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SUPPLEMENTARY MATERIAL TO

Zinc oxide nanoparticles prepared by thermal decomposition of zinc benzenepolycarboxylato precursors: Photoluminescent, photocatalytic and antimicrobial properties

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EXPERIMENTAL

Solid-state kinetics under non-isothermal conditions

The general equation (Eq. (1)) was used to describe the kinetics of thermally induced reactions in the solid state:[1]

$$\frac{\mathrm{d}\alpha}{\mathrm{d}\tau} = A\exp\left(-\frac{E_\mathrm{a}}{RT}\right)f(\alpha) \tag{1}$$

where E_a is the apparent activation energy, A is the pre-exponential factor, and $f(\alpha)$ is an algebraic expression of the kinetic model as a function of conversion degree, α. The value of α, at any temperature and for all heating rates was determined as

$$\alpha = \frac{m_\mathrm{i} - m}{m_\mathrm{i} - m_\mathrm{f}} \tag{2}$$

where m is the mass of a sample at a certain temperature, while m_i and m_f are the initial and final masses, respectively. In DTG data, α represents the ratio of the partial peak surface area for a given temperature in relation to the total peak surface area.

Under non-isothermal conditions, for measurements at constant heating rates, Eq. (1) is usually converted to:

$$\beta\frac{\mathrm{d}\alpha}{\mathrm{d}\tau} = A\exp\left(-\frac{E_\mathrm{a}}{RT}\right)f(\alpha) \tag{3}$$

where β is the heating rate, $\beta = \mathrm{d}T/\mathrm{d}\tau$. The integral form (Eq. (4)) of the reaction can be obtained by integrating Eq. (3) as:

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$$g(\alpha) = \int_0^{\alpha} \frac{\mathrm{d}\alpha}{f(\alpha)} = \frac{AE_a}{R\beta} p(x) \quad (4)$$

where $p(x)$ is the temperature integral for $x = E_a/RT$, which does not have an analytical solution.[2]

The non-isothermal kinetic analysis of complexes **1**–**4** was performed under four heating rates (15, 20, 25 and 30 °C min^{-1}) using the Kissinger method:[3]

$$\ln\frac{\beta}{T^2} = \ln\frac{AR}{E_a} - \frac{E_a}{RT} \quad (5)$$

where T is the temperature corresponding to the maximum of the DTG peak.

The thermodynamic activation parameters, change of activation entropy ($\Delta S^{\#}$), activation enthalpy ($\Delta H^{\#}$) and Gibbs free energy of activation ($\Delta G^{\#}$) were calculated for all degradation steps,[4,5] using Eqs. (6)–(8):

$$\Delta S^{\neq} = R\left[\ln\frac{Ah}{k_B T}\right] \quad (6)$$

$$E_a \approx \Delta H^* - RT \quad (7)$$

$$\Delta G^* = \Delta H^* - T\,\Delta S^* \quad (8)$$

where h and k_B are the Planck's and the Boltzmann's constants, respectively.

RESULTS AND DISCUSSION

TABLE S-I. Thermogravimetric results for precursors **1**–**4**

Precursor	Stage	TG range, °C	DTG peak temperature, °C	Mass loss, % (Calc., %)	Fragment loss	Residue
1	1	30–386	365	36.9 (34.2)	$-C_5H_5N_2 + CO_2$	
	2	386–465	432	26.7 (26.5)	$-C_5H_4N + CO$	
	3	465–548	511	19.0 (17.4)	$-C_6H_4$	ZnO
2	1	30–411	402	30.5 (30.5)	$-C_5H_4N + CO_2$	
	2	411–486	441	30.1 (30.2)	$-C_5H_4N_2 + CO$	
	3	486–560	510	18.7 (18.9)	$-C_6H_4$	ZnO
3	1	30–175	159	4.33 (4.30)	H_2O	
	2	175–348	310	17.0 (17.2)	$CO_2 + CO$	
	3	348–440	391	36.8 (36.8)	$-C_5H_4N + -C_6H_4$	
	4	440–504	491, 502	24.7 (22.0)	$-C_5H_4N_2$	ZnO
4	1	30–461	420	53.5 (53.4)	$2C_{10}H_9N_3 + CO_2$	
	2	461–540	509	21.0 (20.1)	$-C_6H_2 + CO + CO_2$	2ZnO

