Morphology-controllable ZnO rings: ionic liquid-assisted hydrothermal synthesis, growth mechanism and photoluminescence properties

(Supporting information)

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Computational methods

All calculations are performed using the Vienna *ab initio* Simulation Package (VASP).[1,2] The exchange-correlation energy and potential are described by generalized gradient approximation (PW91).[3] The electron-ion interaction is described by the projector-augmented wave (PAW) method,[4,5] and the electronic wave functions are expanded by plane waves up to a kinetic energy of 350 eV. The surface Brillouin zone is sampled using a 3×3×1 Monkhorst–Pack mesh.[6] The selectivity of surface model is based on that the main exposed facets making up the surface of ZnO crystals are $(10\bar{1}0)$ and $(000\bar{1})$, respectively.[7] The surface were modeled by a periodical slab of six atomic layers separated by 15 Å of vacuum region. The slab models (3×3) for ZnO $(10\bar{1}0)$ and $(000\bar{1})$ surfaces were employed with corresponding coverage of 1/3 ML. During the calculation, the top three layers and the adsorbed species are allowed to be relaxed while the bottom layer atoms are fixed. The molecules in the gas phase have been calculated using a $15\times15\times15$ Å^3 cubic unit cell. Spin-polarized calculations were performed when needed.

The adsorption energy (E_{ads}) is calculated according to the formula: $E_{ads} = E_{A/M}-E_A-E_M$, where $E_{A/M}$, E_A, and E_M are the energies of adsorbed system, isolated molecule and substrate, respectively. The surface energy (γ) is calculated as follows: $\gamma=(E_S-E_B)/2A$, where E_S is the energy of the surface block, E_B the energy of the bulk crystal containing in the same number of atoms as the surface block, and A is the surface area. Because only one surface is allowed to relax with the bottom layers of the slab fixed, the coefficient before A is unity. Thus, the surface energy is given as: $\gamma=(E_S-E_B)/A$. The surface energy of the facets with adsorbed ILs is defined by:

$\gamma=(E_{S+E}-nE_E-E_B)/A$, where E_{S+E} is the energy of the facet with adsorbed ILs, E_E is the energy of a isolated IL and n is the number of IL molecules adsorbed to the surface. According to the Bolzmann-Gibbs statistics at a finite temperature T, the adsorption energy determines the density of the ILs on the given surface, and the ratio of the densities at a pair of surface equals, $N_{(10\bar{1}0)}/N_{(000\bar{1})}=\frac{\exp[E_{ads}^{(10\bar{1}0)}/k_BT]}{\exp[E_{ads}^{(000\bar{1})}/k_BT]}$, where k_B is the Bolzmann constant. This ratio is very sensitive to the difference in the adsorption energy. The charge transfers are analyzed here using Bader charges derived from the “Atoms in Molecules” theory of R Bader.[8]

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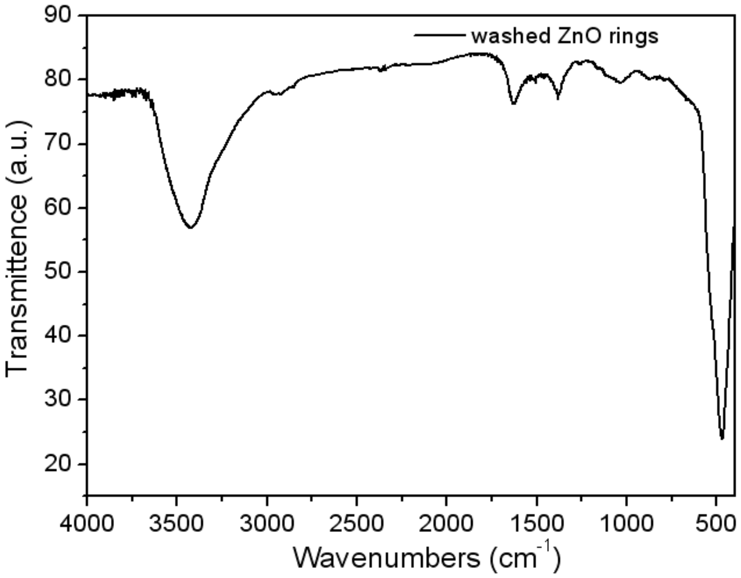
Fig. S1 FTIR spectrum of the thoroughly washed ZnO rings.



