Supplementary Information

A facile method to synthesize nanosized metal oxides from their corresponding bulk materials

Pinhua Zhang,[a] Yingnan Wang,[a] Yongming Sui,[a] Chunzhong Wang,[b] Bingbing Liu,[a] Guangtian Zou[a] and Bo Zou*[a]

a State Key Laboratory of Superhard Materials, Jilin University, Changchun 130012, China

b Key Laboratory of Physics and Technology for Advanced Batteries (Ministry of Education), College of Physics, Jilin University, Changchun, 130012, China

* Corresponding authors. E-mails: zoubo@jlu.edu.cn

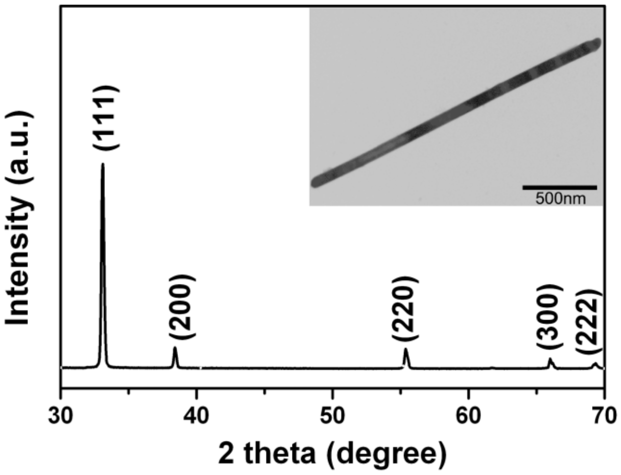


Fig. S1 XRD pattern of CdO nanorods synthesized with less CdO (0.032 g, 0.25 mmol). The inset is TEM image of sample.

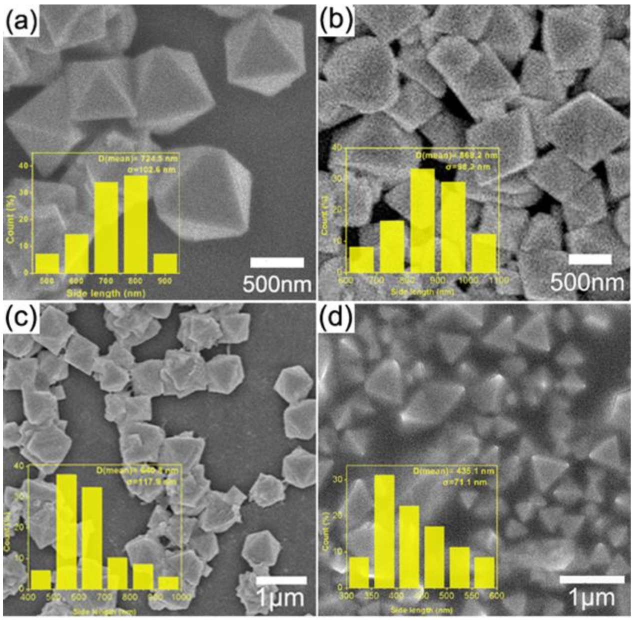


Fig. S2 TEM images of the as-prepared CdO upon changing the parameters in the synthetic system; (a) 300 °C and (b) 320 °C with 1 mmol CdO and the molar ratio of 1:5 (OA: OLA), respectively; (c) 1 mmol CdO and the molar ratio of 2: 4 (OA: OLA); (d) 1 mmol CdO and the molar ratio of 3: 3 (OA: OLA).

We investigated the effect of temperature on the morphology and size of nanosized CdO as shown in Fig. S2. When the temperature was elevated to 300 ^{o}C, the morphology of the obtained nanosized CdO is still octahedral and the mean side length increases to 724.5 nm. At 320 ^{o}C, the mean side length of the CdO octahedrons is 868.2±98.2 nm. In addition, we conducted a series of experiments to discuss the changes of morphology and size by varying the molar ratio between OA and OLA. As shown in Fig. S2c and S2d, we can observe that the morphology of as-prepared products preserved the octahedral shape, only the increased size of octahedrons was presented. When the molar ratio of OA and OLA is 2: 4 and 3: 3, the mean side length of the octahedrons is 640.8±117.9 nm and 435.1±71.1 nm, respectively. Besides that, when the molar ratio is up to 4:2, clear transparent solution was generated and no nanoparticle was obtained.

