

Green, Water-Based Synthesis of ZnO Nanostructures

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We report on the synthesis of zinc oxide (ZnO) nanostructures using a simple, green, water-based process, without the aid of any chemical precursor or external energy source. Zinc plates were immersed in deionized water and kept at ambient conditions in a dark cabinet for up to 21 days. After immersion, the reaction products were analyzed using scanning electron microscopy, X-ray diffraction, X-ray photoelectron spectroscopy, photoluminescence spectroscopy and Raman spectroscopy. After short immersion times (1-3 days), ZnO agglomerates with a high concentration of oxygen defects were formed, which overlapped along the c axis to form ZnO nanoflowers. After long immersion times (21 days), ZnO microspikes with smooth surfaces, well-defined tips, and less oxygen defects were formed. This low-cost, low-energy synthesis process is an attractive alternative to produce ZnO nanostructures with low impact on the environment.

Keywords: ZnO, nanoflowers, nanostructures, growth, water, green

Introduction

Zinc oxide (ZnO) nanostructures have attracted much interest in the last two decades due to their unique properties, which include a wide band gap (3.3 eV), a large exciton binding energy (60 meV) at room temperature, thermal stability, biocompatibility, and piezoelectricity,¹⁻⁴ and can be used in several applications including bioimaging,^{5,6} sensors,⁷⁻⁹ field emission devices,¹⁰⁻¹² photodetectors,^{13,14} and solar cells.^{15,16}

Over the years, several methods have been explored to obtain ZnO nanostructures, including hydrothermal,^{17,18} chemical^{19,20} and physical^{21,22} vapor deposition processes. However, these processing techniques may involve several steps, as well as the use of high-temperature furnaces, high pressure vessels, expensive equipment, and/or harmful chemical reagents. Since these technical difficulties may hinder the implementation of ZnO nanostructures on a large scale,^{4,23} some authors have recently proposed the synthesis of ZnO nanostructures using simple and environmentally friendly routes, such as ZnO nanostructures produced by immersing plasma-treated zinc plates in water exposed to

ultra violet (UV) light,²⁴ which produced different ZnO nanostructures (nanoflowers, dendrites, and nanorods) depending on the UV-exposure time (24 to 72 h). The authors of the work²⁴ proposed a growth mechanism in which ions formed by the photoinduced splitting of water separate themselves between the valleys and hills of the surface of the Zn plate, resulting in the formation of ZnO nanocrystallites. Another proposed green synthesis route consists in the formation of ZnO nanopencils produced by heating ZnS powder using sunlight concentrated by a converging lens,²⁵ which rely on a solid-vapor growth mechanism to produce ZnO nanowires capped with smaller nanorods. A final proposed green synthesis route consists in the formation of ZnO nanoparticles using an eco-friendly tapioca-assisted^{26,27} and corn/potato starch-assisted²⁸ sol-gel process, which resulted in spherical ZnO nanoparticles of controlled sizes depending on the chelating agent and the calcination temperature. However, the majority of these synthesis routes somehow still rely on the use of chemical reagents, energy sources (UV lamps, calcination furnaces), or are only capable of producing suspended ZnO nanostructures.^{29,30} In this work, we report on a simple and green pathway to produce ZnO nanoflowers using a one-step, non-assisted process: the immersion of metallic zinc plates in deionized water, without the aid of any type

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of external power source (e.g., sunlight, UV-light, heat, pressure, etc.), catalyst, or chemical precursor.

Experimental

ZnO nanostructures were produced by immersing zinc plates in deionized water under dark conditions (no sunlight exposure) at room temperature and atmospheric pressure. First, Zn plates (99.9% pure) (Ical, São Paulo, Brazil) with dimensions of 9 mm × 9 mm × 1 mm were cleaned using acetone and isopropyl alcohol (Synth, Diadema, Brazil) for 10 min in an ultrasound bath. Then, batches of five Zn plates were placed in centrifuge tubes (polypropylene) filled with 10 mL of deionized (DI) water and stored at ambient conditions inside a dark cabinet (to avoid any sunlight) for up to 21 days.

