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Letters to the Editor

Synthesis of ZnO nanostructures and H_2 by reactions of Zn with H_2O

A. A. Vostrikov,[*] A. V. Shishkin, and N. I. Timoshenko

S. S. Kutateladze Institute of Thermophysics, Siberian Branch of the Russian Academy of Sciences,
1 prosp. Akad. Lavrent´eva, 630090 Novosibirsk, Russian Federation.
Fax: +7 (383) 330 8480. E-mail: vostrikov@itp.nsc.ru

Development of methods and studies of mechanisms of the controlled synthesis of ZnO nanostructures are stimulated by prospects of their industrial use.[1—3]

In the present work, the synthesis of the ZnO nanostructures during oxidation of solid $(Zn)_S$ and liquid $(Zn)_L$ zinc with sub- and supercritical (temperature $T_w > 647$ K) water was found and studied. The process occurs upon the chemical recondensation with water (CRW) of $(Zn)_{S,L}$. The initial stage of the CRW is the formation of $(ZnO)_n$ clusters due to the collective interaction of n atoms of $(Zn)_{S,L}$ and gaseous water

$$n\,(Zn)_{S,L} + n\,(H_2O)_g = (ZnO)_n + n\,(H_2)_g. \qquad (1)$$

The critical size $n = n^*$ beginning from which reaction (1) becomes exothermic due to a sharp increase in the energy $E_b(n)$ of the $(ZnO)_{n-1}$—ZnO bond can easily be estimated using the dependence $E_b(n) \approx 0.1E_s n$ characteristic[4,5] of small ($2 \le n \le 8$) clusters. (Here $E_s(ZnO) = 496$ kJ mol^{-1} is the sublimation energy of $(ZnO)_S$).[6] Taking into account the energy parameters of the components of reaction (1) and assuming (because the data are lacking) the energy of the bond of $(ZnO)_{n^*}$ with $(Zn)_S$ to be minimum and equal to $E_s(Zn)$, we have $n^* \approx 4$. Small clusters are mobile in $(Zn)_L$, favoring their coagulation into nanoparticles. Epitaxy can be the main mechanism of nanostructure growth in solid $(Zn)_S$

$$(Zn)_S\cdot(ZnO)_{n\geq n^*} + (H_2O)_g = (Zn)_S\cdot(ZnO)_{n+1} + (H_2)_g. \qquad (2)$$

In the present work, three regimes of synthesis of the nanostructures during the CRW of zinc were studied: (1) at a constant pressure of steam P_w (density n_w) and a specified temperature of the reactor T_R with $(Zn)_S$ samples, (2) for the oxidation of $(Zn)_{S,L}$ with supercritical water (SCW) under conditions of decreasing n_w from $n_{w,0}$ to $n_{w,f}$ during the CRW, and (3) by bubbling SCW with a constant flow rate through the $(Zn)_L$ layer. Experiments were carried out in flow-type and batch reactors.[7] The parameters characterizing the conditions and results of experiments are presented in Table 1.

Samples of $(Zn)_S$ were prepared from a zinc melt (high-purity grade, 99.95 wt.% Zn) and mechanically purified from oxide in all cases, except for entries *7—9*. The M_{Zn} and ΔM_{Zn} values were determined from the results of weighing the samples before and after experiment. In entries *1—3* water was supplied in excess to a cool reactor and then rapidly heated. In other entries steam (entries *4* and *5*) or SCW (entries *6—13*) was injected into the preheated reactor containing a zinc sample.

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Table 1. Conditions and final results of zinc oxidation*

Entry	T_R/K	$P_{w,0}$/MPa	$n_{w,0}$	$n_{w,f}$	M_{Zn}	ΔM_{Zn}	$q_{H_2} \cdot 10^2$ /mol	t/s	S/cm^2
			g cm^{-3}		g				
				Solid zinc					
1	546	5.76	0.0295	0.0295	2.1693	0.1177	0.180	3420	2.77
2	576	8.96	0.0485	0.0485	2.5262	1.0423	1.594	14580	2.64
3	599	12.21	0.0717	0.0717	2.1690	0.7193	1.101	2700	2.77
4	608	13.71	0.0844	0.0844	16.6876	3.2636	4.991	1250	28.48
5	626	15.13	0.0861	0.0342	16.4720	3.0203	4.619	1140	25.50
6	671	31.22	0.4227	0.3107	12.7077	4.6839	7.163	347	19.05
				Liquid zinc					
7	705	12.36	0.0448	0.0226	12.9163	0.9187	1.405	1000	8.19
8	744	25.79	0.1039	0.0805	12.3059	0.9741	1.489	806	8.19
9	709	29.53	0.1612	0.1407	12.0615	0.8560	1.309	630	8.19
10	921	30.85	0.0823	0.0445	12.5946	1.5582	2.383	1026	8.19
11	840	28.42	0.0882	0.0363	13.7235	2.0944	3.230	1014	8.19
12	793	28.36	0.0997	0.0220	12.3907	3.2263	4.934	925	8.19
13	694	21.51	0.0999	0.0152	12.7389	3.5095	5.367	985	8.19

* M_{Zn} is the initial weight of the zinc sample, ΔM_{Zn} is the weight od zinc transformed into ZnO during time t, q_{H_2} is the amount of produced hydrogen, and S is the initial geometric surface area of the $(Zn)_S$ and $(Zn)_L$ samples contacting with H_2O.

