Electronic Supplementary Information

The enhanced photoluminescence of hollow $CaWO_4$ microspheres: the fast fabrication, structural manipulation, and the exploration of growth mechanism

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1. The parallel experimental parameters and corresponding morphologies of the as-produced $CaWO_4$

Table S1 Generalization of the experimental data and their structural information of the as-obtained tetragonal $CaWO_4$

Sample	$c(Ca(NO_3)_2)$ (mol L^{-1})	$c(Na_2WO_4)$ (mol L^{-1})	c(SDBS) (mol L^{-1})	Time (min)	Morphology
1	0.200	0.200	0.020	30	Hollow microspheres (diameter: 2.60-5.78 μm) assembled by nanospheres (size: 20.94-64.12 nm)
2	0.025	0.025	0.020	30	Cauliflower-like microstructure (diameter: 3.49-5.33 μm) made of nanosheets (thickness: 89.96-269.87 nm)
3	0.050	0.050	0.020	30	Microspheres (diameter: 4.15-5.41 μm) built up ordered nanoparticles (size: 31.84-131.01 nm)
4	0.100	0.100	0.020	30	Porous microspheres (diameter: 4.18-5.90 μm) aggregated via small nanoparticles (size: 23.37-78.63 nm)
5	0.400	0.400	0.020	30	Monodisperse microspheres (diameter: 1.87-3.41 μm) composed by nanoparticles (size: 18.03-66.68 nm)
6	0.200	0.200	0.020	1	Solid microspheres (diameter: 1.35-3.37 μm) constituted of nanoparticles (size: 14.44-64.91 nm)
7	0.200	0.200	0.020	2	Solid microspheres (diameter: 1.96-3.31 μm) consisted of nanoparticles (size: 13.68-54.08 nm)
8	0.200	0.200	0.020	5	Hollow microspheres (diameter: 2.79-5.06 μm) formed by nanoparticles (size: 16.14-58.56 nm)
9	0.200	0.200	0.020	15	Hollow microspheres (diameter: 2.12-4.01 μm) built up nanoparticles (size: 17.97-53.94 nm)

2. The detailed structural information and corresponding XRD results of the as-prepared $CaWO_4$ samples

(1) Statistics of particle size for hollow $CaWO_4$ microspheres from the FE-SEM image of Fig. 1.

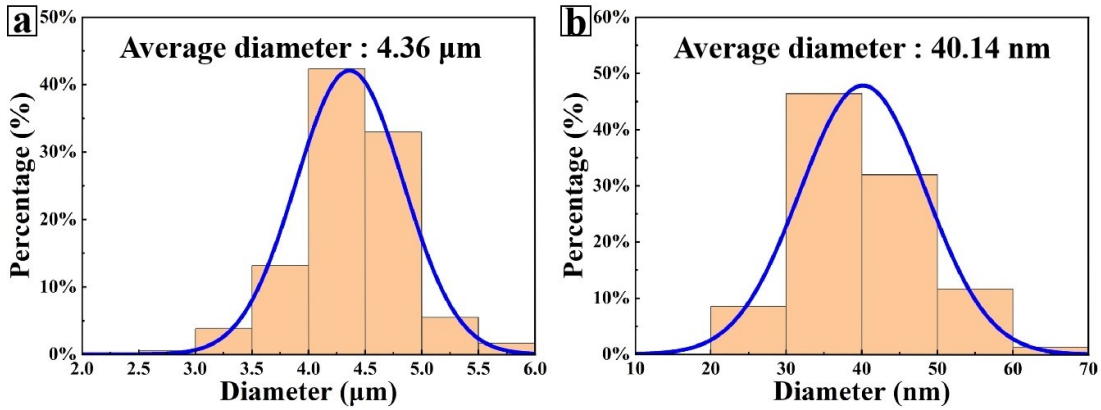

Fig. S1 Statistics results of particle size distribution for hollow $CaWO_4$ microspheres (Sample 1) and nanospheres size distribution on the outer surfaces of selected microspheres: (a) data from **Fig. 1b** in the text: histogram and fitted normal curves of hollow $CaWO_4$ microspheres at a low magnification, and (b) data from **Fig. 1e**: histogram and fitted normal curves of particle size of nanospheres from single hollow $CaWO_4$ microspheres surface at a relatively high magnification.

(2) Statistics of particle size of $CaWO_4$ synthesized at different conditions from the FE-SEM image of Fig. 2 and Fig. 3.