For each immersion time (1, 2, 3, 4, 5, 6, 7, 14, and 21 days) there was a corresponding centrifuge tube with five Zn plates inside it. After each immersion time was completed, the Zn plates were removed from the water and dried under ambient conditions, without using heat or pressurized air. The reaction products at the surface of the Zn plates were analyzed using a JEOL JMS-6701F field-emission scanning electron microscope (FE-SEM) (Tokyo, Japan) operated at 1 kV of acceleration voltage; a Bruker AXS D8 Focus X-ray diffractometer (XRD) (Karlsruhe, Germany) set to scan between 30 and 60 degrees using a step of 0.02 degrees and 1 s of collection for each step; a Thermo Scientific K-Alpha X-ray photoelectron

spectrometer (XPS) (Waltham, MA, USA) equipped with an Al K α X-ray beam of 400 μ m in size; a Horiba T64000 Raman spectrometer (Kyoto, Japan) equipped with a 523-nm laser; and a Varian Cary Eclipse fluorescence spectrophotometer (Agilent, Santa Clara, CA, USA) equipped with a xenon lamp (set to 325 nm excitation wavelength) and a solid sample holder.

Results and Discussion

Figure 1 shows FE-SEM images of the reaction products found at the surface of the Zn plates as a function of immersion time in water (from 1 to 21 days). After 1 day of immersion, a porous film consisting of agglomerated nanoparticles with no obvious long-range organization was formed. After 2 and 3 days of immersion, more organized clusters started to form in some regions, while others remained porous-like. After 4 days of immersion, we can already see the formation of small and well-defined nanoflowers with hexagonal symmetry throughout the surface. Between 7 and 14 days of immersion, these nanoflowers grew in size reaching the micron scale, became more complex (i.e., more petals in each nanoflower), maintained their hexagonal symmetry, and adopted a sword-like morphology. Finally, after 21 days of immersion, the microswords collapsed into a dense agglomerated bed of swords mostly parallel to one another, and perpendicular to the surface, from which microswords with well-defined tips and smooth surfaces stood out.

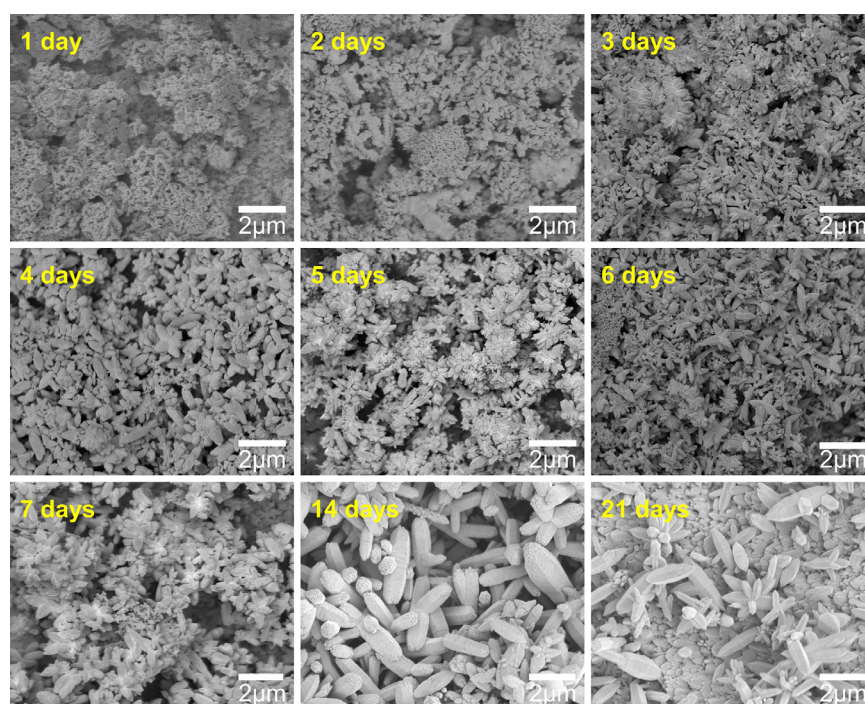


Figure 1. FE-SEM images obtained after 1, 2, 3, 4, 5, 6, 7, 14, and 21 days of immersion.