TABLE S-II. Thermodynamic and kinetic parameters of the thermal degradation of 1–4

Precursor	Stage	E_a / kJ mol^{-1}	ln(A / min^{-1})	$\Delta H^{\#}$ / kJ mol^{-1}	$\Delta S^{\#}$ / J mol^{-1} K^{-1}	$\Delta G^{\#}$ / kJ mol^{-1}
1	1	235.7 ± 1.9	44.7 ± 10.6	230.4	86.2	175.4
	2	163.9 ± 2.4	27.8 ± 10.3	158.0	–54.6	196.5
	3	75.8 ± 2.9	10.4± 9.6	69.3	–200.3	226.4
2[6]	1	284.1 ± 9.0	51.0 ± 12.0	278.5	138.6	191.1
	2	254.9 ± 10.6	43.1 ± 12.8	248.9	72.2	203.3
	3	105.6 ± 6.5	15.4 ± 10.5	99.1	–160.2	231.1
3	1	100.6 ± 1.3	28.3 ± 9.8	97.0	–46.5	117.1
	2	136.6 ± 2.2	28.1 ± 10.2	131.8	–50.8	161.4
	3	294.2 ± 13.4	52.7 ± 12.9	288.7	152.9	187.1
	4	196.5 ± 6.7	29.9 ± 11.1	190.1	–37.8	219.4
4	1	296.5 ± 11.4	51.8 ± 14.2	290.7	145.0	190.2
	2	68.1 ± 0.6	9.1 ± 8.1	61.5	–211.1	226.7

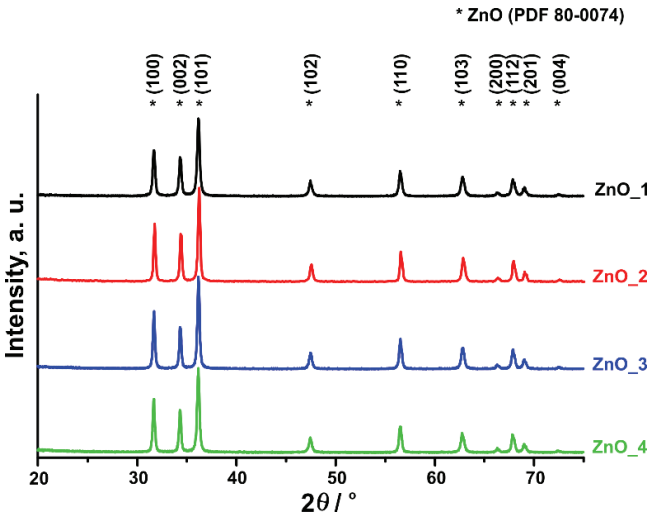

Fig. S-1. XRPD patterns of ZnO_1–ZnO_4.
Diffraction peaks are indexed according to PDF 80-0074.