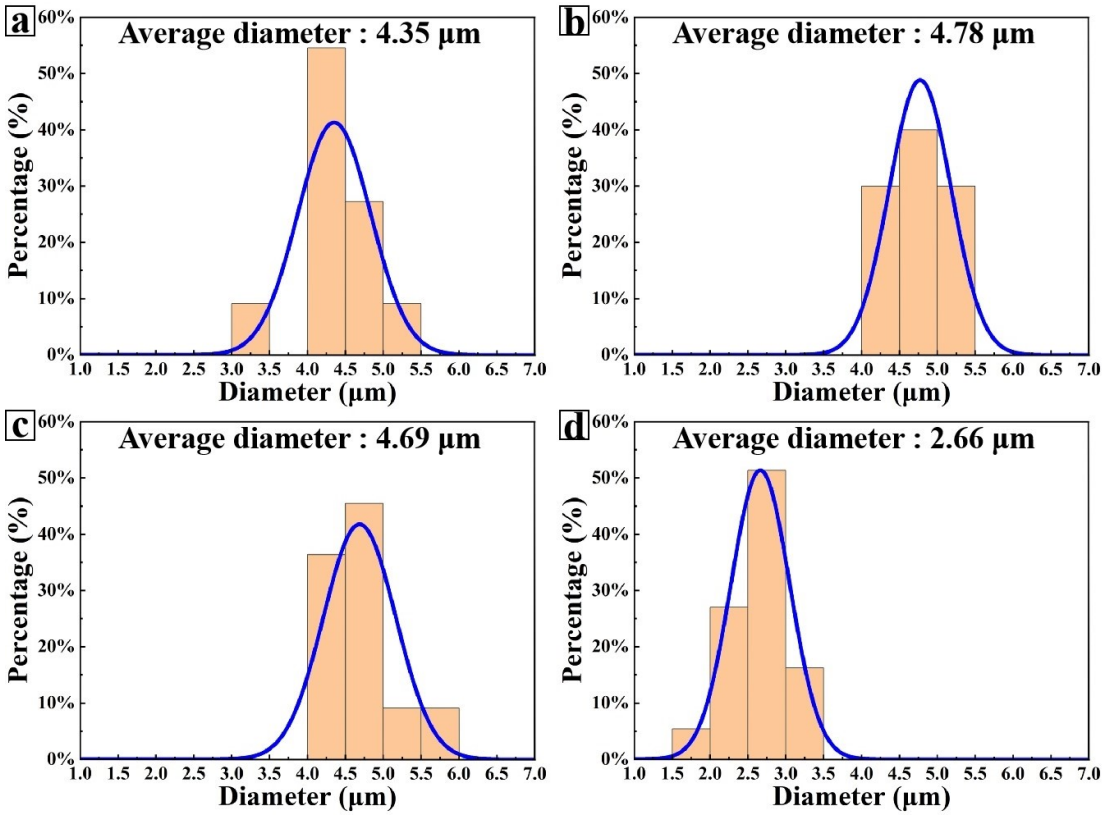

Fig. S2 Histogram and fitted normal curves of size distribution of $CaWO_4$ microspheres (Sample 2-5) synthesized at different concentrations of raw materials but with a constant concentration ratio (Na_2WO_4: $Ca(NO_3)_2$ = 1 : 1): (a) data from **Fig. 2a**: 0.025 mol L^{-1} (Sample 2), (b) data from **Fig. 2d**: 0.050 mol L^{-1} (Sample 3), (c) data from **Fig. 2g**: 0.100 mol L^{-1} (Sample 4), and (d) data from **Fig. 2j**: 0.400 mol L^{-1} (Sample 5).