XRD measurements were conducted to assess the phases present in the reaction products. The XRD patterns of the samples as a function of immersion in water (Figure 2a) indicate only the presence of ZnO (wurtzite structure, space group $P6_3mc$) confirmed using JCPDS card number 36-1451, and metallic zinc arising from the substrate (hcp structure, space group $P6_3/mmc$), confirmed using JCPDS card number 04-0831. No other diffraction peaks were observed. It can also be noticed that the intensity of the ZnO diffraction peaks increased as the immersion time increased, which indicates that the volume fraction of ZnO nano/microstructures increased as a function of time (i.e., ZnO growth), in agreement with the FE-SEM observations. In order to further investigate the structure of the reaction products, Raman spectroscopy measurements were conducted on samples after 1 and 21 days of immersion in water, as shown in Figure 2b. Both samples exhibited a predominant peak at 439 cm^{-1} , which is known as the E_2 (high) Raman active optical phonon mode of wurtzite ZnO. We can also observe a shoulder in this predominant peak, which consists of two peaks located at 380 and 410 cm^{-1} , assigned to the A_1 (TO) vibration mode and multiple phonons, respectively. A broad peak located at 583 cm^{-1} can also be observed for both samples, assigned to the E_1 (LO) vibration mode, which is caused by defects such as oxygen vacancies and interstitial zinc.^{31,32} Interestingly, after 1 day of immersion the intensity of this broad peak was higher than after 21 days of immersion, indicating that at the initial stages of the reaction (1 day) the concentration of oxygen vacancies and/or interstitial zinc was higher than at the final stages (21 days). Finally, the peak located at 331 cm^{-1} corresponds to second-order Raman modes.^{31,33}

The samples were also analyzed using XPS to study their chemistry and oxidation state. Figure 3 shows the survey spectrum of the sample after 21 days of immersion, as well as the high-resolution Zn 2p and O 1s spectra after

1, 3, 7 and 21 days of immersion. The wide survey spectrum only shows the presence of Zn, O and C, with carbon being related to adventitious carbon contamination from the atmosphere. All high-resolution XPS spectra were corrected using the C–C component of the C 1s peak at 284.6 eV as reference.^{34,35} The high-resolution Zn 2p XPS spectra of the samples after 1, 3, 7 and 21 days of immersion (Figure 3b) all exhibit doublet peaks corresponding to Zn $2p_{3/2}$ and Zn $2p_{1/2}$ at 1021.1 and 1044.1 eV , respectively (spin-orbit splitting). Moreover, all Zn $2p_{3/2}$ peaks were fitted to only one sharp Gaussian, related to the Zn^{2+} chemical state in Zn–O bonds.^{34,35} On the other hand, the high-resolution O 1s XPS spectra of the samples after 1, 3, 7 and 21 days of immersion were all fitted to 3 peaks at 529.7 , 530.8 and 531.7 eV (Figures 3c–3f). The peak located at 529.7 eV can be attributed to Zn–O bonds in a hexagonal array (wurtzite structure),^{35,36} while the peak located at 530.8 eV can be attributed to oxygen deficient regions caused by oxygen vacancies in ZnO.^{37,38} The peak located at 531.7 eV can be attributed to adsorbed oxygen on the surface, arising from H_2O , O_2 and oxygenated carbon impurities.^{37,39} Although the position of these peaks did not vary as a function of immersion time, their intensities did. It can be observed that the peak related to oxygen vacancies in ZnO (530.8 eV) dominated the chemical state of oxygen after 1 day of immersion. However, its relative importance decreased as the immersion time proceeded (i.e., the peak intensity decreased), until reaching a steady-state after 7 days of immersion. Concomitantly, the intensity of the peak related to stoichiometric ZnO (529.7 eV) rapidly increased from 1 to 7 days of immersion, also a reaching steady-state after 7 days of immersion. In other words, the ZnO nanostructures formed at the initial stages of the reaction exhibited a high concentration of oxygen defects, which then decreased as a function of time, giving rise to a more stoichiometric ZnO after 7 days of immersion. These results are in good agreement with our Raman analyses. Finally,