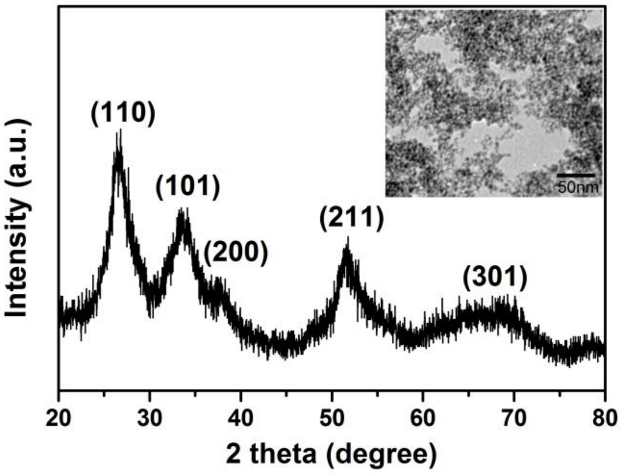


Fig. S3 XRD pattern of SnO_2 nanocrystals. The inset is TEM image of sample.

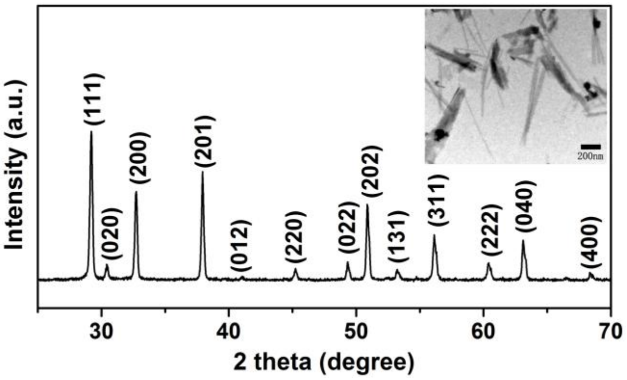


Fig. S4 XRD pattern of the obtained orthorhombic PbO. The inset is TEM image of sample.

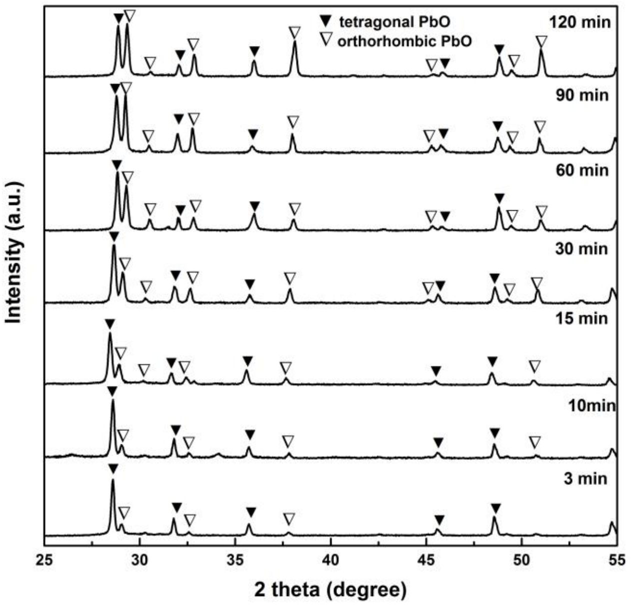


Fig. S5 Temporal XRD patterns evolution of tetragonal PbO/orthorhombic PbO mixture synthesized at 230 ^{o}C.

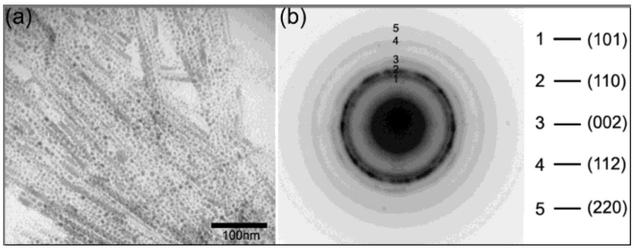


Fig. S6 (a) High-magnification TEM image of tetragonal PbO. (b) SAED of the as-prepared tetragonal PbO.