The vibration band at 470 cm^{-1} corresponds to the stretching frequency of ZnO.[1] The broad band around 3500 cm^{-1} corresponds to the symmetric and asymmetric stretching vibrations of the water molecules. The band at 1633 cm^{-1} is assigned to the H-O-H bending vibrations. The band at 1380 cm^{-1} is assigned to the bending vibrations of the O–H bonds of the free hydroxyl groups.[2] According to the FTIR analysis, no vibration bands of other adsorbed species (specially, [C_3mim]Br[3]) are detected, and render a cleaning ZnO surface.

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Fig. S2 A) XRD patterns of the samples synthesized at various concentrations of [C_3mim]Br with a fixed concentration of $Zn(NO_3)_2 \cdot 6H_2O$ (0.1 mol/L) and NaOH (0.1 mol/L) in 25 mL aqueous solution at 120 °C for 24 h. (a) without ILs, (b) 0.2 mol/L [C_3mim]Br, (c) 0.8 mol/L [C_3mim]Br, (d) 1.2 mol/L [C_3mim]Br. B) Ratio of the (0002)/(10$\bar{1}$0) peak intensities.

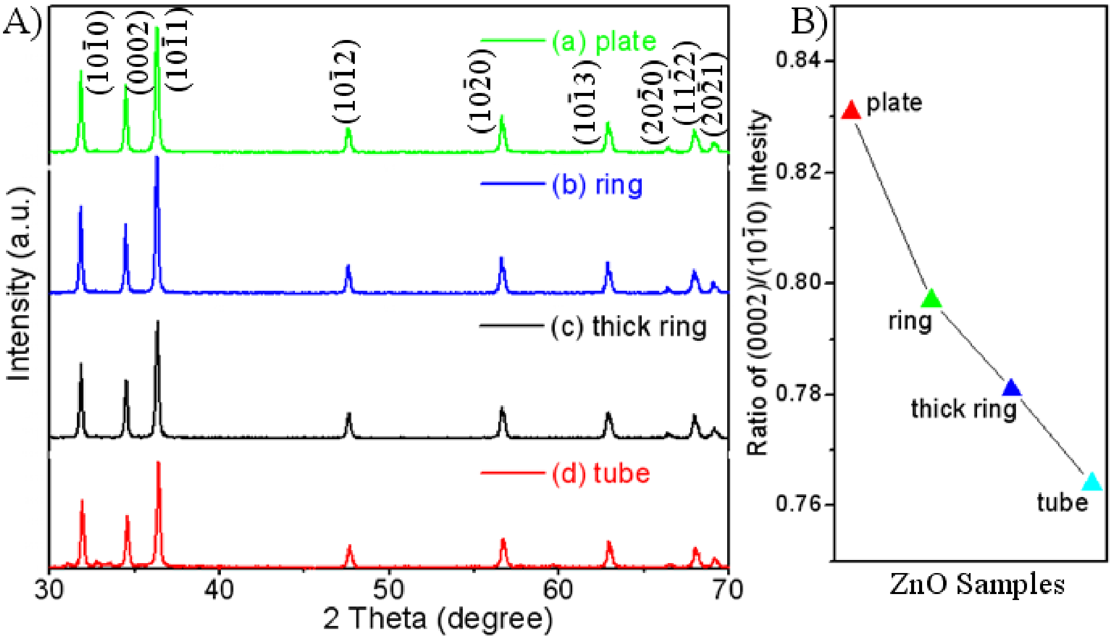

Fig. S3 FTIR spectra of (a) slightly washed [C_3mim]Br/ZnO rings, (b) pure [C_3mim]Br.