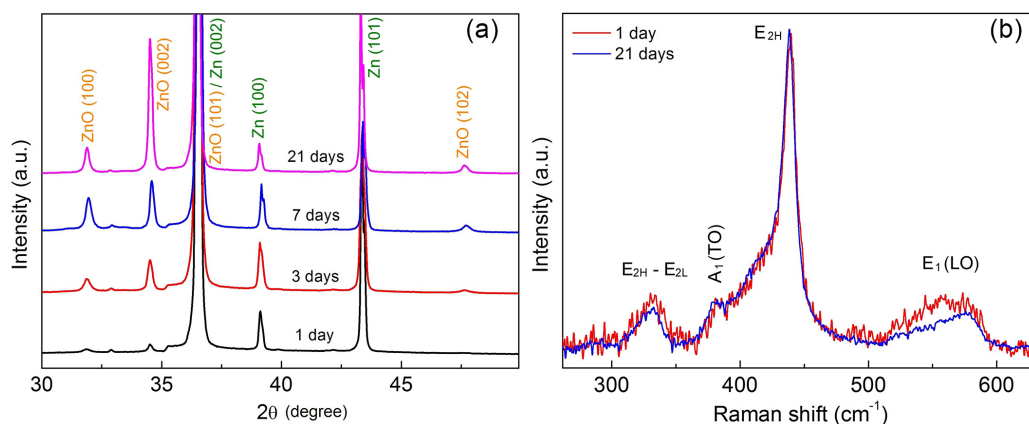


Figure 2. (a) XRD as a function of immersion time, (b) Raman shift after 1 and 21 days of immersion.

the peak related to adsorbed oxygen (531.7 eV) steadily decreased with immersion time. This could be explained using our FE-SEM results, since the initially porous ZnO nanostructures evolved into less porous and smoother ZnO structures, decreasing the surface area available for adsorption of H₂O, O₂ and oxygenated carbon impurities.

We also analyzed the immersed samples using photoluminescence (PL) spectroscopy, which can provide valuable information on the nature of defects, impurities and band gap in materials.⁴⁰ The PL spectra of the samples after 1, 3, 7 and 21 days of immersion in water are shown in Figure 4a. All samples presented a peak centered at 361 nm ($E_1 = 3.43$ eV) in the region of UV emission. This peak can be related to interband transitions between the 3d

band and the sp-conduction band originating from the Zn substrate.⁴¹ All our samples showed an UV-blue emission band between 373 to 409 nm (3.32 to 3.03 eV). This band was decomposed into 3 peaks at approximately 380, 390 and 403 nm ($E_2 = 3.3$, $E_3 = 3.2$, and $E_4 = 3.1$ eV), as shown in Figures 4b to 4e. The high energy emission (E_2) can be related to near band edge transitions in ZnO which originate from excitonic recombination.⁴² The sub-UV emission (E_3) can be related to free transitions between electrons and acceptors, and recombination of shallow donors.⁴² The emission in the visible (E_4 - E_{10}) can be related to deep level defects states of ZnO. In particular, blue emission can be related to transitions involving Zn defects, while green emission can be related to transitions involving oxygen