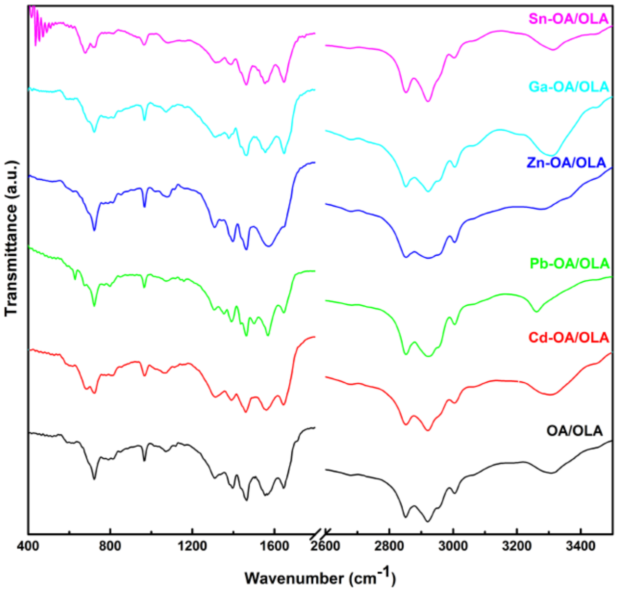
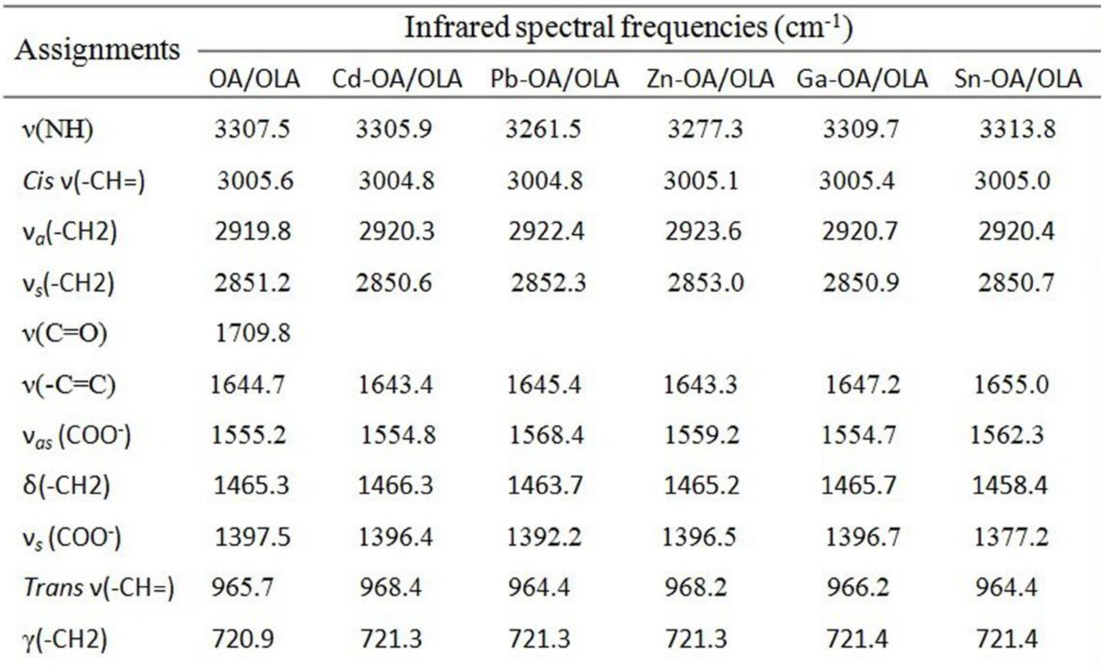


Fig. S7 FTIR spectra of OA/OLA, Cd-OA/OLA, Pb-OA/OLA, Zn-OA/OLA, Ga-OA/OLA and Sn-OA/OLA.

Table 1: Infrared Spectral Frequencies (cm^{-1}) with Their Assignments for OA/OLA, Cd-OA/OLA, Pb-OA/OLA, Zn-OA/OLA, Ga-OA/OLA and Sn-OA/OLA.



