Environ. Chem. **2013**, *10*, 306-312
doi:10.1071/EN12202_AC

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Supplementary material

Agglomeration and dissolution of zinc oxide nanoparticles: role of pH, ionic strength and fulvic acid

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Fluorescence Correlation Spectroscopy (FCS)

A laser light is focussed into a sample of interest using confocal optics. In this manner, an open, illuminated volume element (confocal volume) with dimensions of ~0.5–1.0 µm^3 is created. At any point in time, the confocal volume is occupied by only a few fluorescent molecules. In the absence of chemical reactions or other dynamic processes, temporal fluctuations in the measured fluorescence intensity in the confocal volume can be attributed solely to the translational diffusion of the fluorescent particle. An autocorrelation function that assumes a three-dimensional Gaussian distribution ($G(t)$) is used to analyse the variations in the fluorescence intensity. For example, for a 1-component system in the absence of phosphorescence[1]:

$$G(t) = a + \frac{1}{N}\left(1 + \frac{t}{\tau_D}\right)^{-1}\left(1 + \frac{t}{(\omega_0 / z_0)^2 \tau_D}\right)^{-1/2} \qquad \text{(S1)}$$

where a is the limiting value of $G(t)$ for $t \rightarrow \infty$ (usually $a = 1$), N is the average number of fluorescent particles diffusing in the confocal volume, τ_D is the characteristic diffusion time of the fluorescent species through the sample volume, t is the delay time, and ω_0 and z_0 are the respective transversal and longitudinal radii of the sample volume. The values of ω_0 and z_0 can be determined by the calibration of the system with rhodamine 110 (R110, Fluka), which has a known diffusion coefficient of 4.4×10^{-10} m^2 s^{-1}.[2]

The values of diffusion times for the bare nZnO (labelled with R6G) and for the nZnO in the presence of SRFA were determined from a best fit of an autocorrelation function that assumed a three-dimensional Gaussian distribution, and which was given as the weighted sum of a number *i* of individual G_i[3]:

$$G(t) = \frac{1}{N}\prod_{i=1}^{n}\left[1 + A_i \exp\left(-t/\tau_i\right)\right]\frac{1}{\left(1+t/\tau_D\right)\left(1+t/\left[\left(z_o/\omega_0\right)^2\tau_D\right]\right)^{1/2}} \quad \text{(S2)}$$

where $A_i = F_i/(1 - F_i)$, *F* corresponds to the fraction of molecules that resided in the dark state at any time. Diffusion coefficients (*D*) of the nZnO were subsequently calculated from measured diffusion times using the following relationship:

$$D = \omega_0^2 / 4\tau_D \quad \text{(S3)}$$

Scanned Stripping Chronopotentiometry technique (SSCP)

In stripping chronopotentiometry, reoxidation of electrode-accumulated metal is made by application of a constant oxidising current (stripping current, I_s). In this manner, the analytical signal is given by the time needed to reoxidise the amalgamated metal, i.e. the transition time (τ). SSCP curves are constructed from a series of τ measurements made over a range of deposition potentials (E_d). The limiting value of the transition time (τ*), which is obtained for deposition potentials much larger than the standard potential, reflects the magnitude of the original flux, irrespective of its nature, i.e. diffusion control (fully labile complexes) or kinetic control (non-labile complexes).[4] For a metal complex, the shift in the SSCP half-wave deposition potential as compared to the free metal ($\Delta E_{d,1/2}$) is directly related to the complex stability, irrespective of the degree of lability.[4] In a labile system, the amalgamated metal is higher than that in a kinetic regime, which also results in a higher $\Delta E_{d,1/2}$ value.

A thermodynamic complex stability constant (*K*′) for the metal complex can be calculated from the shift in the half-wave deposition potential ($\Delta E_{d,1/2}$) (analogous to the DeFord–Hume expression[5]), irrespective of the degree of lability of the system[4]:

$$\Delta E_{d,1/2} = -\left(\frac{RT}{nF}\right)[\ln\left(1+K'\right) + \ln\left(\frac{\tau_{ML}^*}{\tau_M^*}\right)] \quad \text{(S4)}$$

where τ_{ML}* and τ_M* are the respective limiting wave heights in the presence and absence of ligands, *R* is the gas constant, *F* is the Faraday constant, *n* is the number of electrons involved in the Faradaic process and *T* is the temperature.