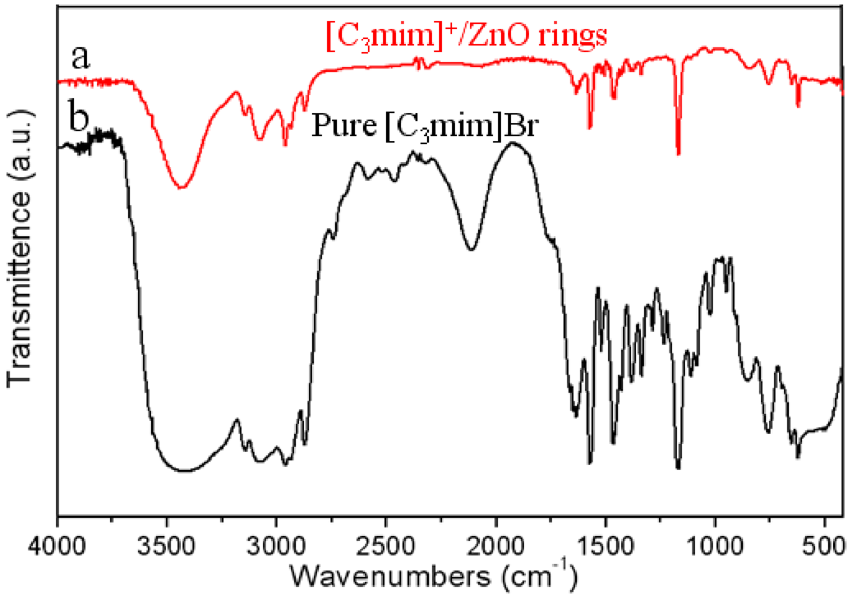

Table S1 Frequencies of FTIR vibration bands for the pure [C_3mim]Br and [C_3mim]Br/ZnO rings.

Frequencies of vibration bonds (cm^{-1})		Assignments
Pure [C_3mim]Br	ZnO/[C_3mim]Br	
3086	3080	C(2)–H bonds of imidazole ring stretching vibration
2960, 2874	2961, 2874	C–H bonds of alkyl chains stretching vibration
1568, 1463, 1169	1573, 1464, 1169	imidazole ring skeleton stretching vibration
1022	1021	C–N bonds of imidazole ring stretching vibration
1633	1634	C=C stretching vibration
----	460	Zn–O vibration of ZnO

The adsorption of [C_3mim]Br on ZnO crystals was confirmed by the FTIR of as-prepared ZnO rings (Fig. S3). The main frequencies of peaks are listed in Table S1, which shows weak vibration bands at 1568, 1463 and 1169 cm^{-1}, consistent with that of the imidazole ring skeleton stretching vibration.[1] The bands around 2960 and 2874 cm^{-1} are assigned to the C–H bonds of alkyl chains. The bands at 1633 cm^{-1} is assigned to the C=C stretching vibration. The bands at 3086 cm^{-1} are assigned to the stretching vibration of C(2)–H of imidazole ring.[2] All the above vibration bands are consistent with the literature.[3] Compared with that of the pure [C_3mim]Br, the relative intensity of the H−C(2) stretching vibration in the [C_3mim]Br/ZnO is weakened. Based on the analysis of FTIR spectra, it can be concluded that [C_3mim]Br adsorbs on ZnO surfaces, and the interactions focus on the H–C(2) of the imidazole ring and surface O atoms.

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Fig. S4 Structural model of the isolated [C_3mim]Br. Deep gray: C; sky-blue: N; white: H; deep red: Br.