Assignments	Infrared spectral frequencies (cm^{-1})					
	OA/OLA	Cd-OA/OLA	Pb-OA/OLA	Zn-OA/OLA	Ga-OA/OLA	Sn-OA/OLA
ν(NH)	3307.5	3305.9	3261.5	3277.3	3309.7	3313.8
Cis ν(-CH=)	3005.6	3004.8	3004.8	3005.1	3005.4	3005.0
ν_a(-CH2)	2919.8	2920.3	2922.4	2923.6	2920.7	2920.4
ν_s(-CH2)	2851.2	2850.6	2852.3	2853.0	2850.9	2850.7
ν(C=O)	1709.8					
ν(-C=C)	1644.7	1643.4	1645.4	1643.3	1647.2	1655.0
ν_{as} (COO$^-$)	1555.2	1554.8	1568.4	1559.2	1554.7	1562.3
δ(-CH2)	1465.3	1466.3	1463.7	1465.2	1465.7	1458.4
ν_s (COO$^-$)	1397.5	1396.4	1392.2	1396.5	1396.7	1377.2
Trans ν(-CH=)	965.7	968.4	964.4	968.2	966.2	964.4
γ(-CH2)	720.9	721.3	721.3	721.3	721.4	721.4

The FTIR spectra of M-OA/OLA were recorded and compared with the results of the OA/OLA mixture. Fig. S7 shows FTIR spectra of the mixture of the M-OA complex and oleylamine. As the FTIR spectra for the other M-OA/OLA are very similar to that of Cd-OA/OLA, we focus our discussion on this spectrum. The important infrared frequencies attributed to the vibrations of the mixtures are listed in Table 1. The important infrared frequency, characteristic of the aliphatic chain of the OA/OLA mixture, remains almost unchanged upon formation of the Cd-OA complex from the acid. The spectrum of the OA/OLA mixture reveals modes characteristic of the oleyl groups:[1] the peaks at 2851.2 and 2919.8 cm^{-1} are due to the symmetric and asymmetric CH_2 stretching modes, and the peak at 3005.6 cm^{-1} is attributed to a cis –HC=CH– arrangement.[2] In addition there are modes characteristic of the amine group: the peak at 3305.9 cm^{-1} due to the ν(N-H) stretching mode. Importantly, the absence of the 1710 cm^{-1} band corresponding to C=O stretch bond of the carboxyl group (of pure oleic acid) and the appearance of two new bands characteristic of asymmetric ($\nu_{as}(COO^-)$) and symmetric ($\nu_s(COO^-)$) stretch at 1554.8 cm^{-1} and 1396.4 cm^{-1} (curve Cd-OA/OLA), confirm that the conversion of oleic acid to Cd-OA is complete and that these complexes possess an ionized structure.[3,4] The peaks of M-OA/OLA had shifted comparing with the OA/OLA mixture. These shifts may be attributed to the changes in counter ions associated with carboxylate anions, suggesting that acidic groups, carboxyl is the predominant contributor in metal ion uptake.[5,6]

Furthermore, based on previous studies of carboxylate, the wavenumber separation (Δν), between the ($\nu_{as}(COO^-)$ and $\nu_s(COO^-)$ IR bands can be used to diagnose the type of interaction between the carboxylate moiety and the metal ion.[7,8,9] For Δ > 200 cm^{-1}, a unidentate ligand is expected,[7] whereas for Δ < 110 cm^{-1}, it is a bidentate ligand. For a bridging ligand, Δ is between 140 and 200 cm-1. In our case, the Δν values differences range from 158 to 185.1 cm^{-1}, revealing bridging coordination.

References

1 N. Shukla, C. Liu, P. M. Jones and D. Weller, *J. Magn. Magn. Mater.*, 2003, **266(1–2)**, 178.

2 C. Cannas, A. Musinu, A. Ardu, F. Orr, D. Peddis, M. Casu, R. Sanna, F. Angius, G. Diaz and G. Piccaluga, *Chem. Mater.*, 2010, **22**, 3353.

3 K. N. Mehrotra, M. Chauhan and R. K. Shukla, *Bull. Chem. Soc. Jpn.*, 1995, ***68***, 1825.

4 G. Z. Liu, C. E. Conn and C. J. Drummond, *J. Phys. Chem. B*, 2009, **113**, 15949.

5 R. Ashkenazy, L. Gottlieb and S. Yannai, *Biotechnol. Bioeng.*, 1997, **55**, 1.

6 M. Iqbal, A. Saeed and S. I. Zafar, *J. Hazard. Mater.*, 2009, **164**, 161.

7 K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds; Wiley, New York, c1978, p. 220.

8 G. B. Deacon and R. J. Phillips, *Coord. Chem. Rev.*, 1980, **33**, 227.

9 S. Crisp, H. J. Prosser and A. D. Wilson, *J. Mater. Sci.*, 1976, **11**, 36.