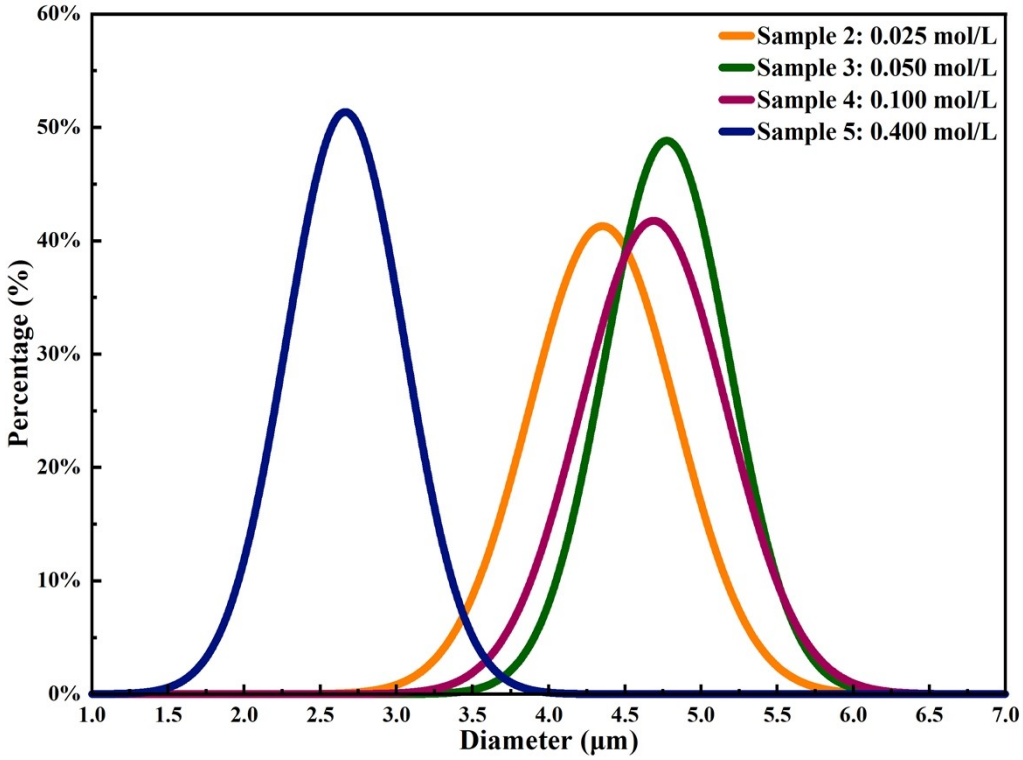

Fig. S3 Data from **Fig. 2a, d, g, and j**: merged the fitted normal curves of size distribution of hollow $CaWO_4$ microspheres (Sample 2-5) synthesized at different concentrations of raw materials but with the same concentration ratio (Na_2WO_4: $Ca(NO_3)_2$ = 1 : 1).

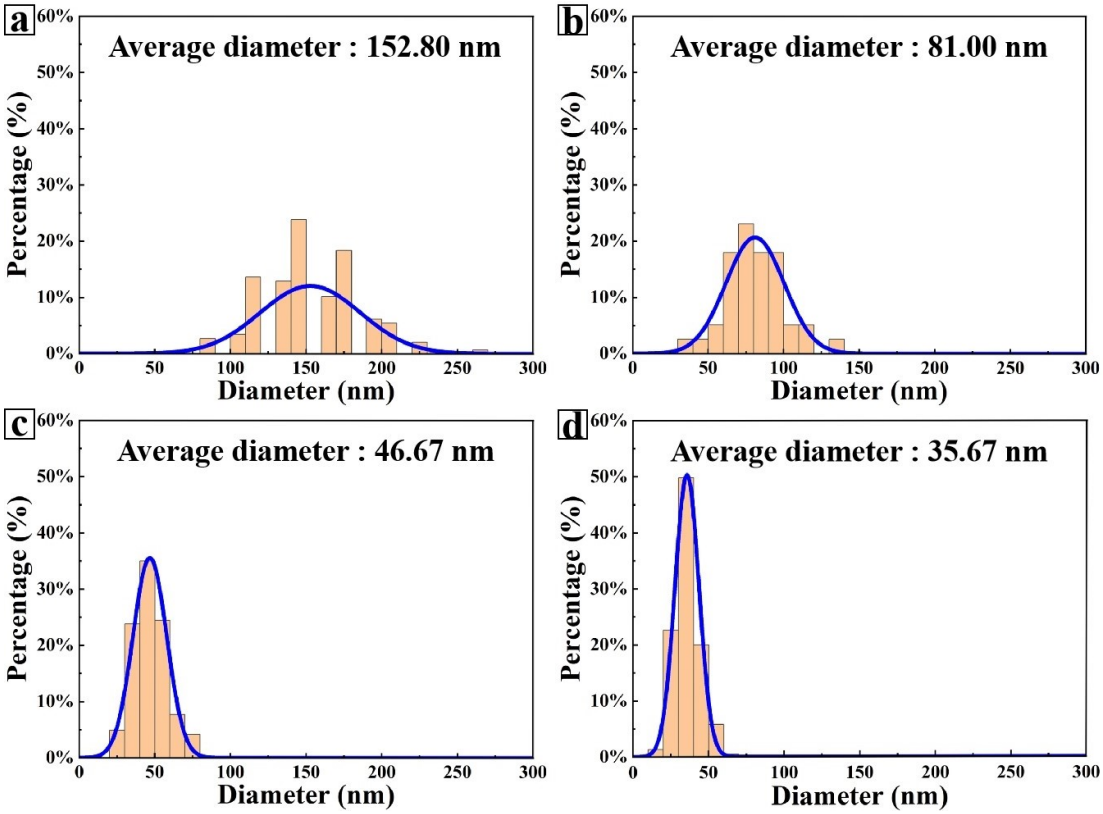

Fig. S4 Histogram and fitted normal curves of nanoparticles size distribution on the outer surfaces of $CaWO_4$ microspheres (Sample 2-5) synthesized at different concentrations of raw materials but with the same concentration ratio (Na_2WO_4: $Ca(NO_3)_2$ = 1 : 1) : (a) data from **Fig. 2c**: 0.025 mol L^{-1} (Sample 2), (b) data from **Fig. 2f**: 0.050 mol L^{-1} (Sample 3), (c) data from **Fig. 2i**: 0.100 mol L^{-1} (Sample 4), and (d) data from **Fig. 2*l***: 0.400 mol L^{-1} (Sample 5).