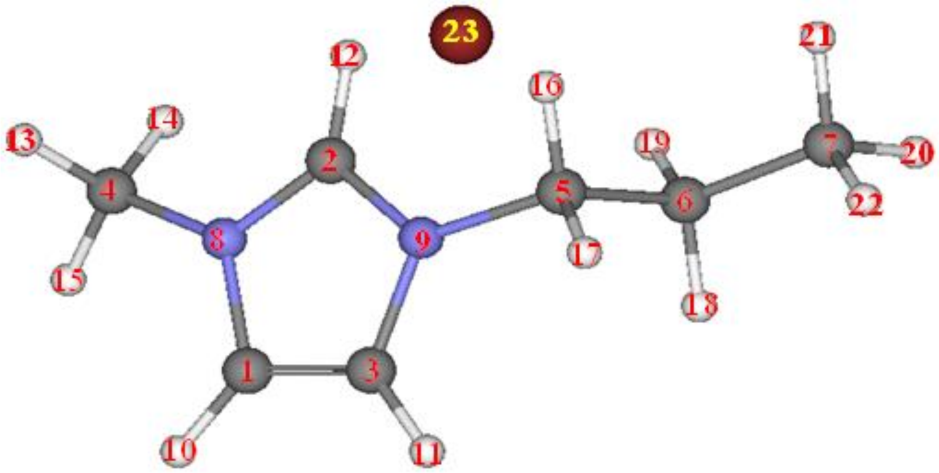
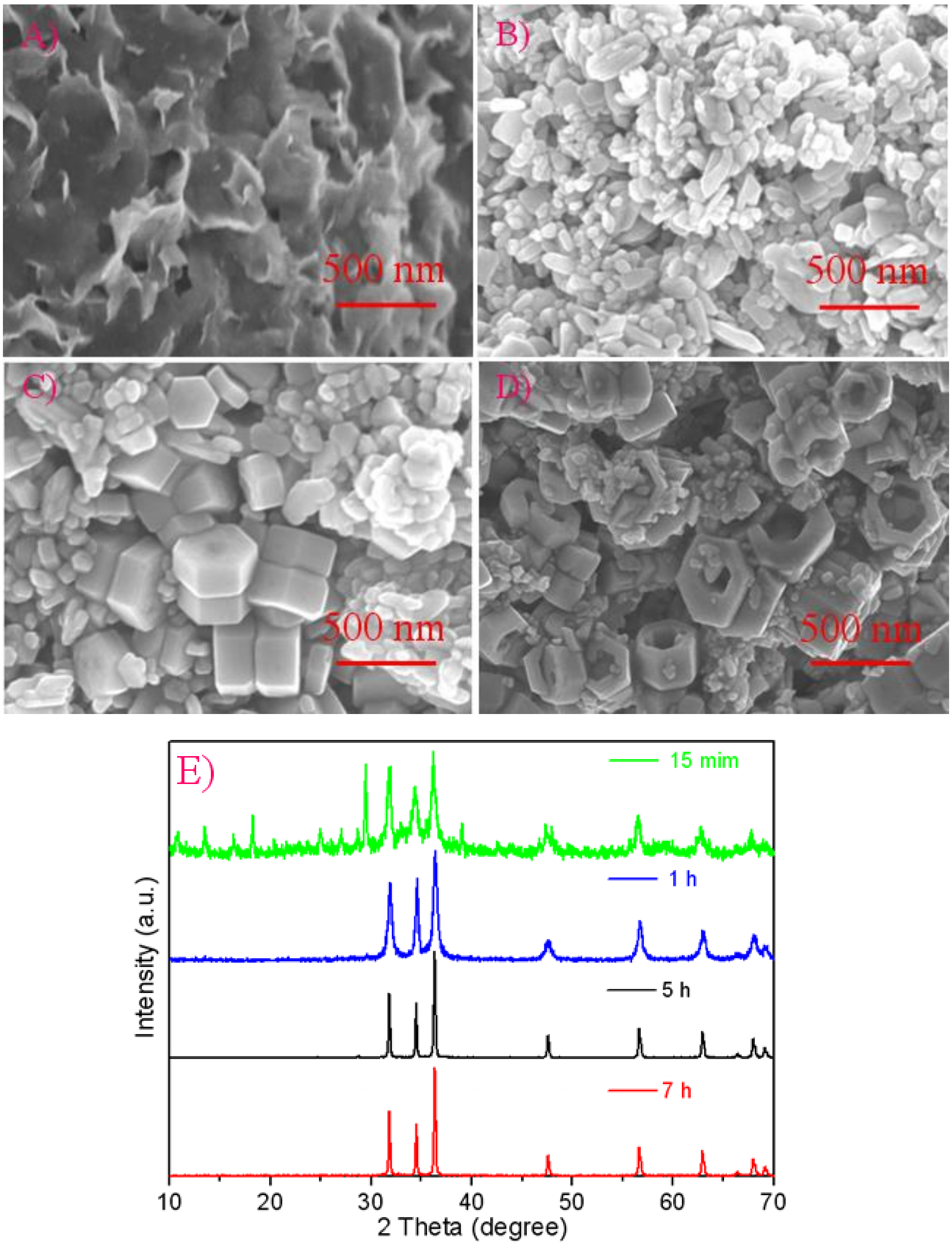


Table S2 Bader charge analysis of the isolated and adsorbed $[C_3mim]Br$ on the ZnO $(10\bar{1}0)$ and $(000\bar{1})$ facets (*e*).