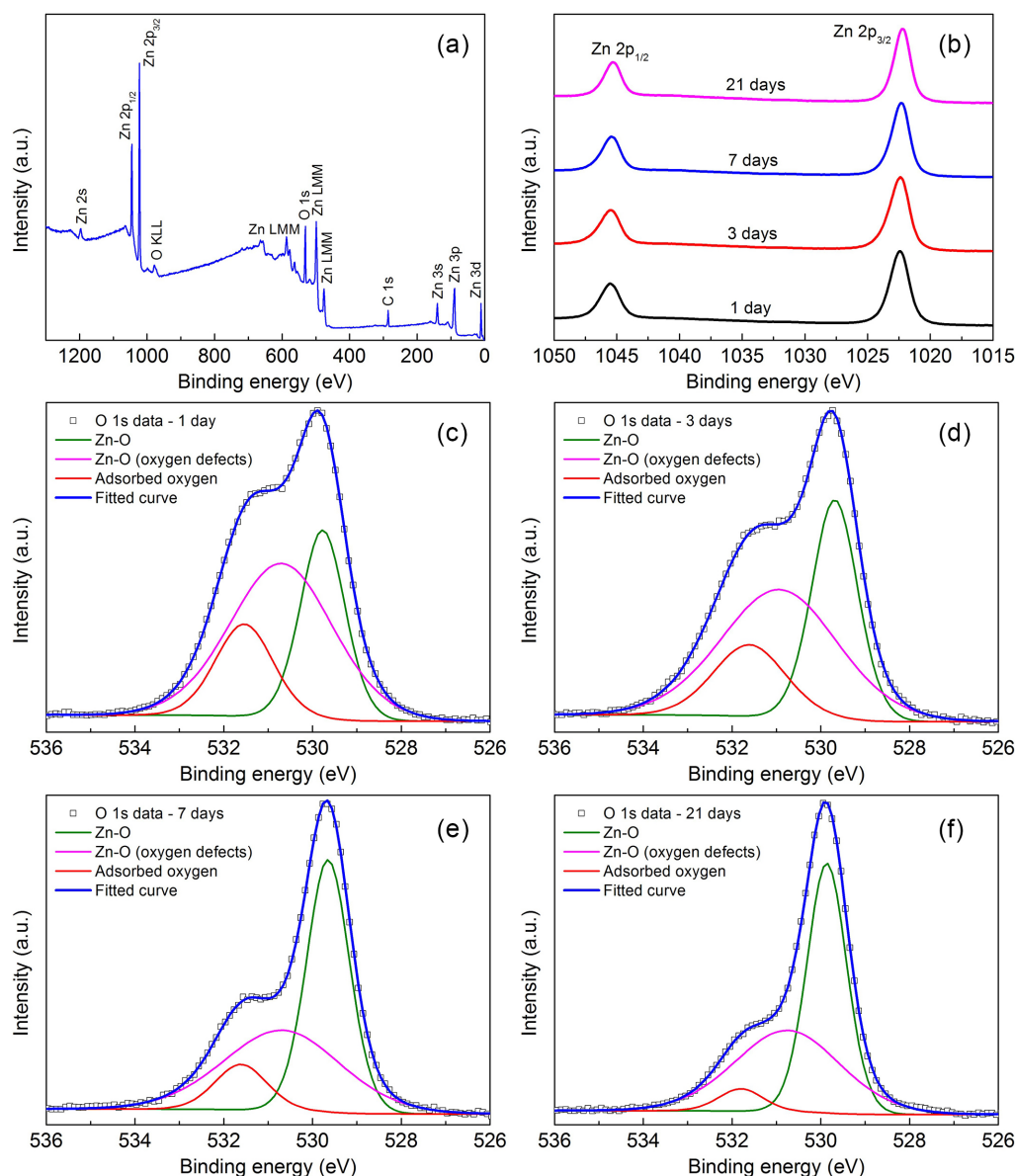
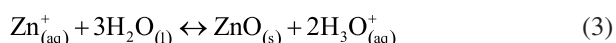
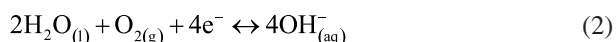


Figure 3. XPS spectra: (a) wide survey spectrum after 21 days of immersion; (b) Zn 2p after 1, 3, 7 and 21 days of immersion; and O 1s after (c) 1, (d) 3, (e) 7 and (f) 21 days of immersion.