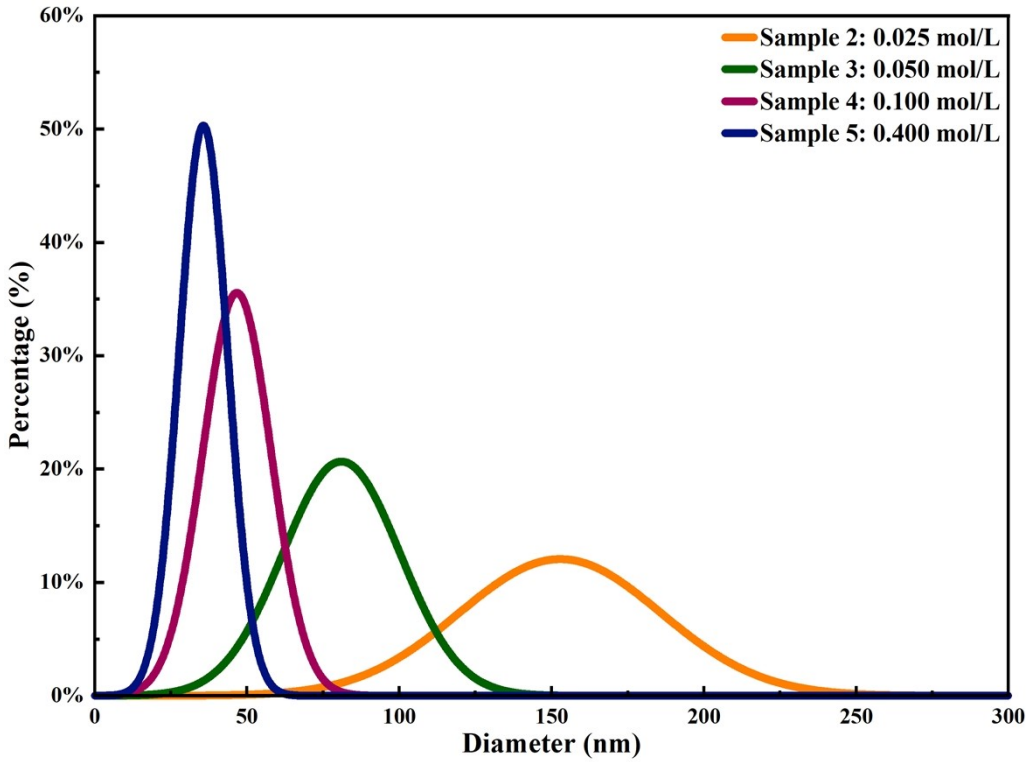

Fig. S5 Data from **Fig. 2c, f, i, and *l***: merged the fitted normal curves of nanoparticles size distribution on the outer surfaces of $CaWO_4$ microspheres, synthesized at different concentrations of raw materials but with the same concentration ratio (Na_2WO_4: $Ca(NO_3)_2$ = 1 : 1) for Sample 2-5.

