL	V_2O_3 nanoparticles	Fig.S3d

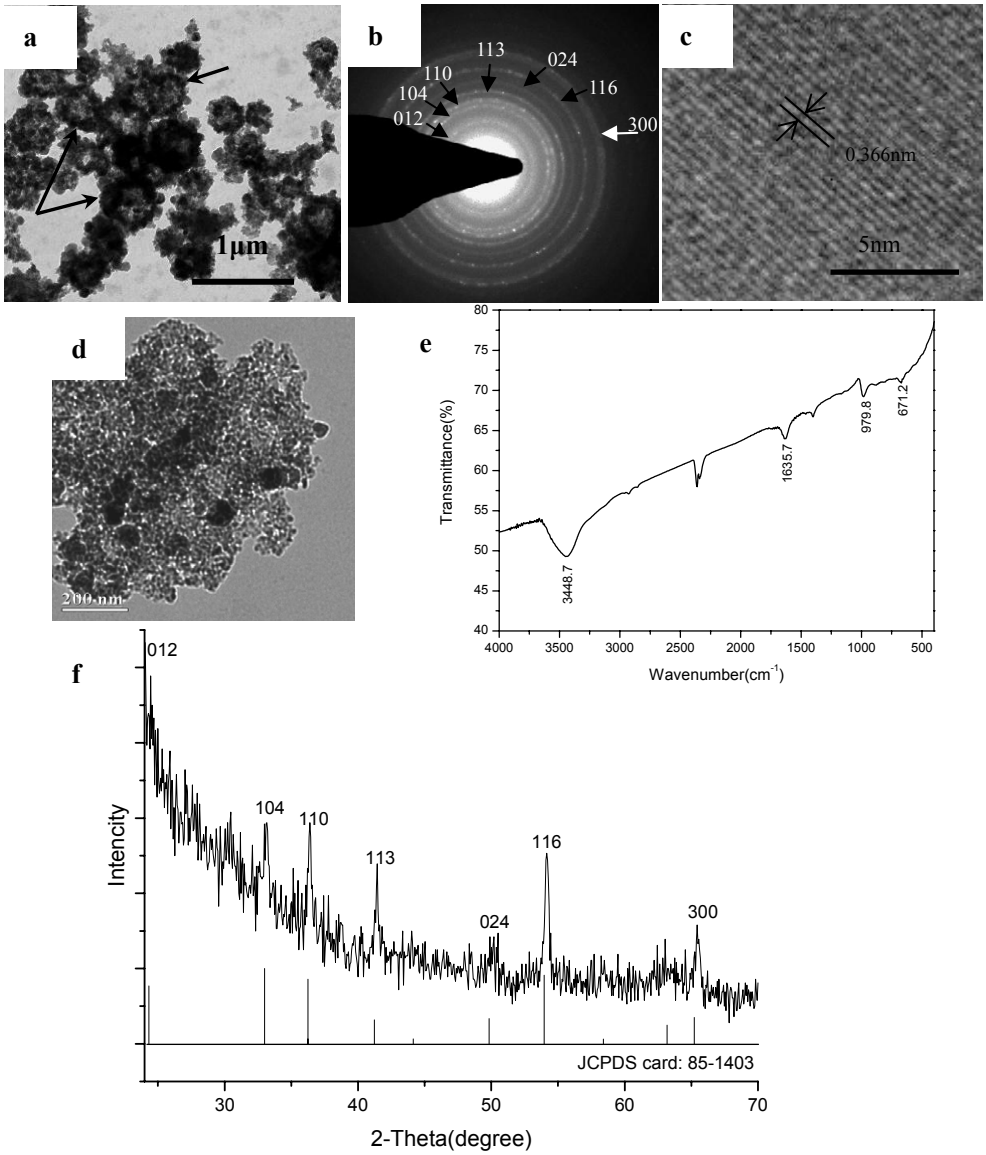

Figure S3. TEM image(a), SAED pattern(b) and HRTEM image(c) of the sample 1 in the above table. TEM image(d), FTIR spectrum (e) and XRD result (f) of the sample 2.

Fig.S3a indicates the sample1 is mainly composed of loose hollow spheres (as noted by black arrows) and dispersed nanoparticles, and clear diffraction circles shown in its SAED pattern (Fig.S3b) can be well attributed to the diffraction of (012), (104), (110), (113), (024), (116) and (300) planes of karelianite V_2O_3 from inside to outside. The lattice fringe with a spacing of 0.366nm in HRTEM image ((Fig.S3c) is in agreement with the d value of (012) plane of karelianite V_2O_3. Fig.S3d indicates the sample2 is mainly composed of dispersed nanoparticles, and the peaks in XRD spectrum ((Fig.S3e) can be indexed to the diffraction peaks of karelianite V_2O_3 (JCPDS card: 85-1403). The lines at the bottom of Fig.S3e are the standard XRD pattern of karelianite V_2O_3.

ESI 4.

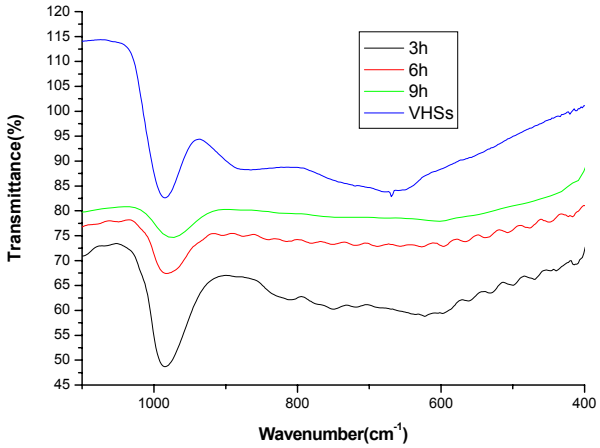

Figure S4. FTIR spectra of samples obtained at 3h, 6h and 9h in the time-dependent experiments and VHSs.

ESI 5. Electrochemical measurement.

Electrochemical properties of samples were examined by assembled three-electrode cell. The working electrode was made by dropping 0.1 mL of 5 mg/mL sample solution in ethanol onto a polished glass-carbon electrode, then depositing 0.02 mL of 2.5 mg/mL polystyrene solution in tetrahydrofuran to immobilize and drying in air ambient. Cyclic voltammetry was carried out in a voltage range of -0.8~0.8 V (VOHSs) and -1.4~1.4 V (V_2O_5 hollow spheres) on a CHI660A electrochemical workstation with a Pt flag as a counter electrode, a saturated calomel electrode (SCE) as a reference electrode, and 2 M KCl aqueous solution as electrolyte. A scan rate of 10mV/s was employed.