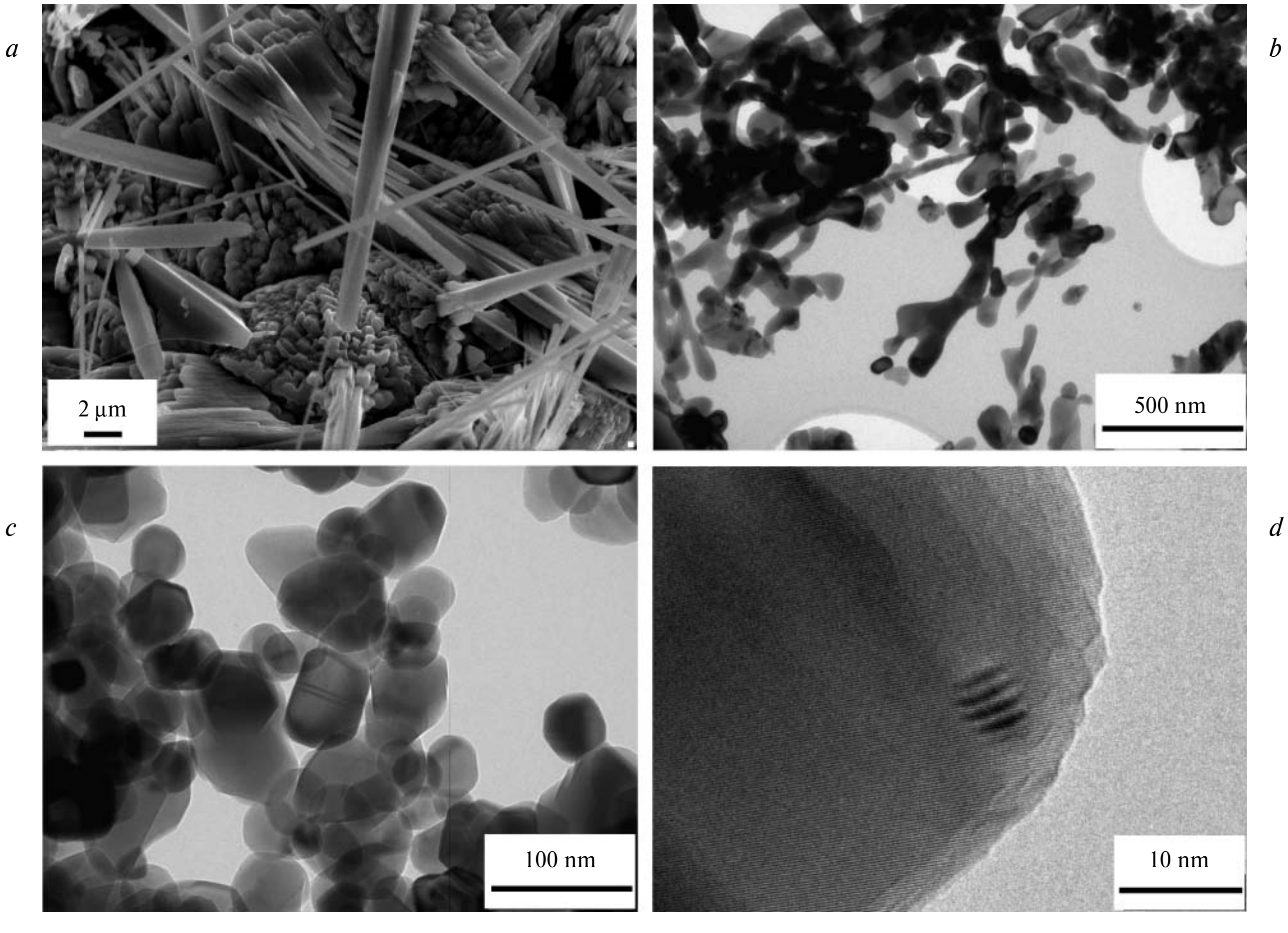

Fig. 1. Nanostructures of ZnO: nanorods (*a*), nanofilaments (*b*), and nanoparticles obtained by the CRW process of $(Zn)_L$ (*c*) and using SCW (*d*).