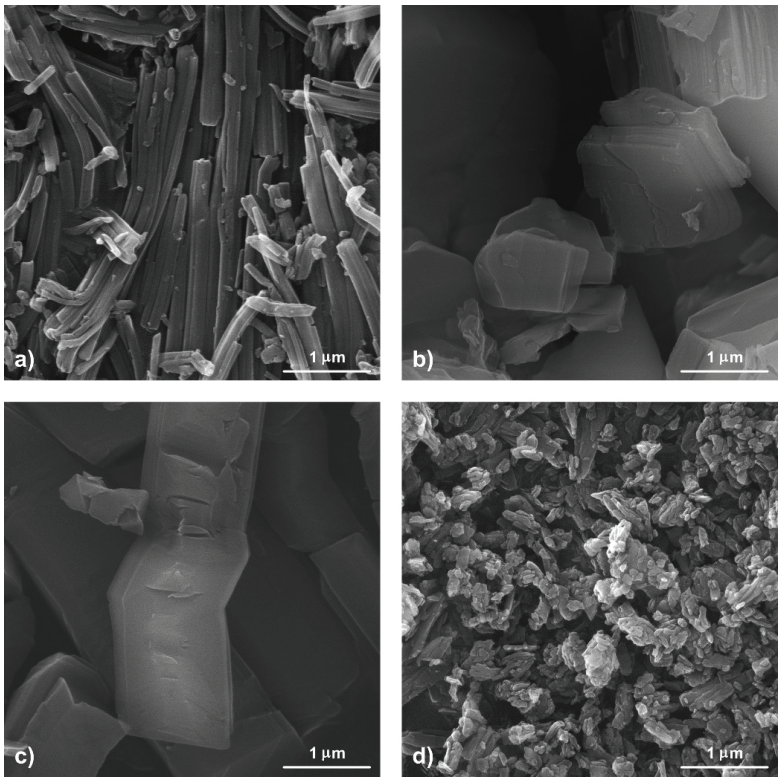

Fig. S-2. FESEM images of precursors **1** (a), **2** (b), **3** (c) and **4** (d).

