Anomalous Dissolution Kinetics of Nanocrystals

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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 (*7–8*), had established that these processes are usually—i.e. at near-ambient conditions—kinetically controlled. The kinetics may be treated on two levels. One may either consider merely the elementary process of addition or removal of a single atom or formula unit (*1–2, 5*). Or one may take a broader view of the temporal evolution of the overall surface topology comprising many atoms (*3–4, 6–8*). Adopting the latter view, we shall show that with very small nanocrystals, the specific rate of dissolution (i.e. rate per unit surface area) is markedly dependent on the crystal size. This—to our knowledge—novel and quite pronounced nanoeffect may be rationalized in terms of a frustrated multiple nucleation of surface steps and kinks.

Like crystal growth (*9*), crystal dissolution is known to proceed at the atomic level via the propagation of surface steps (*3–4, 6–8*), aptly termed 'dissolution stepwaves' (*3*). Depending on conditions, e.g. undersatura-tion (driving force), the moving steps follow each other at a certain distance D_S (step spacing, Fig. 1a). The movement results from kinks receding at constant speed, on average a distance D_K apart. In general, $D_K < D_S$, since kinks have a low energy of formation (*9*). Thus, at fixed experimental conditions, a change, or crossover, in the kinetics of dissolution should occur when 1. the crystal size D_P ('particle size') gets smaller than D_S, and 2. when $D_P < D_K$. In regime 1, each facet of the crystal may accommodate only a single atomic step at a time (frustrated nucleation of additional steps because $D_S > D_P$), though the step may still contain a sufficient number of kinks so as to advance at a constant speed.

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

Size-dependent dissolution rate data on nanocrystals of NiO (bunsenite) corroborate these predictions. The characteristic time t_c needed to completely dissolve nanocrystals of a given average size D_P in 1M sulfuric acid at constant temperature T was measured (Fig. 1b). t_c should be a linear, quadratic or cubic function of D_P, depending on whether conventional dissolution kinetics, regime 1 or regime 2, respectively, applies (*11*). In the doubly 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_P= 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_P (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.
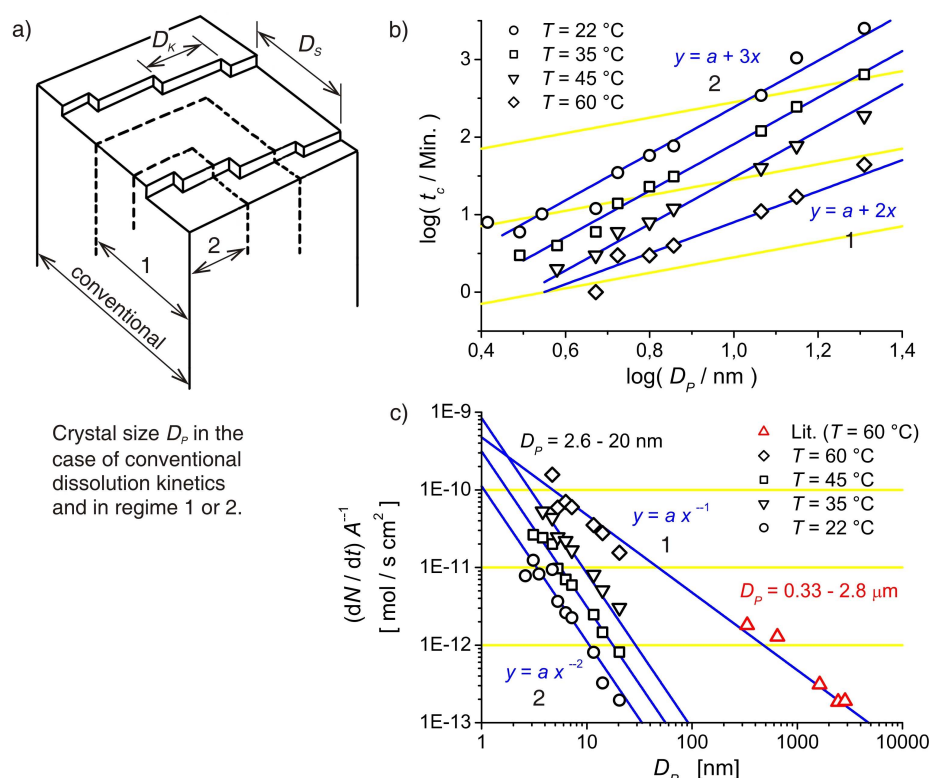

Fig. 1. a) Essential features of a dissolving crystal facet (see text). b) Time t_c needed for complete dissolution of NiO in 1 M H_2SO_4 (isotherms) versus crystal size D_P. Yellow lines: slope expected for conventional dissolution kinetics. c) Specific dissolution rate (*11*), including literature data for NiO in 0.72 M HNO_3 (*10*).

References and Notes

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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_2SO_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, t_c 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 $(dN/dt)A^{-1}$ (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 ($D_P < D_S$), 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 $dN/dt \sim D_P^2/D_P \sim D_P$. Since A scales as D_P^2, $(dN/dt)A^{-1} \sim 1/D_P$. In regime 2 ($D_P < D_K$), 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_c on D_P (Fig. 1b).

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

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 unevaluated data from the literature are shown to be in good accord with the proposed theory.
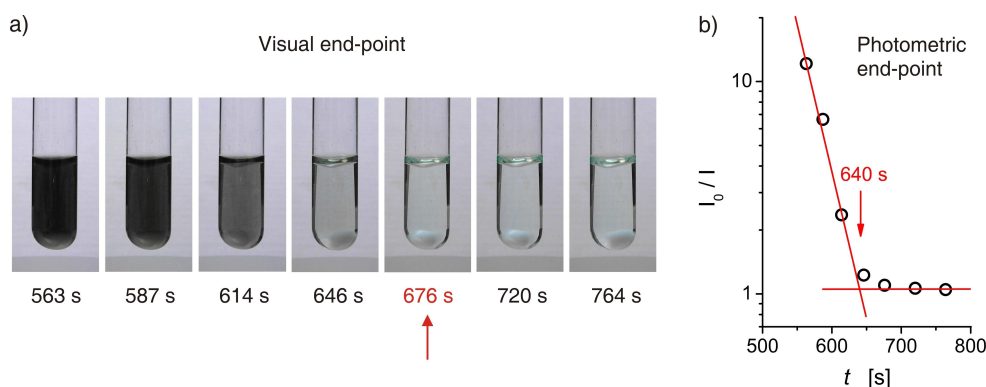
Fig. s1. a) NiO (D_P= 3.5 nm, 9.8 mg) dissolving in magnetically stirred 0.91 M H_2SO_4 (4.3 mL, T= 22 °C). b) Photometric evaluation of the photographs shown in a).

Additional Reference

s1. M. Petrik, B. Harbrecht, Z. Kristallogr. Proc. 1, 253 (2011).