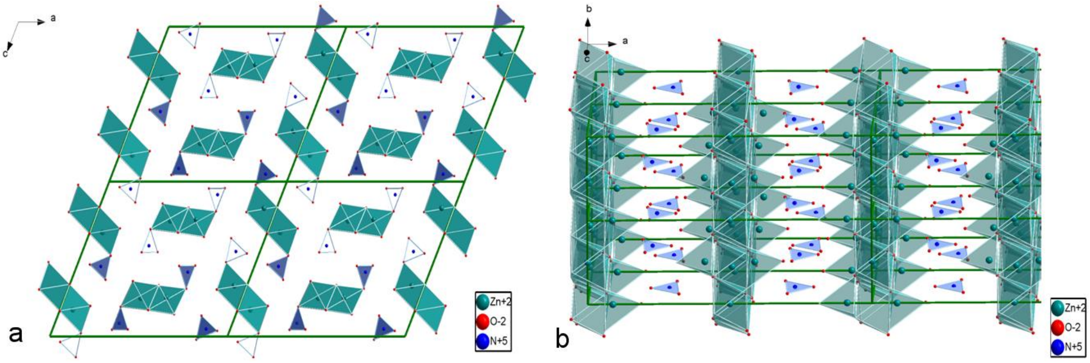
Atoms	Isolated $[C_3mim]Br$	Adsorbed $[C_3mim]Br$ on $(000\bar{1})$	Adsorbed $[C_3mim]Br$ on $(10\bar{1}0)$
C1	3.1239	2.9975	3.1160
C2	1.4932	2.0271	1.8930
C3	3.1269	3.3279	3.3098
C4	3.5369	3.6766	3.7951
C5	3.4578	3.6653	3.5708
C6	4.0870	4.1131	3.9294
C7	4.1072	4.2273	4.0273
N8	7.7911	7.7666	7.6417
N9	7.7417	7.6974	7.6493
H10	0.8658	0.8594	0.7437
H11	0.8612	0.7435	0.7968
H12	0.8445	0.3270	0.4914
H13	0.9356	0.7211	0.8985
H14	0.8157	0.8335	0.6075
H15	0.9259	0.9447	0.9427
H16	0.9222	0.7764	0.8920
H17	0.9253	0.8881	0.9339
H18	0.8840	0.8773	1.0299
H19	0.9263	0.9055	0.9592
H20	1.0079	0.8417	0.9272
H21	0.9832	0.9497	0.9613
H22	0.9009	0.9709	1.0109
$[Br^-]$23	7.7360	7.5691	7.6188
$[C_3mim]^+$	50.2642	50.1376	50.1274
Total	58.0002	57.7076	57.7462

Fig. S5 SEM images of the samples which had been hydrothermal treated for (A) 15 min, (B) 1 h, (C) 5 h, and (D) 7 h. The corresponding XRD patterns of the samples are in (E).



To investigate the morphological evolution and formation mechanism of ZnO rings, time-dependent experiments were carried out and the products obtained at different reaction stages were investigated. The SEM images of these products are displayed in Fig. S5. Fig. S5A shows that irregular thin plates were formed at the initial stage (15 min), and the product was a mixture of $ZnNO_3(OH)\cdot H_2O$, $Zn_5(NO_3)_2(OH)_8\cdot 2H_2O$ and ZnO, which was confirmed by the XRD result (JCPDS No. 24-1460, 47-0965, and 36-1451, Fig. S5E). For the reaction proceeding for 1 h, product with plate-like shape and nanoparticles was obtained (Fig. S5B). When the reaction time is prolonged to 5 h, the hexagonal disk was formed and corrosion pits appeared in the middle of the hexagonal disk surface, as shown in Fig. S5C. When the reaction time was increased to 7 h, the corrosion pits have penetrated through the disks, forming hexagonal rings, as shown in Fig. S5D. The XRD patterns of the ZnO samples, obtained at 1, 5 and 7 h, are similar, which are all pure phase ZnO (JCPDS No. 36-1451). But the ratios of the relative peak intensities for (0002) and $(10\bar{1}0)$ planes are decreased gradually, indicating that ZnO crystals have performed elongation along the [0001] direction and the dominate facets, $(10\bar{1}0)$, increases, which is consistent with the SEM results. All these results indicate that $[C_3mim]Br$ will protect the lateral $(10\bar{1}0)$ facets of ZnO crystals, and promote the formation of ring-like structures.

Fig. S6 Crystal structure diagram: a) $ZnNO_3(OH)\cdot H_2O$; b) $Zn_5(NO_3)_2(OH)_8\cdot 2H_2O$.[1,2]



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