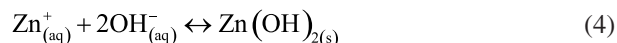
defects. These can include transitions from the conduction band to zinc vacancies, transitions from interstitial zinc trap to the valence band, transitions from interstitial zinc to zinc vacancy, and the recombination of electrons from deep levels or trap levels to oxygen defect states.⁴²⁻⁴⁴

The sub-UV emission can also be related to the presence of hydrogen and stacking fault defects.⁴² The integrated intensity ratio sub-UV/UV (E_3/E_2) can be used to compare hydrogen concentration and stacking fault defects among different samples. The integrated intensity ratios obtained after 1 and 3 days of immersion (ca. 6) were two times as large as the ratios obtained after 7 and 21 days of immersion (ca. 3), indicating a higher concentration of defects after short immersion times, in agreement with our XPS and Raman results.

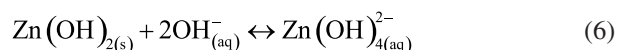
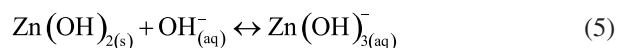
Based on our results, we propose the following pathway for the growth of ZnO nano/microstructures, schematically represented in Figure 5 (along with high-resolution FE-SEM images). After 1 day of immersion, the reaction between Zn and water resulted in the formation of small ZnO nanoparticles of approximately 10 nm in size (Figure 5a). This process starts with the dissolution of zinc and hydroxide ions provided by the oxidation of metallic zinc (equation 1) and the reduction of oxygen in the aqueous environment (equation 2), respectively.⁴⁵ The oxidation of zinc is thermodynamically spontaneous in aqueous media and can take place either in basic or acidic environments.⁴⁵ The zinc cations react with water (hydrolysis) producing hydronium and crystalline ZnO (equation 3), which acts as nuclei for the ZnO nanostructures observed in Figure 5a.



The reduction of oxygen (equation 2) can stimulate a local alkalinity due to the production of hydroxide ions, and this local pH increase can result in the formation zinc hydroxide, $\text{Zn}(\text{OH})_2$, according to equation 4.



The local pH increase can also induce the reaction of zinc hydroxide resulting in the formation of $\text{Zn}(\text{OH})_3^-$ and $\text{Zn}(\text{OH})_4^{2-}$ complexes according to equations 5 and 6, which are thermodynamically unlikely to occur in neutral environments.⁴⁵ However, these complexes can be obtained spontaneously from the interaction of pure zinc and water at 25 °C, depending on the pH of the system.⁴⁶⁻⁴⁸



Continuing with the description of Figure 5, after 2 days of immersion, the ZnO nanoparticles coalesced into hexagonal ZnO clusters (more stable shape of the wurtzite structure),⁴⁹ as shown in Figure 5b. After 4 days of immersion, the hexagonal ZnO clusters started to grow along the c-axis. This process is governed by the ZnO spontaneous dipole moment along the c-axis, which is due to the ZnO (0001) planes being positively charged (terminated by Zn^{2+}), and the (000 $\bar{1}$) planes being negatively charged (terminated by O^{2-}). The positive surfaces (Zn^{2+}) of the ZnO cluster can attract $\text{Zn}(\text{OH})_3^-$ and $\text{Zn}(\text{OH})_4^{2-}$ complexes forming ZnO according to equations 7 and 8, resulting in the anisotropic growth along the c-axis⁴⁹ (Figure 5c).

