

Electronic Supplementary Information (ESI) available for:

**Cation non-stoichiometry in multi-component oxide nanoparticles by solution chemistry: A case study on  $\text{CaWO}_4$  for tailored structural properties**

Wanbiao Hu, Wenming Tong, Liping Li, Jing Zheng, and Guangshe Li\*

*State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter and Graduate School of Chinese Academy of Sciences, Fuzhou 350002 (P. R. China)*

*E-mail: guangshe@fjirsm.ac.cn*

**Supporting Online Materials**

**Table S1.** Elemental analysis before and after  $\text{Ar}^+$  ion bombarding on the as-prepared  $\text{CaWO}_4$  nanocrystals using XPS.

**Fig. S1.** XRD patterns of  $\text{Zn}^{2+}$  doped  $\text{CaWO}_4$  samples with varied initial doping level of  $\text{Zn}^{2+}$  comparing with un-doped sample.

**Fig. S2.** TEM and HRTEM images of  $\text{Zn}^{2+}$  doped  $\text{CaWO}_4$  nanocrystals with the initial molar ratio of  $\text{Zn}^{2+}/(\text{Ca}^{2+}+\text{Zn}^{2+})$  at 0.15.

**Fig. S3.** XRD patterns of the sample after firing the as-prepared  $\text{Zn}^{2+}$  doped  $\text{CaWO}_4$  nanocrystals at  $800\text{ }^\circ\text{C}$  in air for 2 h.

**Fig. S4.** Raman spectroscopy of the samples prepared with and without involving citric acid.

**Fig. S5.** High-resolution XPS spectra of O1s for  $\text{Ca}_{1-x}\text{Zn}_x\text{WO}_4$  nanocrystals at given dopant contents.

**Fig. S6.** XRD patterns of the samples prepared with and without involving citric acid.

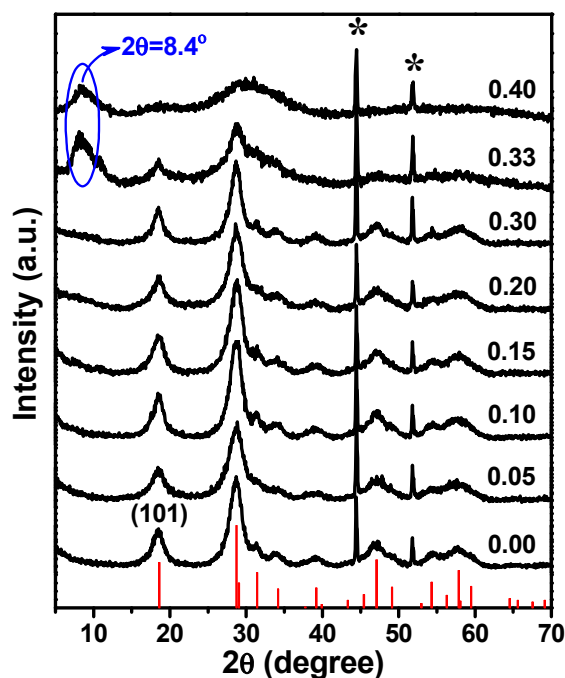
**Table S1.** Elemental analysis for the as-prepared CaWO<sub>4</sub> nanoparticles before and after Ar<sup>+</sup> ion bombarding using XPS.\*

| <b>Bombarding time (0 s)</b> |         |            |         |             |              |             |
|------------------------------|---------|------------|---------|-------------|--------------|-------------|
| Name                         | Peak/BE | Height/CPS | FWHM/eV | Area/CPS.eV | At. %        | Ca2p/W4f    |
| C1s                          | 284.62  | 10388.61   | 2.15    | 33914.4     | 32.19        | <b>3.03</b> |
| O1s                          | 530.59  | 57275.1    | 2.1     | 144247      | 48.97        |             |
| W4f                          | 35.21   | 19648.59   | 1.39    | 49823.2     | <b>4.68</b>  |             |
| Ca2p                         | 346.95  | 26491.59   | 1.41    | 74909.71    | <b>14.16</b> |             |