The plots of *τ v.* E_d are very rich in speciation information since they can cover a large part of the stability distribution spectrum in addition to the corresponding portions of the rate constant distributions. A rigorous equation is also available for the full wave in the kinetic current regime for the complete depletion mode.[6] Its features allow the heterogeneity of the metal complexation to be unambiguously quantified.

Computation of the dissolved ZnO

The $E_{d,1/2}$ values for all pH are slightly more negative (~5 mV) than observed for the metal-only system, indicating that virtually all of the dissolved Zn was uncomplexed. Under these conditions, quantification of the total dissolved Zn using SSCP data is straightforward; the dissolved metal ion concentration will be directly proportional to the limiting value of the electrolysis time with a proportionality factor (that can be obtained by calibration).

Dissolution as a function of particle size

Classically, the dependence of solubility upon particle size, assuming a spherical particle, can be expressed with a modified form of the Kelvin equation[7]:

$$S / S_0 = \exp\left[\left(2\gamma\bar{V}\right)/\left(RTr\right)\right] \quad \text{(S5)}$$

where S is the solubility of the particles with a radius r, S_0 is the solubility of the bulk material, γ is the surface free energy and $\bar{V}$ is the molecular volume. According to this relation, as the particle dimensions decrease the solubility increases exponentially relative to the bulk solubility. Various examples of this relationship have been observed for several NP systems including quartz grains with particle radius of 1 to 100 nm,[8] silica NP,[9] $nTiO_2$[10] and nZnO.[11,12] Despite these examples, it is still not clear if this classical relationship between particle size and solubility apply to all nanoparticulate systems, e.g. some chemical processes such as photocatalysed oxidation may also affect the NP dissolution.[13]

Debye layer thickness

The Debye length was calculated using the following equation[14]:

$$\kappa = \left(\frac{\varepsilon_0 \varepsilon kT}{2N_A e^2 I}\right)^{\frac{1}{2}} \quad \text{(S6)}$$

where ε_0 is the vacuum permittivity, ε is the relative permittivity of the medium, k is the Boltzmann constant, T is the temperature, N_A is the Avogadro constant, e is the elementary charge and I is the ionic strength.

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Evolution of ZnO diameters measured by FCS

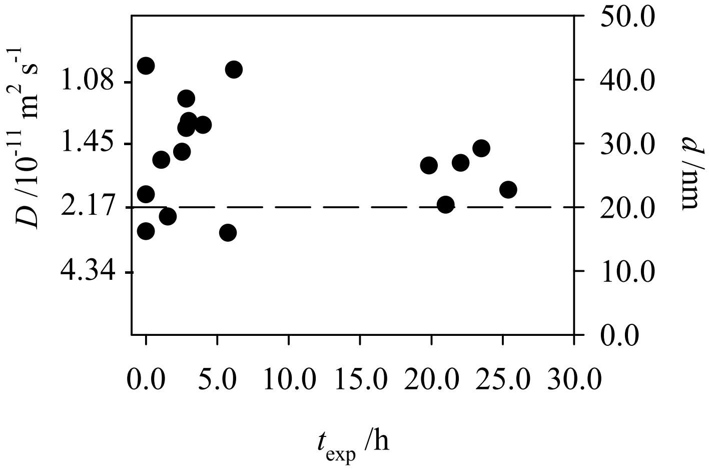

Fig. S1. Variation of the diffusion coefficients and weight average hydrodynamic diameters of 1.0 mg L^{-1} of the bare (R6G labelled) nZnO as a function of exposure time at I = 0.01 M, and pH 6.0). In these experiments, a small volume of stock solution was rapidly mixed with the buffered (pH 6.0, 5.0 × 10^{-3} M MES) experimental media such that measurements were initiated within 10 min. The dashed line indicates the size of the disaggregated nZnO as provided by the supplier (NanoAmor).

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