Effects of Surface Chemistry on the Morphology Transformation of $ZnWO_4$ Nanocrystals: Investigated from Experiment and Theoretical Calculations

Pan Li [a)], Xian Zhao [b)], Yanlu Li [b)], Honggang Sun [b)], Liming Sun [b)], Xiufeng Cheng [b)], Xiaopeng Hao[b)], and Weiliu Fan [a)*]

[a)] Department of Chemistry and Chemical Engineering, and [b)] State Key Laboratory of Crystal Materials, Shandong University, Jinan 250100, China

* To whom correspondence should be addressed.

Tel: 86-531-88366330, Fax: 86-531-88365174,

E-mail: fwl@sdu.edu.cn

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Supporting Information

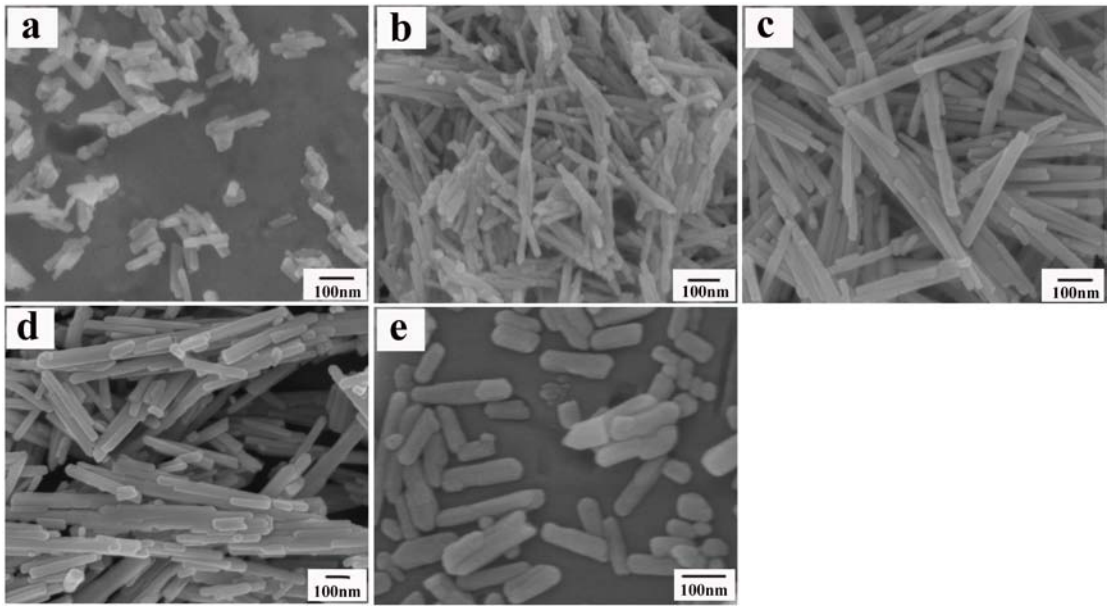

Fig. S1. SEM images of $ZnWO_4$ nanocrystals prepared under different pH conditions. (a) pH = 7.5; (b) pH = 8.5; (c) pH = 9.0; (d) pH = 9.5; (e) pH = 10.0.

Procedure for calculating surface energy of the polar facets as a function of μ_{Zn}:

The chemical potential μ_{ZnWO4} of a condensed and stoichiometric phase of zinc tungstate is written as a sum of three terms representing the chemical potential of each species within the crystal:

$$\mu_{ZnWO_4} = \mu_{Zn} + \mu_W + 4\mu_O \quad (1)$$

Since the surface is in equilibrium with the bulk $ZnWO_4$, we have $\mu_{ZnWO4} = E_{bulk}$. The zinc, tungsten and oxygen atoms are assumed to form no condensate on the surface. Consequently, the chemical potential of each species must be lower than the energy of an atom in the stable phase of the considered species:

$$\Delta\mu_{Zn} = \mu_{Zn} - E_{Zn}^{bulk} < 0 \quad (2)$$

$$\Delta\mu_W = \mu_W - E_W^{bulk} < 0 \quad (3)$$

$$\Delta\mu_O = \mu_O - \frac{1}{2}E_{O_2}^{gas} < 0 \quad (4)$$

The two inequations (2) and (4) define the upper boundaries of the zinc and oxygen chemical potentials. By combining Eqs. (3) and (1), we obtain the following lower boundaries:

$$\Delta\mu_{Zn} + 4\Delta\mu_O > -E_{ZnWO_4}^{f} \quad (5)$$

With

$$-E_{ZnWO_4}^{f} = E_{ZnWO_4}^{bulk} - E_{Zn}^{bulk} - E_{W}^{bulk} - 2E_{O_2}^{gas} \quad (6)$$

$E_{ZnWO_4}^{f}$ is the formation energy of $ZnWO_4$ with respect to the Zn and W atoms in their bulk phases, and the O atom in the gas phase, which is positive defined.

The surface energy of the bottom surface γ_{bottom} was calculated using

$$\gamma_{bottom} = \frac{1}{2A}(E_N^{surface} - N_{Zn}\mu_{Zn} - N_W\mu_W - N_O\mu_O) \quad (7)$$

Here, we define the O chemical potential as a particular value $\Delta\mu_O = 0$, then the surface energies are represented as functions of $\Delta\mu_{Zn}$, as it was shown in the following Table S1:

Table S1. The surface energies γ (J/m^2) for the polar surfaces as a function of μ_{Zn}.

	$\Delta\mu_{Zn}$ =0 (Zn rich)	$\Delta\mu_{Zn}$ = - $E_{ZnWO_4}^{f}$ (Zn poor)
$\gamma_{bottom}(100)$	4.85	-3.57
$\gamma_{bottom}(\bar{1}00)$	2.43	10.84
$\gamma(100)$	1.91	10.32
$\gamma(\bar{1}00)$	4.31	-4.10
$\pm\gamma(100)$	3.11	

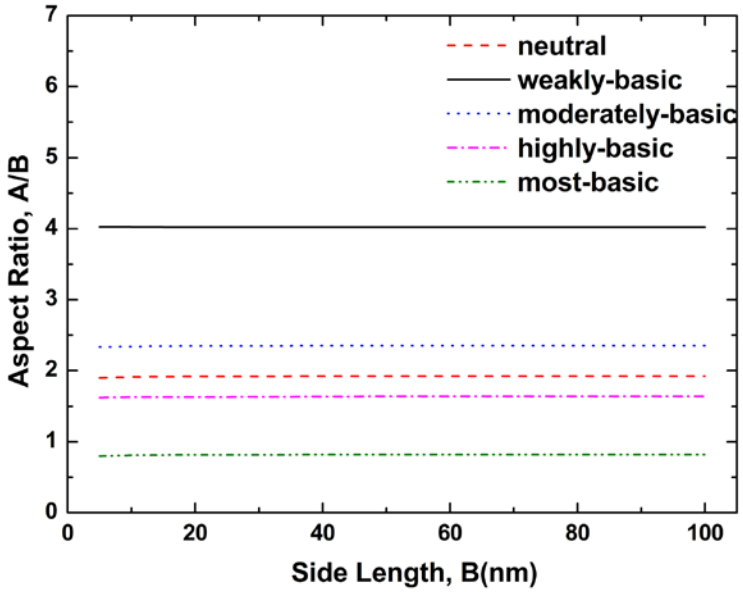

Fig. S2. Plot of optimized aspect ratio A/B of $ZnWO_4$ nanocrystals for each type of surface chemistry, with a side length B = 5 to 100 nm.