The structure, elemental composition, and size distribution of the ZnO nanoparticles were studied on a JEM-2010 transmission electron microscope equipped with an EDAX spectrometer with an energy resolution of at least 130 eV and a LEO-420 scanning electron microscope.

Some ZnO nanostructures obtained under different experimental conditions are shown in Fig. 1. Analysis of the nanostructures showed that at low T_R predominantly nanorods (*a*) are formed in $(Zn)_S$, whereas nanofilaments and dendrite-like and equiaxed (20—100 nm) nanostructures (*b*) are formed with an increase in T_R. The Moire effect is often observed on the ZnO nanoparticles produced with SCW (*d*). Measurements of the interplanar distance using the two-dimensional Fourier transform identified the $(Zn)_n$ clusters about 2 nm in size conjugated with ZnO. Epitaxial accretion of these structures is favored by close parameters of the Zn and ZnO lattices. Only nanoparticles from 1.5 to 150 nm in size (average size ~60 nm) were formed during the CRW (*c*). Note that the fraction of the ZnO nanoparticles increased sharply at $T_R \to T_m = 692$ K (melting point of Zn). We explain this phenomenon by the local melting of Zn and formation and coagulation of $(ZnO)_n$ in melt.

The plots of the specific rate of synthesis $v_{ZnO} = M_{ZnO}/(St)$ *vs.* $n_{w,0}$ and T_R (Fig. 2) show that (1) for $(Zn)_L$ purified from oxide (entries *10—13*) v_{ZnO} increases sharply with an increase in $n_{w,0}$ and at a weak dependence of T_R, *i.e.*, ZnO formation is determined by multiparticle reaction (1); (2) for $(Zn)_L$ with the oxide films (entries *7—9*) the behavior of $v_{ZnO}(n_{w,0}, T_R)$ is determined by inoculum; (3) for $(Zn)_S$ the v_{ZnO} rate increases with an increase in T_R and $n_{w,0}$. The obtained $q_{H_2}(t)$ plots (Fig. 3) show that for $(Zn)_S$ at $T_R \to T_m$ the CRW process is self-accelerated with an increase in *t*: the v_{ZnO} rate increases despite a decrease in n_w and the surface area of contact between H_2O and Zn. This is a consequence, most likely, of local melting of $(Zn)_S$ due to the great thermal effect of reaction (2) and outflow of $(Zn)_L$ onto the ZnO surface.

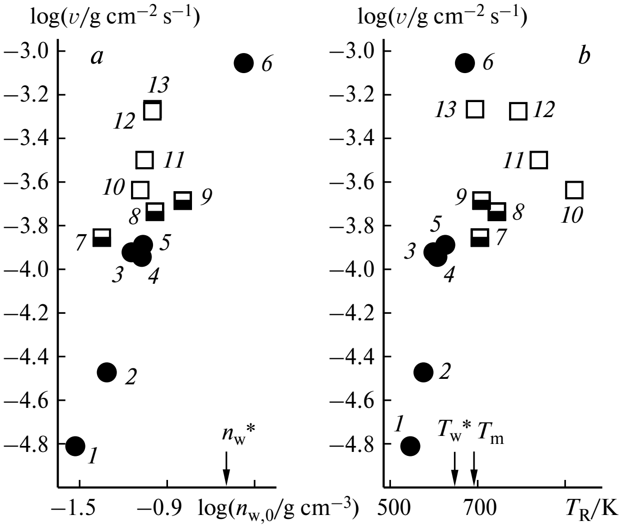

Fig. 2. Plots of the specific rate of ZnO formation *vs.* starting density of H_2O (*a*) and temperature of the reactor (*b*) according to the data of entries *1—13*. Arrows indicate the critical density n_w^* and temperature T_w^* of water and the melting point of zinc T_m.

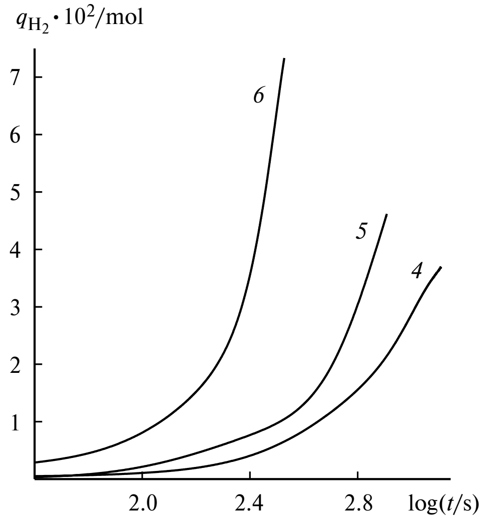

Fig. 3. Time plots of the amount of hydrogen produced by the oxidation of solid zinc in entries *4—6*.

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