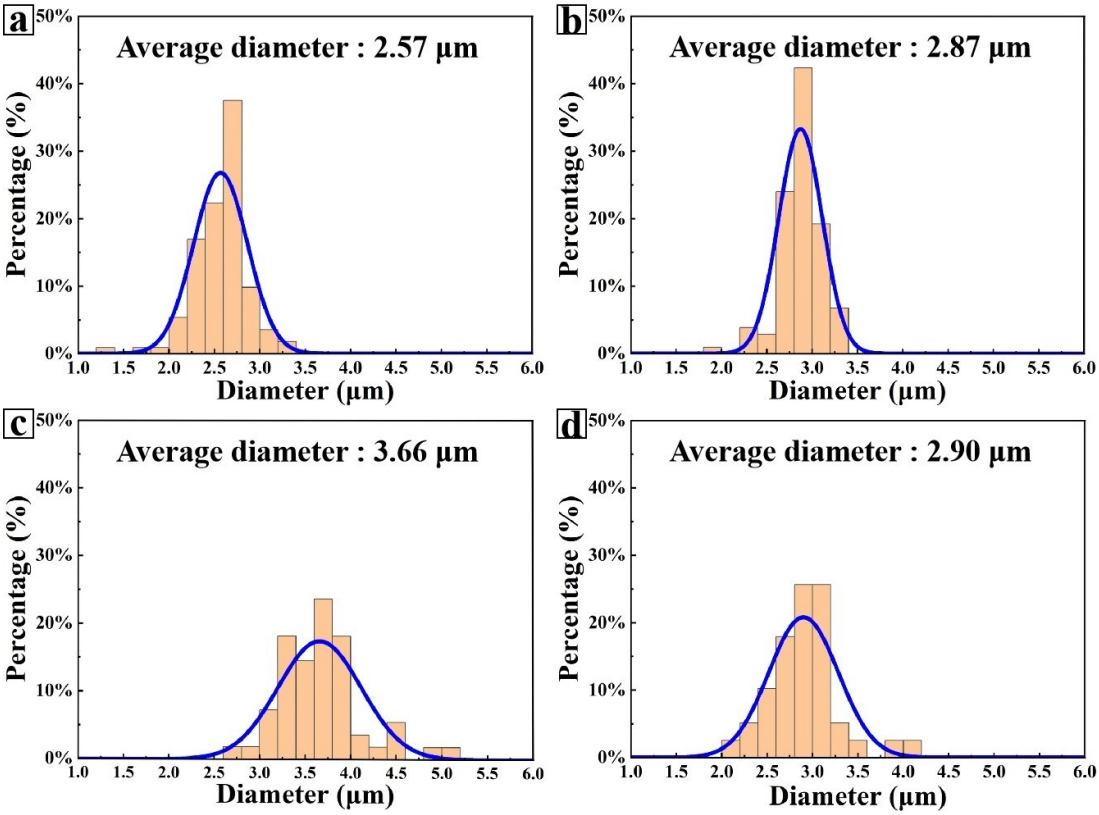

Fig. S6 Histogram and fitted normal curves of particle size distribution for porous-shell hollow $CaWO_4$ microspheres (Sample 6-9), fabricated by the microwave irradiation process at continuous reaction intervals: (a) data from **Fig. 3a**: 1 min (Sample 6), (b) data from **Fig. 3e**: 2 min (Sample 7), (c) data from **Fig. 3i**: 5 min (Sample 8), and (d) data from **Fig. 3m**: 15 min (Sample 9).

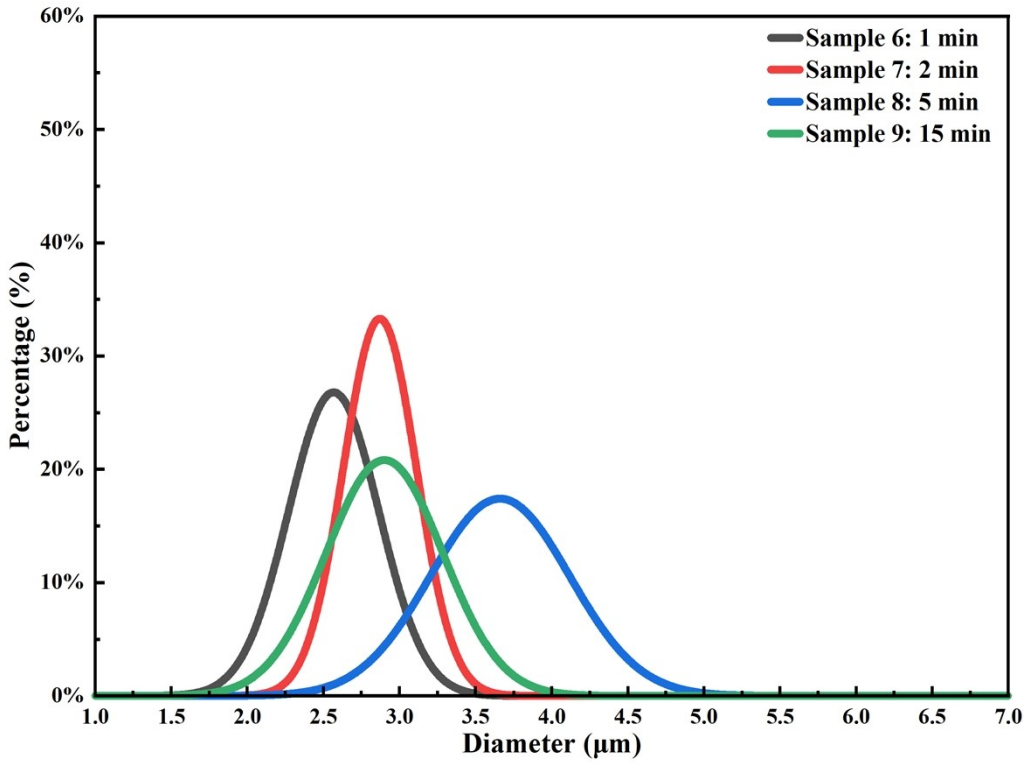

Fig. S7 Data from **Fig. 3a, e, i, and m**: merged the fitted normal curves of particle size distribution for porous-shell hollow $CaWO_4$ microspheres, prepared by the microwave irradiation process at continuous reaction timespans (Sample 6-9).

