Crystal dissolution has been studied extensively, more recently by the groups of Stumm, Casey, Lasaga, Lüttge, Nancollas, Hochella Jr., De Yoreo and many others (1–6). Early classical work on both crystal growth and dissolution, culminating in two seminal papers by Kossel and Stranski (1–2, 5) and also in a more general perspective by Harbrecht et al. (6). It is the purpose of this contribution to discuss recent results on the dissolution of nanocrystals (7) and to suggest possible mechanisms for the pronounced anomaly that has been observed for these systems. (Fig. 1).

**Fig. 1.** a) Essential features of a dissolving crystal facet (see text). b) Time $t_i$ needed for complete dissolution of NiO in 1 M HSO$_4$ (isotherms) versus crystal size $D_k$. Yellow lines: slope expected for conventional dissolution kinetics. c) Specific dissolution rate ($\frac{\partial k}{\partial D_k}$) versus crystal size $D_k$.

Similarly, in regime 2, only one kink may be accommodated, therefore the step advances at a speed proportional to its reciprocal length, i.e. approximately $D_k^{-1}$.

Size-dependent dissolution rate data on nanocrystals of NiO (bunsenite) corroborate these predictions. The characteristic time $t_i$ needed to completely dissolve nanocrystals of a given average size $D_k$ in 1 M sulfuric acid at constant temperature $T$ was measured (Fig. 1b). $t_i$ should be a linear, quadratic or cubic function of $D_k$ depending on whether conventional dissolution kinetics, regime 1 or regime 2, respectively, applies (11). In the double logarithmic plot, the slope is found to be close to either 3 (cubic) or 2 (quadratic), depending on temperature. A slope of unity is never observed, conventional dissolution—i.e. a constant rate per unit surface area—is, therefore, ruled out. Remarkably, in the size range studied ($D_k = 2.6–20$ nm), a thermally induced crossover from regime 2 to 1 takes place at $T = 45–60$ °C. Complementary data at $T = 60$ °C for larger NiO crystals by Jones et al. and Smart (10)—published long ago but not evaluated then—match our results quite well, when plotted as the specific dissolution rate vs. $D_k$ (Fig. 1c).

Thus, although for nanocrystals the specific dissolution rate may be enhanced by orders of magnitude (depending on size, as illustrated in Fig. 1c), it is not necessary to invoke fundamental changes in surface free energy (5) to explain this pronounced nanoeffect. Rather, it follows straightforwardly from the established microscopic model of crystal growth and dissolution.

**References and Notes**

11. See supporting material.
12. We thank Hui-Hui Wang for helping with the experiments.

**Supporting Material**

Materials and Methods

Fig s1. Additional Reference

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Supporting Material

General

We believe that the results presented herein are particularly convincing since the data (including that from the literature, Fig. 1c) span about three orders of magnitude in both the particle size and the dissolution rate. The general conclusions, therefore, remain largely unaffected by the observed scatter (uncertainty) of the numerical data.

Materials

The synthesis, via SDPP (sub-decomposition-point pyrolysis), of both shape-isotropic and anisotropic ultrafine NiO nanoparticles, their controlled growth and methods of characterization were outlined elsewhere (s1).

Methods

Typically, 4 mg of nanocrystalline NiO powder are magnetically stirred with 4 mL of 1 M H$_2$SO$_4$ in a test tube immersed in a thermostated aluminium heating block or water bath. Since nanocrystalline NiO is black, the colour changes from dark-gray to green-blue upon completion of the dissolution, which is readily detected visually or photometrically (Fig. s1). Without magnetic stirring, the rate is not changed significantly, hence mass transport is not limited by diffusion. In most of the experiments, visual detection was used, without magnetic stirring. A number of control experiments were carried out, with or without magnetic stirring, by means of a photometric setup employing a digital camera (Fig. s1).

Theory

With conventional dissolution kinetics, the specific dissolution rate (dN/dt)$\propto 1$ (number of mols over time and surface area) remains constant whatever the crystal size $D_p$, because the stepwave and kink densities remain constant. In regime 1 ($D_p < D_0$), only one step at a time traverses each facet, at a constant speed regardless of $D_p$. The time needed to dissolve a complete monolayer, therefore, scales as $D_p$, while the number of atoms or molecules per monolayer scales as $D_p^2$, hence dN/dt $\sim D_p^2/D_0 \sim D_p$. Since $A$ scales as $D_p^2$, (dN/dt)$A^{-1}$ $\sim 1/D_p$. In regime 2 ($D_p < D_0$), the step velocity is no longer constant but proportional to the reciprocal step length, or $D_p^{-1}$—for there is now only a single kink receding at constant speed—, so that the time it takes to dissolve a monolayer scales as $D_p^2$. The same reasoning as above leads to (dN/dt)$A^{-1} \sim 1/D_p^2$. Thus, in a doubly logarithmic plot of (dN/dt)$A^{-1}$ over $D_p$, the slope is 0, –1 or –2 for conventional kinetics, regime 1 or regime 2, respectively (Fig. 1c). Further elementary calculus discloses a linear, quadratic or cubic dependence, respectively, of $t$ on $D_p$ (Fig. 1b).

To convert $t$ into (dN/dt)$A^{-1}$ (Fig. 1c), the derivative dN/dt = $D_p^2$ or dN/dt = $D_p/3t$ is calculated for each experimental point belonging to the quadratic ($D_p \sim t^{-1/3}$) or cubic ($D_p \sim t^{-1/5}$) regime (Fig. 1b), respectively. Then (dN/dt)$A^{-1}$ = $(\rho M A$ (dN/dt)/2$A$ = $(\rho M) (dN/dt)/2$, where $\rho$ is the density of NiO (6807.8 kg/m$^3$) and $M$ its molar weight (0.074692 kg/mol).

Fig. s1. a) NiO ($D=3.5$ nm, 9.8 mg) dissolving in magnetically stirred 0.91 M H$_2$SO$_4$ (4.3 mL, $T=22^\circ$C). b) Photometric evaluation of the photographs shown in a).

Additional Reference


Summary

Crystal dissolution, like crystal growth, is a long-standing subject of study. Yet, so far, little is known about the dissolution of nanocrystals. In this note, it is shown that the (surface-area-normalized) rate of dissolution of small nanocrystals should be orders of magnitude higher than that of large crystals. Starting from an established microscopic model, two power-laws relating the rate of dissolution to the crystal size are derived and verified by dissolution rate measurements on bunsenite (NiO) nanocrystals in dilute sulfuric acid. In addition, previously unevulated data from the literature are shown to be in good accord with the proposed theory.