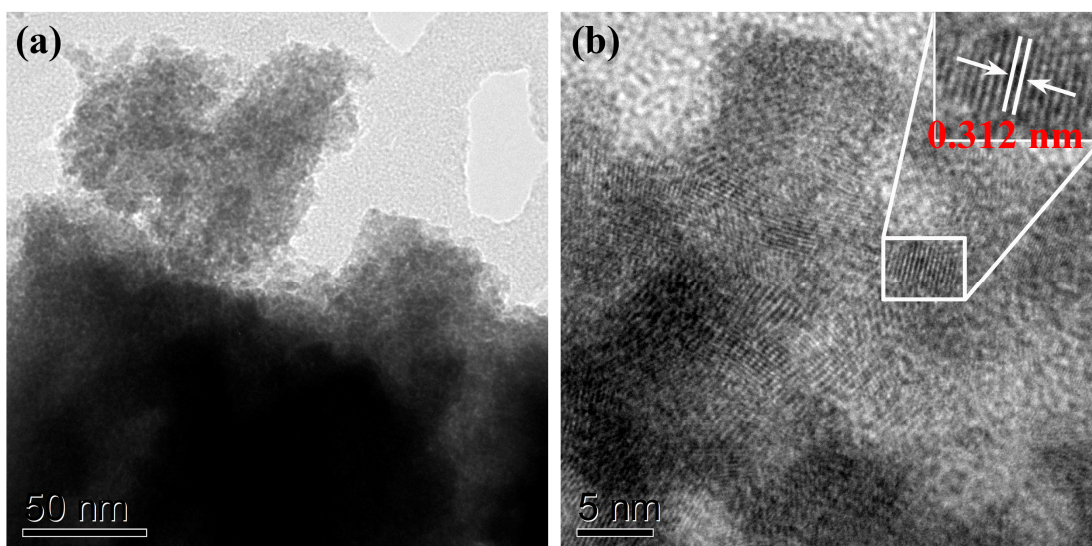
| <b>Bombarding time (5 s)</b> |         |            |         |             |              |             |
|------------------------------|---------|------------|---------|-------------|--------------|-------------|
| Name                         | Peak/BE | Height/CPS | FWHM/eV | Area/CPS.eV | At. %        | Ca2p/W4f    |
| C1s                          | 284.63  | 9502.31    | 1.85    | 30701.78    | 29.59        | <b>2.97</b> |
| O1s                          | 530.57  | 59949.68   | 1.99    | 147494.02   | 50.84        |             |
| W4f                          | 35.29   | 20107.61   | 1.44    | 51755.83    | <b>4.93</b>  |             |
| Ca2p                         | 346.98  | 27521.94   | 1.57    | 76245.64    | <b>14.64</b> |             |

| <b>Bombarding time (10 s)</b> |         |            |         |             |              |             |
|-------------------------------|---------|------------|---------|-------------|--------------|-------------|
| Name                          | Peak/BE | Height/CPS | FWHM/eV | Area/CPS.eV | At. %        | Ca2p/W4f    |
| C1s                           | 284.62  | 11277.79   | 1.75    | 34633.51    | 33.5         | <b>2.91</b> |
| O1s                           | 530.59  | 54037.56   | 2.16    | 141793.03   | 49.06        |             |
| W4f                           | 35.21   | 18423.49   | 1.4     | 46609.84    | <b>4.46</b>  |             |
| Ca2p                          | 346.94  | 24909.52   | 1.52    | 67359.87    | <b>12.98</b> |             |

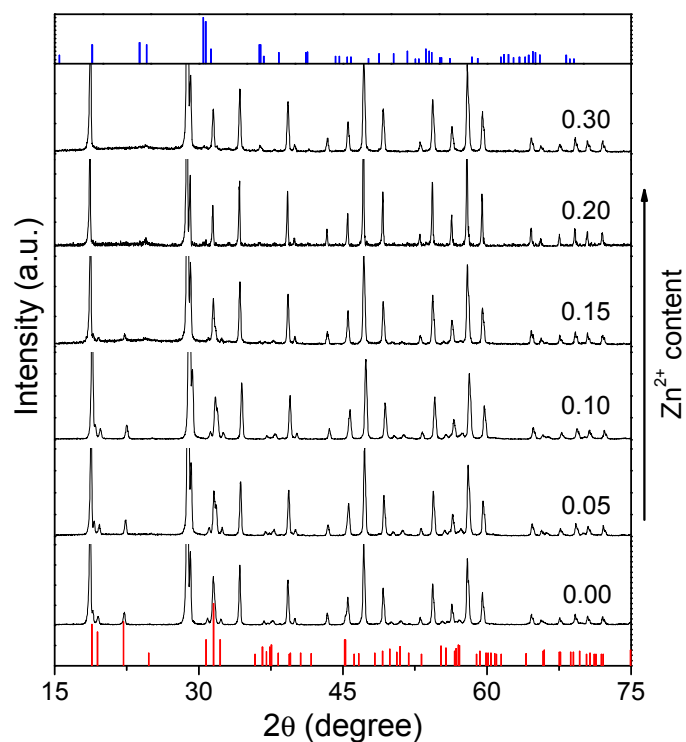
5 \* From the above table, it is clear that the ratio of Ca2p/W4f was decreased after Ar<sup>+</sup> ion bombarding on the sample for once, i.e., 5 s, which was further decreased after the second bombarding, i.e., the bombarding of 10 s. This indicated that the excessive cation should occur on the nanoparticles' surfaces.