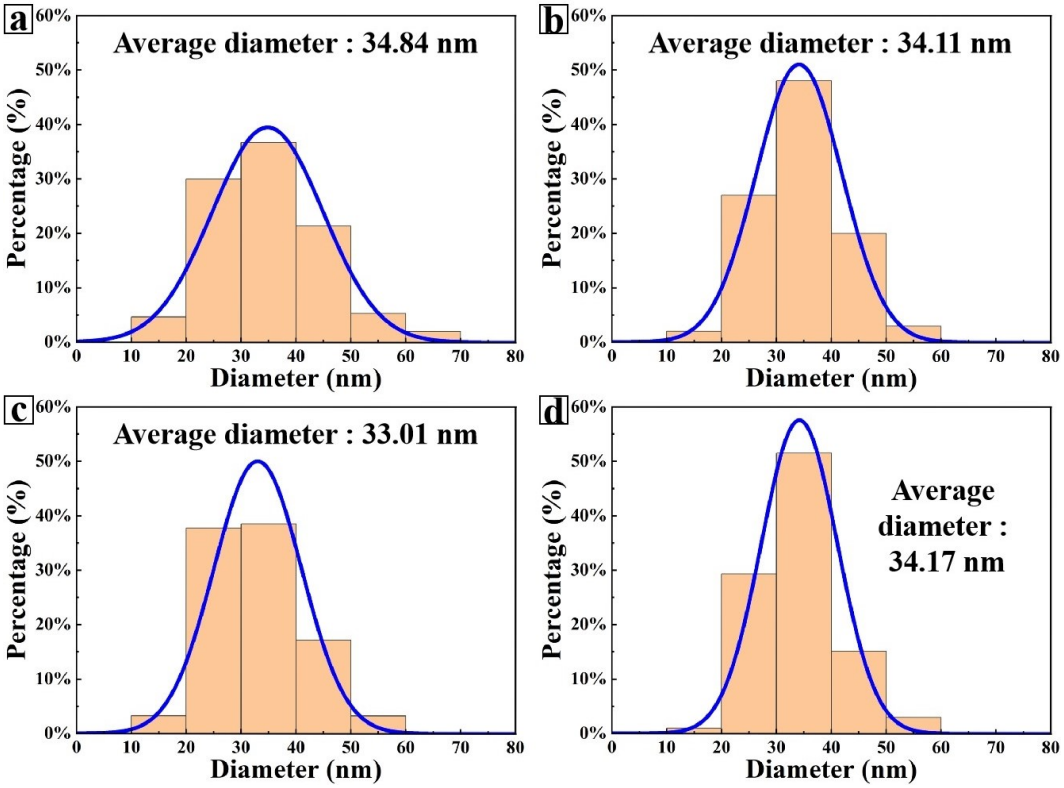

Fig. S8 Histogram and fitted normal curves of nanoparticles size distribution on the outer surfaces for porous-shell hollow $CaWO_4$ microspheres (Sample 6-9), obtained by the microwave irradiation process at continuous reaction intervals: (a) data from **Fig. 3d**: 1 min (Sample 6), (b) data from **Fig. 3h**: 2 min (Sample 7), (c) data from **Fig. 3*l***: 5 min (Sample 8), and (d) data from **Fig. 3p**: 15 min (Sample 9).