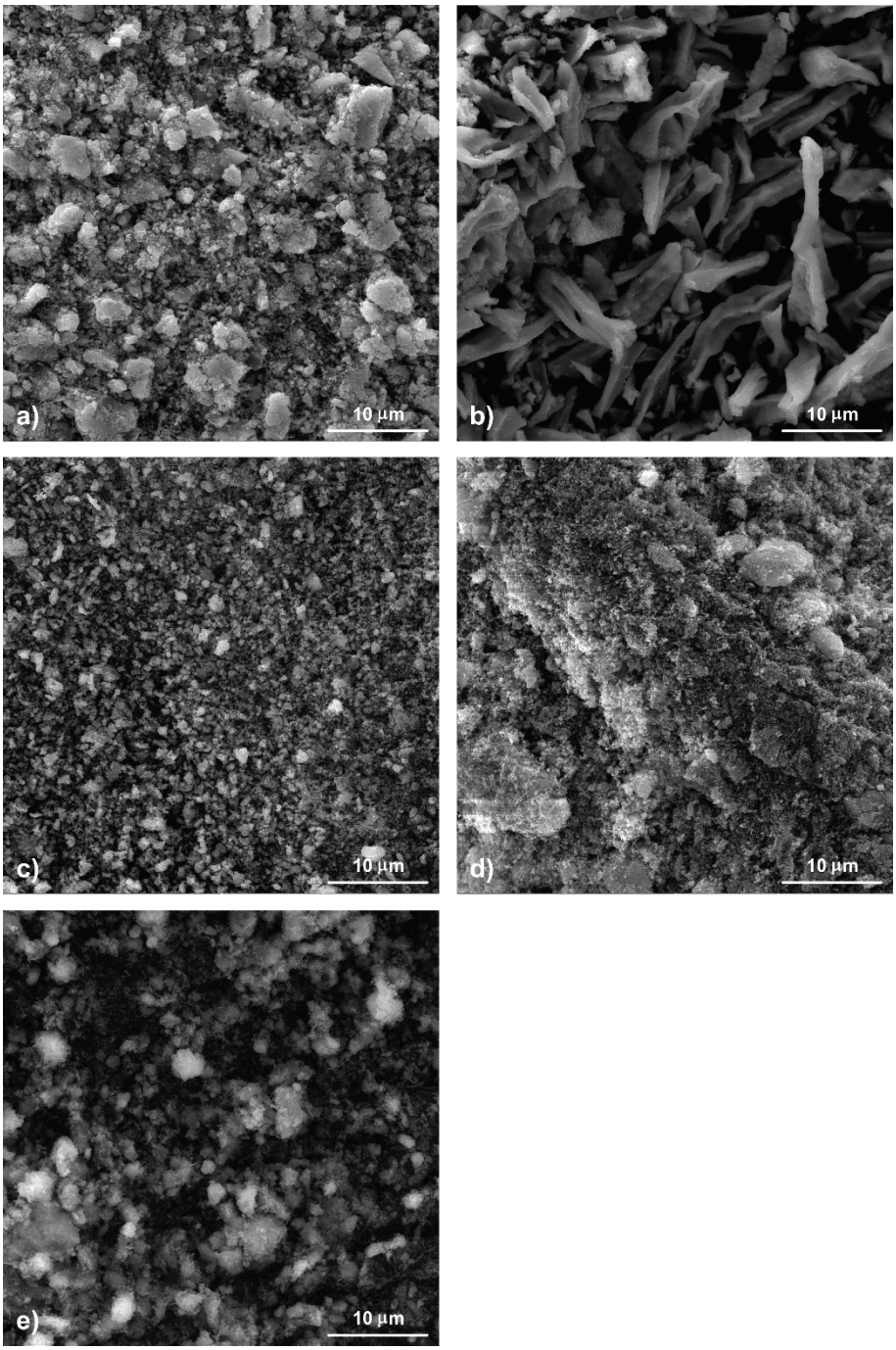

Fig. S-3. FESEM images of aglomerated ZnO_1 (a), ZnO_2 (b), ZnO_3 (c), ZnO_4 (d) and ZnO_com (e) at magnification of 5000×.

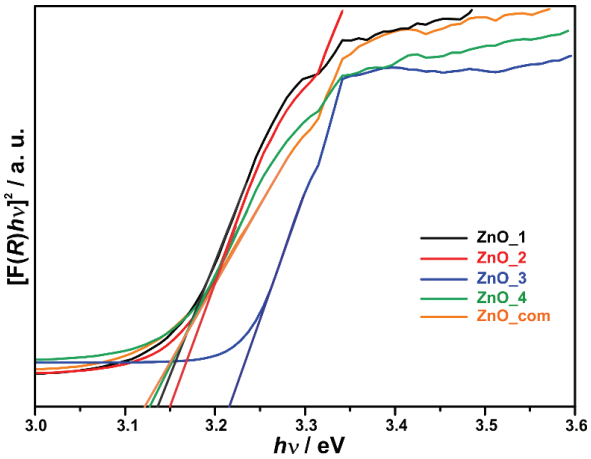

Fig. S-4. Plot of $(F(R)h\nu)^2$ as a function of photon energy for ZnO_1–ZnO_4 and ZnO_com.

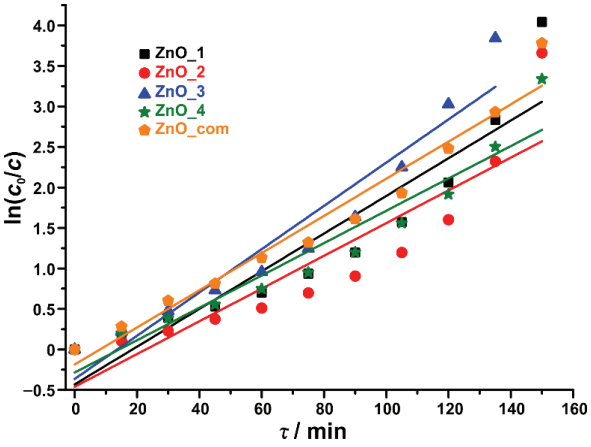

Fig. S-5. Linear plots of pseudo-first order kinetic model of RO16 degradation on the investigated ZnO powders.

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