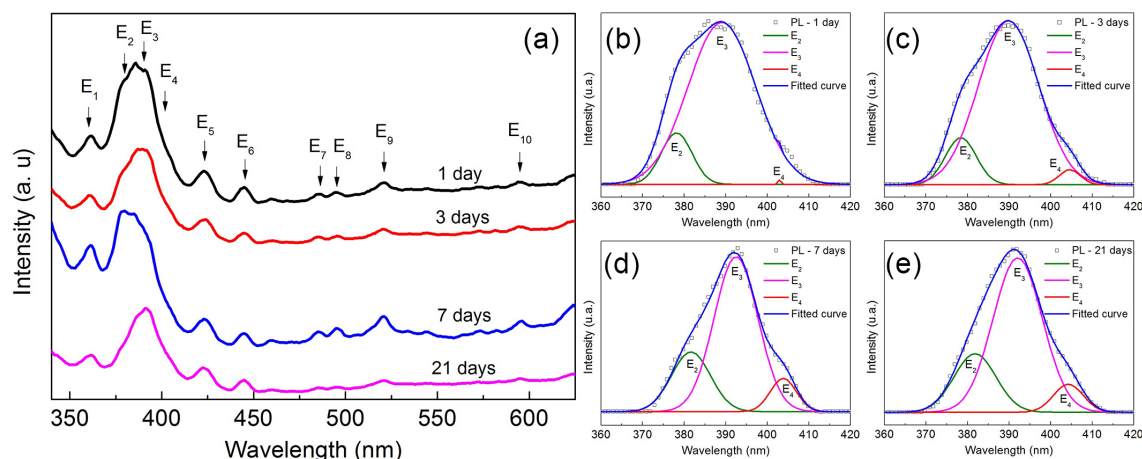
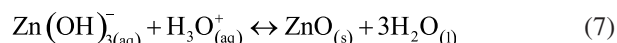
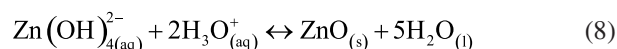


Figure 4. (a) Photoluminescence spectra after 1, 3, 7, and 21 days of immersion; Gaussian fitting of UV-blue emission after (b) 1, (c) 3, (d) 7, and (e) 21 days of immersion.



The stochastic nature of these reactions gives rise to the observed uneven (irregular) surfaces. Moreover, the ZnO clusters can be attached to other clusters, resulting in the formation of ZnO nanoflowers, in agreement with reports elsewhere.⁵⁰ After 14 days of immersion, the ZnO nanoflowers continued to grow along the c-axis, resulting in a sword-like morphology with a step-layered structure (Figure 5d), which arises from the differences in growth velocity (V) among the ZnO planes:⁵¹ $V_{(0001)} > V_{(\bar{1}01\bar{1})} > V_{(\bar{1}010)}$. After 21 days of immersion, a dense bed of ZnO microswords was formed (as shown in Figure 1), which acted as a barrier for the reaction, decreasing the concentration of the $\text{Zn}(\text{OH})_3^-$ and $\text{Zn}(\text{OH})_4^{2-}$ complexes in the aqueous solution, which in turn decreased the number of new nanoflowers being created and their growth rate. Finally, the tendency of the system to reduce its total surface energy led to the smoothing of the step-layered surface and uneven tips, resulting in well-defined and smooth ZnO microswords (Figure 5e). Recently, Jeem *et al.*²⁴ proposed a simple and environmentally friendly synthesis route to produce ZnO nanostructures: the immersion of plasma-

treated zinc plates in water under UV-light exposure (the so-called submerged photosynthesis of crystallites (SPSC) process). This photocatalytic process is accompanied by the generation of hydroxide ions, which is essential for the formation of the ZnO nanostructures. Extending the work of Jeem *et al.*,²⁴ in this work, we propose an even simpler and greener pathway to synthesize ZnO nanostructures using a single-step, water-based, non-assisted process: the immersion of zinc plates (without any surface treatment, such as plasma) in deionized water, without the aid of any type of external energy source (UV-lamp, heat, or pressure), catalyst, or chemical reagents. However, it can be noticed that the kinetics of formation of ZnO nanostructures in our experiments (dark conditions) is slower compared to the one obtained in the photocatalytic synthesis process (UV-radiation) used by Jeem *et al.*²⁴ (one week compared to 24 h, respectively). This difference can be explained in term of the rate of formation of hydroxide ions, which is faster in the UV-radiation activated process. Another interesting low-cost, green route to synthesize ZnO nanostructures was proposed by Almeida *et al.*,²⁶⁻²⁸ which uses a sol-gel process assisted by starch from botanical sources followed by calcination. The authors found that spherical ZnO

