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Preparation of Uniform Zinc Oxide Particles by Homogeneous Precipitation from Zinc Sulfate and Nitrate Solutions

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Monodispersed, hexagonal prismatic and spindle-shaped zinc oxide particles have been prepared by hydrolyzing zinc sulfate and nitrate solutions at elevated temperatures in the presence of urea.

Zinc oxide is used in a variety of ceramic applications such as varistor, semiconductor and so on. The use of monodispersed(as submicrometer as possible), spherical or equiaxed ceramic powders is desirable to achieve an uniform sintered microstructure. We have recently reported the preparation of monodispersed, spherical particles of hydrated alumina(≈ 0.7 μm in size) by hydrolyzing aluminum sulfate solution at 90 °C in the presence of urea.[1] Subsequently, we have succeeded in preparing monodispersed, hexagonal prismatic and spindle-shaped zinc oxides by the homogeneous hydrolysis of dilute solutions of zinc sulfate and nitrate. Until this study was conducted, the preparation of spherical[3] and rodlike[4] particles of zinc oxide had been limited to very complex and expensive organic routes.

Table 1 shows the preparation conditions of zinc oxide particles. All stock solutions were prepared from guaranteed-grade $ZnSO_4 \cdot 7H_2O$, $Zn(NO_3)_2 \cdot 6H_2O$ and $CO(NH_2)_2$ in doubly distilled water. The solutions of zinc sulfate

or zinc nitrate(1l) and urea(1l) were kept in a flask(2l) and heated up to 95 °C at a rate of 0.5 °C min^{-1}. The solution became turbid at ca. 90 °C. After given aging periods, the solution was rapidly quenched to room temperature. Subsequently, the precipitates were separated on a microfilter(0.22 μm pore size), washed with fourth 20 ml portions of doubly distilled water, dried at 110 °C for 12 h and kept in a desiccator.

Table 1. Preparation conditions of zinc oxide particles

	$ZnSO_4 \cdot 7H_2O$ (mol/l)	$CO(NH_2)_2$ (mol/l)	Aging temp °C	Aging time h
S-1	1×10^{-3}	5×10^{-2}	95	0
S-2	1×10^{-3}	1×10^{-1}	95	0
S-3	1×10^{-3}	1.5×10^{-1}	95	0
S-4	1.2×10^{-3}	6×10^{-2}	95	0
S-5	2×10^{-3}	5×10^{-2}	95	0
S-6	2×10^{-3}	8×10^{-2}	95	2
S-7	2×10^{-3}	8×10^{-2}	95	2
	+ $(CH_2CH_2OH)_3N$ 6×10^{-3}(mol/l)			

	$Zn(NO_3)_2 \cdot 6H_2O$ (mol/l)	$CO(NH_2)_2$ (mol/l)	Aging temp °C	Aging time h
N-1	1×10^{-3}	1×10^{-1}	95	0
N-2	1×10^{-3}	1×10^{-1}	95	2
N-3	1×10^{-3}	5×10^{-2}	95	0
N-4	2×10^{-3}	8×10^{-2}	95	0
N-5	1×10^{-3}	1×10^{-1}	95	0
	+ $(NH_4)_2SO_4$ 5×10^{-4}(mol/l)			

Figures 1 and 2 show the scanning electron micrographs and X-ray diffraction patterns of the precipitated zinc oxides. In Fig. 1 the zinc oxides precipitated in the sulfate and nitrate solutions showed the monodispersed, hexagonal prismatic(S-1) and spindle-shaped(N-1) morphology, respectively. In the former case, a very small amount of fibrous basic zinc carbonate, $4ZnO \cdot CO_2 \cdot 4H_2O$, was also observed, though not detected on X-ray diffraction pattern(Fig. 2). The particle size and morphology of precipitated zinc oxide depended on the concentration of the stock solutions and the aging time. With increasing concentration of zinc sulfate solution, the precipitated zinc oxide particles became wide and