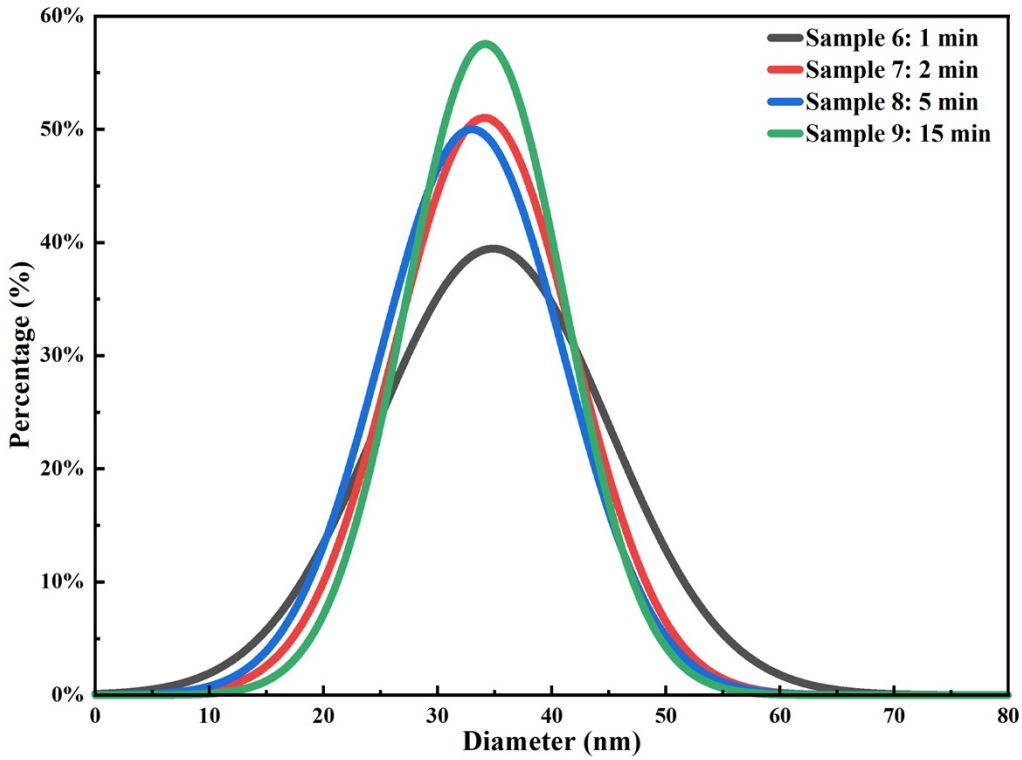

Fig. S9 Data from **Fig. 3d, h, *l*, and p**: merged the fitted normal curves of nanoparticles size distribution on the outer surfaces of porous-shell hollow $CaWO_4$ microspheres (Sample 6-9).

(3) XRD patterns of porous-shell hollow $CaWO_4$ microspherical structures synthesized at different concentrations of raw materials.

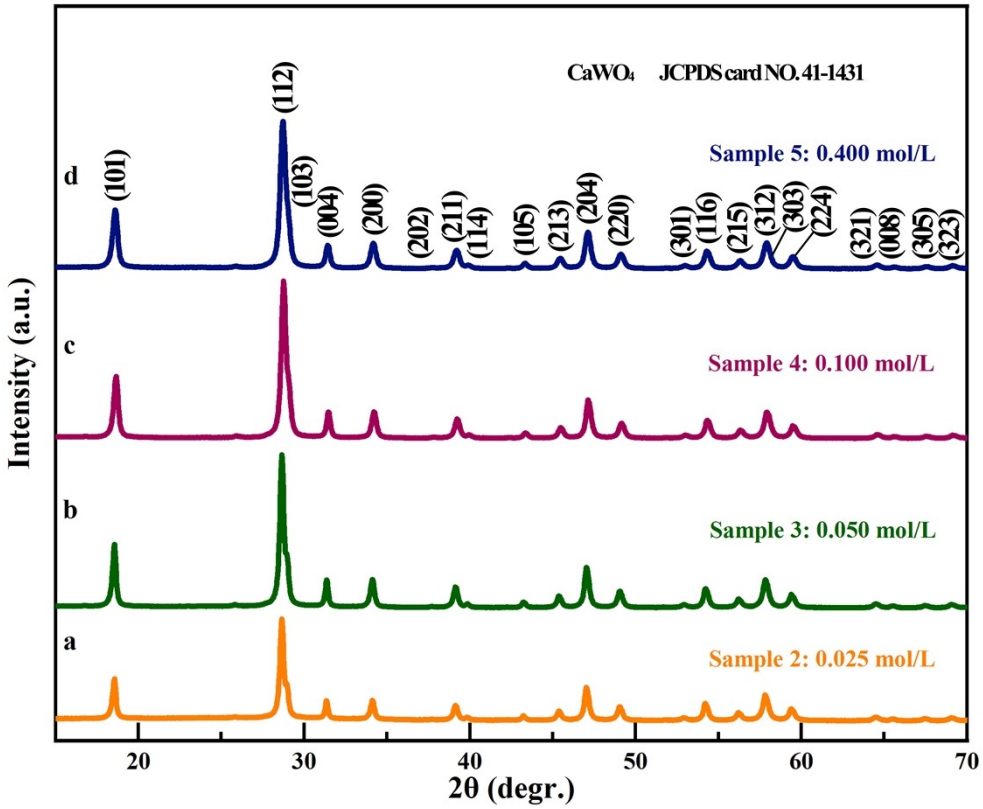

Fig. S10 XRD patterns of $CaWO_4$ microspherical structures (Sample 2-5) fabricated through a facile microwave irradiation route with the same dwell time (30 min) under different concentrations of raw materials but with the same concentration ratio (Na_2WO_4: $Ca(NO_3)_2$ = 1 : 1): (a) 0.025 mol L^{-1} (Sample 2), (b) 0.050 mol L^{-1} (Sample 3), (c) 0.100 mol L^{-1} (Sample 4), and (d) 0.400 mol L^{-1} (Sample 5).