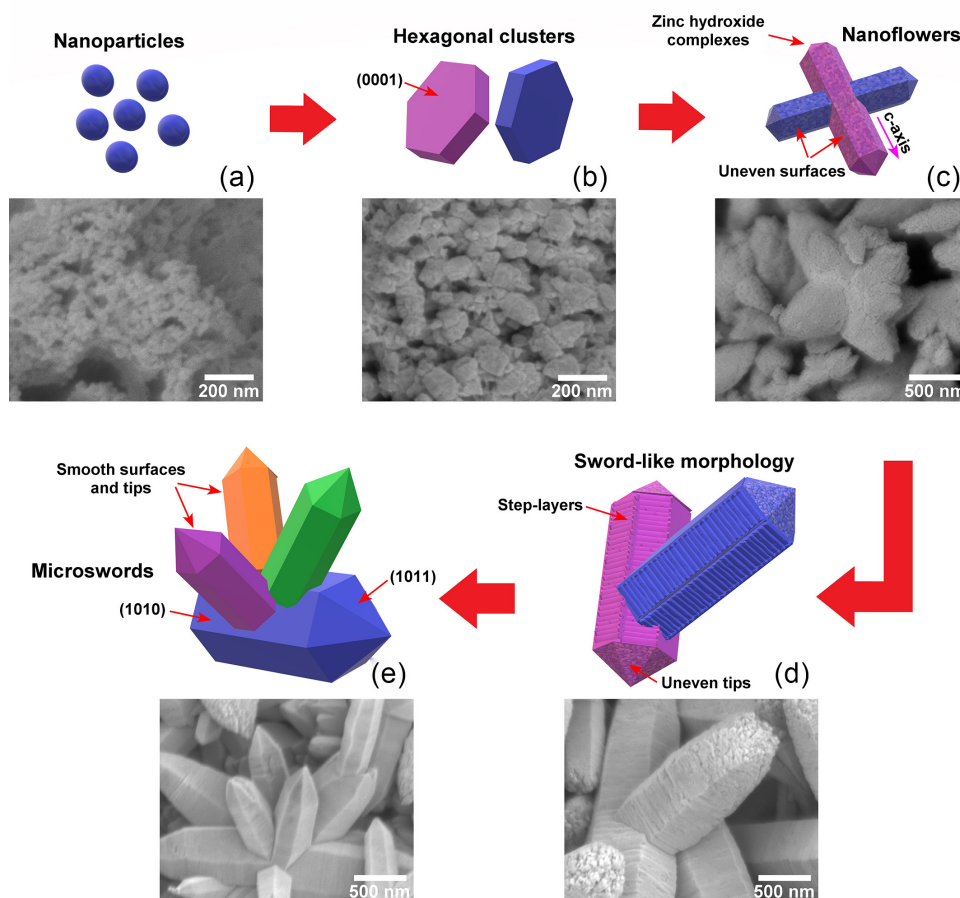


Figure 5. FE-SEM images and schematic representation of the pathway for growing ZnO nanostructures by immersing Zn plates in deionized water.

nanostructures of different sizes were produced depending on the type of the starch (corn, potato, tapioca) and calcination temperature. Despite Almeida *et al.*^{26–28} route being low cost, it still makes use of a chemical reagent (zinc nitrate hydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$)), and thermal energy for calcination at temperatures between 500 and 700 °C. Our results, however, show that it is possible to obtain ZnO nanostructures (nanoflowers) using a single-step, green approach that does not rely on any type of precursor or external energy source.

Conclusions

In this work, we report on the formation of ZnO nano/microstructures grown by immersing metal zinc plates into deionized water at room temperature, ambient pressure and under dark conditions, without the aid of any external energy source or catalyst. ZnO nanoporous agglomerates, nanoflowers and microswords were produced at different immersion times in water. It was also shown that as the immersion time increased, the concentration of oxygen defects in ZnO decreased, the size of the ZnO nano/microstructures increased, while their surface roughness decreased.

Acknowledgments

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