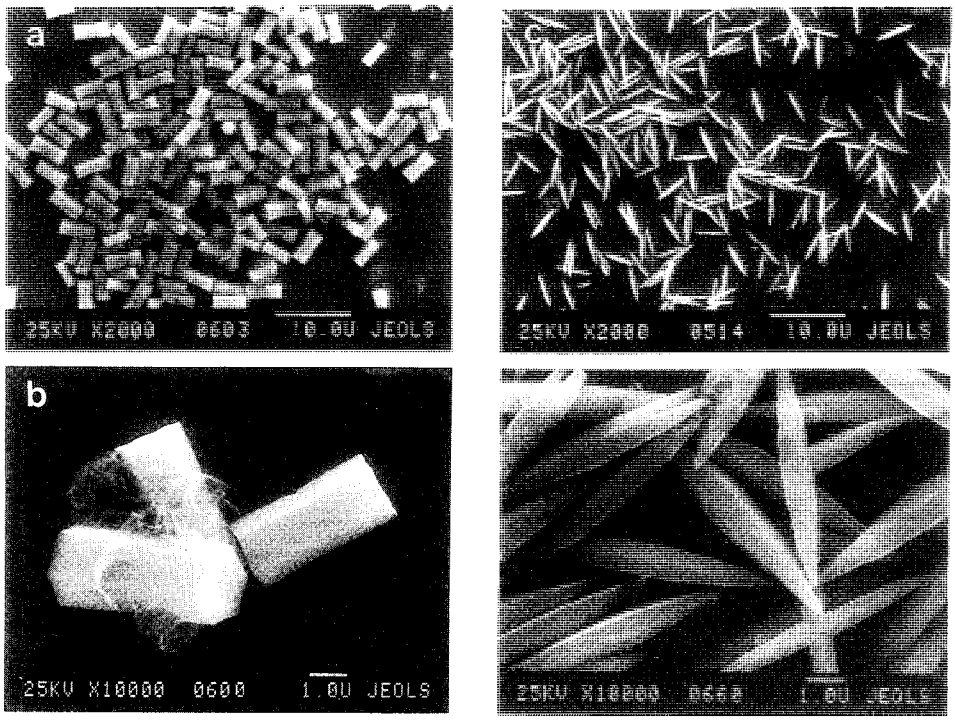
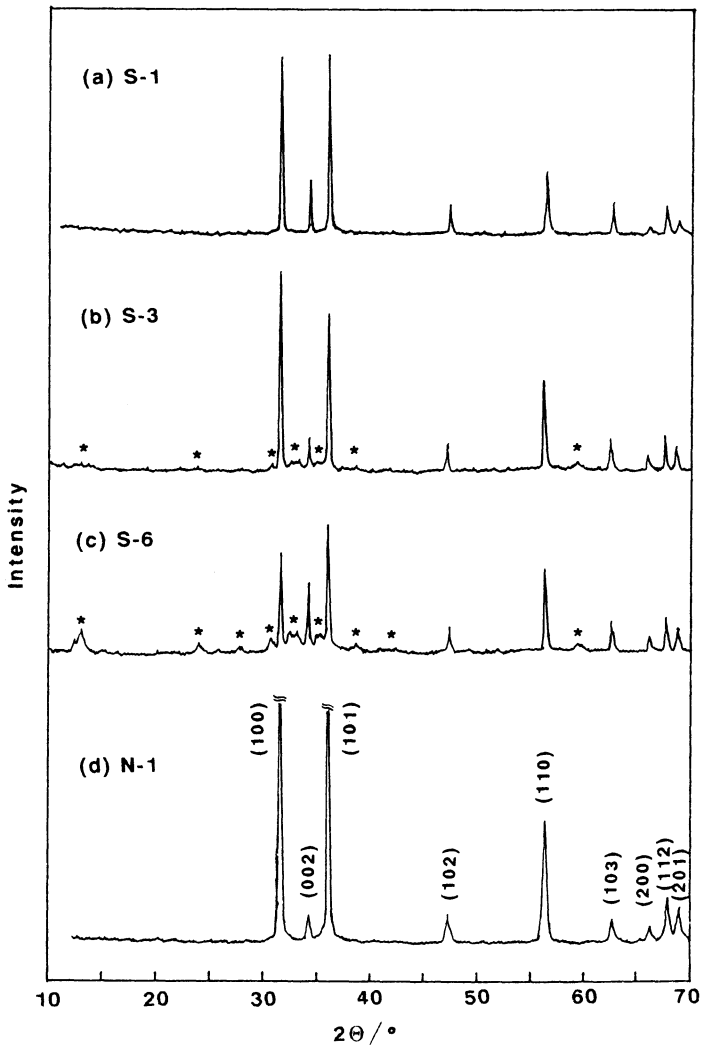


Fig. 1. Scanning electron micrographs(SEM) of zinc oxide particles prepared under the conditions described in Table 1.

a, b: S-1 ; c, d: N-1

short; for example, 1.9 μm x 4.3 μm for S-1, 2.0 μm x 2.8 μm for S-4 and 2.4 μm x 2.5 μm for S-6. On the other hand, as shown in Fig. 2, S-1 - S-6, with increasing concentration of urea and aging time, the amount of $4ZnO \cdot CO_2 \cdot 4H_2O$ increased. Addition of triethanolamine(Table 1, S-7) to the S-6 solution yielded single phase of basic zinc carbonate with low crystallinity. In the hydrolysis in zinc nitrate solutions, similar results were obtained. Addition of a small amount of $(NH_4)_2SO_4$ to zinc nitrate solution (Table 1, N-5) yielded hexagonal prismatic zinc oxide particles, indicating that the presence of sulfate ions in the solutions is essential to the formation of hexagonal prism morphology. In fact, the homogeneous precipitation in zinc chloride ($ZnCl_2$ 1×10^{-3} mol/l + $CO(NH_2)_2$ 1×10^{-1} mol/l) and zinc acetate ($Zn(CH_3COO)_2 \cdot 2H_2O$ 1×10^{-3} mol/l + $CO(NH_2)_2$ 1×10^{-1} mol/l) yielded spindle-shaped zinc oxide particles. Furthermore, compared the X-ray diffraction patterns of S-1 with N-1 in Fig.2, the



intensity ratio I_{002}/I_{100} or I_{002}/I_{101} remarkably decreased in the latter case.[5] This reflects the spindle-shaped morphology which has not hexagonal basal plane as shown in Fig.1(b).

Fig. 2. X-Ray diffraction patterns of zinc oxide particles.
* : $4ZnO \cdot CO_2 \cdot 4H_2O$

References

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5) The magnitude of this intensity ratio for S-1 and N-1 samples hardly changed, even when in order to avoid a preferential orientation of particles the samples were mixed with pasty starch, dried and then subjected to XRD.

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