(4) TEM/HRTEM images of selected nanospheres on porous-shell hollow $CaWO_4$ microspherical structures (Sample 1)

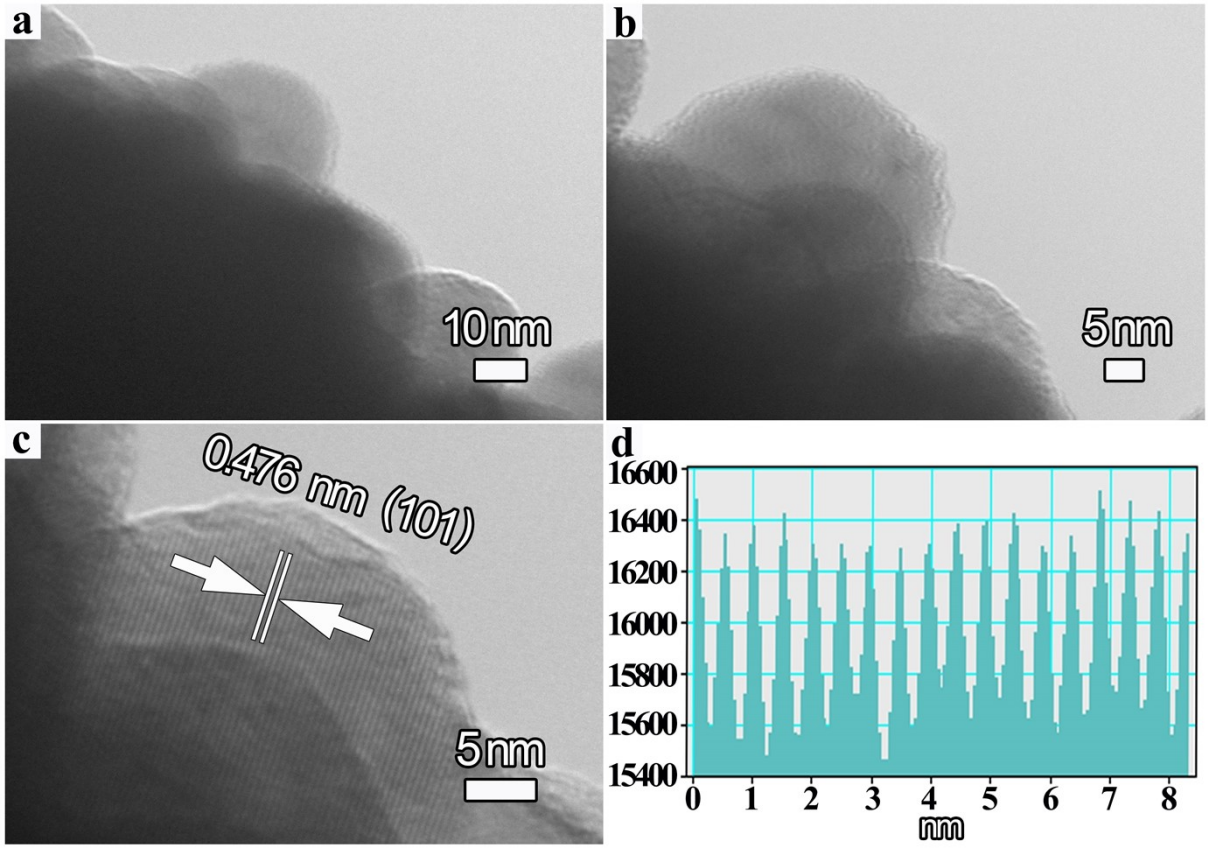

Fig. S11 (a) and (b) Low magnification TEM images of representative nanospheres of the porous-shell hollow $CaWO_4$ microspheres (Sample 1), illustrating crystal nature in different regions. (c) High magnification HRTEM images of a single nanosphere, showing the interplanar distance and plane and consisting with the results of Fig. 1g. (d) The corresponding lattice spacing profile of Fig. S11 c.

(5) The structural information of the as-produced $CaWO_4$ samples

Table S2 The corresponding structural data of these $CaWO_4$

Sample	Morphology	Size	Data Sources
1	Hollow microspheres	2.60-5.78 μm	Fig. S1a
	Nanospheres	20.94-64.12 nm	Fig. S1b
2	Cauliflower-like microstructures	3.49-5.33 μm	Fig. S2a
	Nanosheets	89.96-269.87 nm	Fig. S4a
3	Microspheres	4.15-5.41 μm	Fig. S2b
	Ordered nanoparticles	31.84-131.01 nm	Fig. S4b
4	Porous microspheres	4.18-5.90 μm	Fig. S2c
	Small nanoparticles	23.37-78.63 nm	Fig. S4c
5	Monodisperse microspheres	1.87-3.41 μm	Fig. S2d
	Nanoparticles	18.03-66.68 nm	Fig. S4d
6	Solid microspheres	1.35-3.37 μm	Fig. S6a
	Nanoparticles	14.44-64.91 nm	Fig. S8a
7	Solid microspheres	1.96-3.31 μm	Fig. S6b
	Nanoparticles	13.68-54.08 nm	Fig. S8b
8	Hollow microspheres	2.79-5.06 μm	Fig. S6c
	Nanoparticles	16.14-58.56 nm	Fig. S8c
9	Hollow microspheres	2.12-4.01 μm	Fig. S6d
	Nanoparticles	17.97-53.94 nm	Fig. S8d