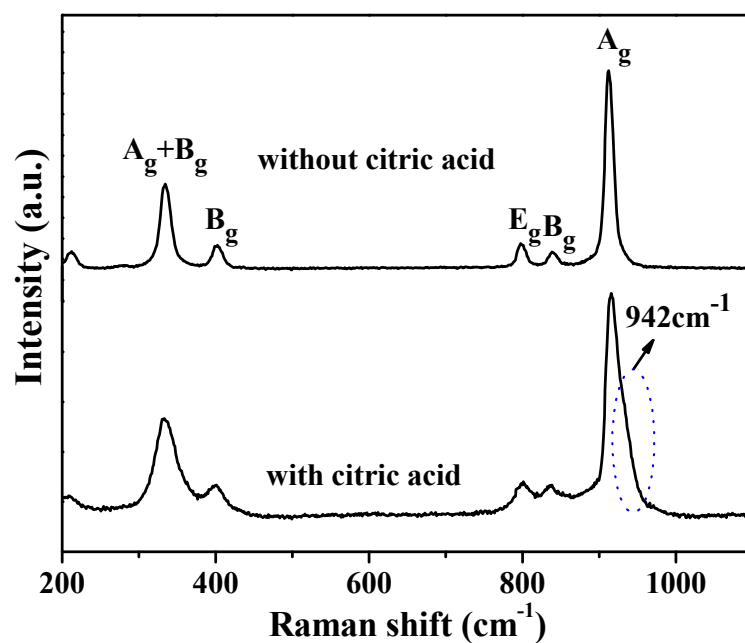
**Fig. S1.** XRD patterns of CaWO<sub>4</sub> samples with varied initial doping level of Zn<sup>2+</sup> comparing with undoped sample. The numbers denote the initial doping ratio of Zn<sup>2+</sup>/(Zn<sup>2+</sup>+Ca<sup>2+</sup>). Vertical bars at the bottom denote the standard data for scheelite structure of bulk CaWO<sub>4</sub> (JCPDS, No. 77-2233). Symbols "\*" denote the internal standard of Ni. It was found that when the ratio of Zn<sup>2+</sup> was below 0.30, no traces of possible impurities like monoclinic wolframite-typed ZnWO<sub>4</sub> or ZnO were observed. Doping Zn<sup>2+</sup> did not lead to the width variations of diffraction peaks. Strong diffraction intensities of all samples characterized the high crystallinity. Using Scherrer formula, crystallite sizes of all samples were estimated to be around 6 nm from diffraction line (101). When the initial ratio of Zn<sup>2+</sup>/(Zn<sup>2+</sup>+Ca<sup>2+</sup>) was beyond 0.30, an impurity phase centered at 2θ=8.4° appeared.



**Fig. S2.** TEM and HRTEM images of  $\text{CaWO}_4$  nanocrystals with an initial ratio of  $\text{Zn}^{2+}/(\text{Zn}^{2+}+\text{Ca}^{2+})$  at 0.15.

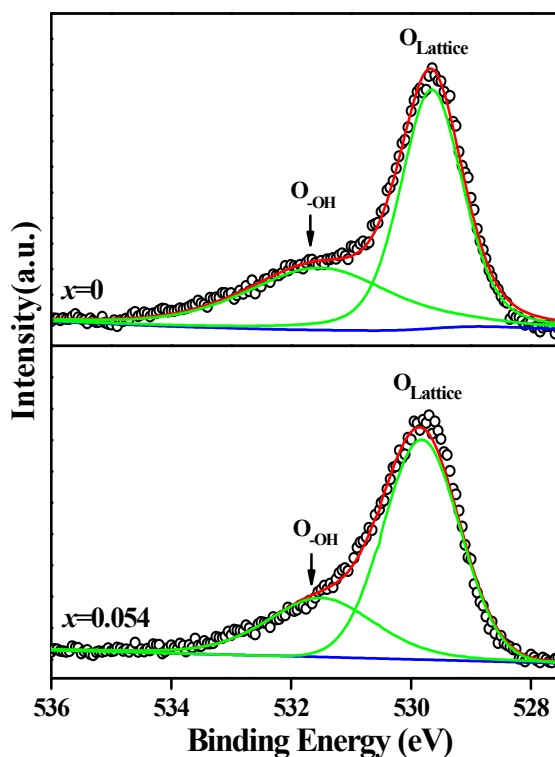


**Fig. S3.** XRD patterns of the samples after firing CaWO<sub>4</sub> nanocrystals with given doping levels at 800 °C in air for 2 h. Vertical bars at the bottom and top denote the standard data for monoclinic Ca<sub>3</sub>WO<sub>6</sub> (S.G.: P2<sub>1</sub>/n; JCPDS No. 22-0541) and monoclinic wolframite-typed ZnWO<sub>4</sub> (S.G.: P2/c; JCPDS No. 89-0447), respectively.

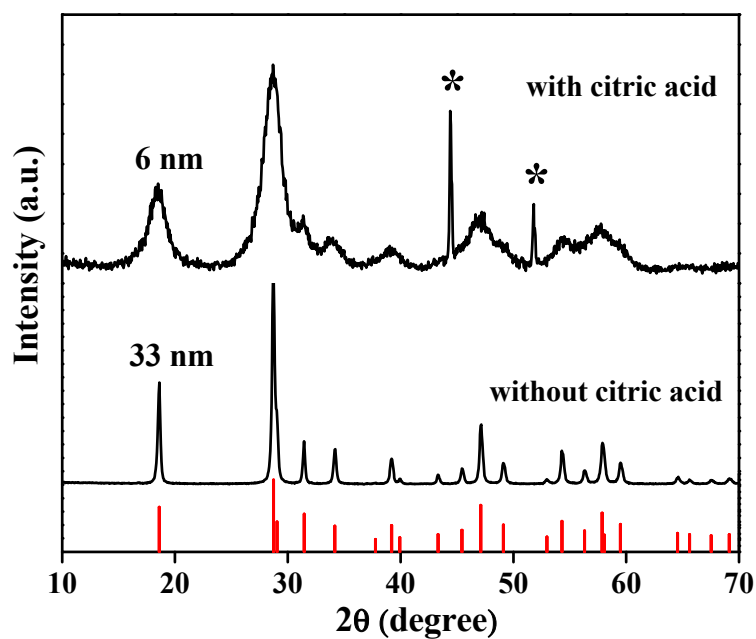


**Fig. S4.** Raman spectra of the samples prepared with and without involving citric acid. A shoulder centered at 942 cm<sup>-1</sup> was noticeably observed at the presence of citric acid, which cannot be ascribed to any vibrations of CaWO<sub>4</sub> or other possible adsorbed species, but a new vibration of surface disordered layer as reported for MnWO<sub>4</sub> nanocrystals<sup>ref\*</sup> prepared using the similar preparation conditions.

ref\*: W. M. Tong, L. P. Li, W. B. Hu, T. J. Yan, X. F. Guan and G. S. Li, *J. Phys. Chem. C*, 2010, **114**,



**Fig. S5.** High-resolution XPS spectra of O1s for  $\text{Ca}_{1-x}\text{Zn}_x\text{WO}_4$  nanocrystals at given dopant contents. It is seen that the XPS data for both samples contained a dominant signal centered at 529.8 eV with a shoulder at 531.6 eV. The dominant signal is associated with the lattice oxygen, while the shoulder is originated from the adsorbed oxygen of the hydrated surfaces as indicated by TG data in Fig. 4.



**Fig. S6.** XRD patterns of the samples prepared with and without involving citric acid. Vertical bars at the bottom denote the standard data for scheelite structure of bulk CaWO<sub>4</sub> (JCPDS, No. 77-2233). The average sizes were estimated to be 6 and 33 nm, which suggested that citric acid played an important role for the preparation of CaWO<sub>4</sub> nanocrystals.