

Even you, reactant!

What else do you say when the very same reactants that are supposed to induce the reaction works against it, inhibiting the product formation!

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The spectacular size dependent properties of nanomaterials, not achievable in bulk materials have led to extensive research on these materials as the materials of future generation. The bottom-up approach of synthesizing semiconducting nanocrystals has generated tremendous excitement as it offers unprecedented flexibility and control of shape and size of the generated nanocrystals. However, there is little fundamental understanding so far of the complex chemical reactions that are employed to generate such high-quality samples of nanocrystals, often leaving the task of controlling the shape and the size to the realm of empiricism. Typically, various sizes of nanocrystals are stabilized in their metastable states by careful control of the chemical reactions carried out using a source of the cation and a source of the anion which are mixed together to form the desired compound. Stabilizing a specific size is achieved by arresting the reaction and hence the growth of the nanocrystal using a third chemical, termed as the capping agent, whose sole purpose is to stick to the surfaces of the growing nanocrystals either physically or chemically or to alter the activity of the other reactants to arrest the growth. The reasonable, working thumb-rule within the community is that the presence of the capping agent slows down or completely arrests the reaction, while increasing the concentration of the reactants, providing cations and anions, speeds up the reaction. Moreover, the folklore in the literature is that the growth in most of these cases, particularly in absence of any capping agent, follows the celebrated Ostwald ripening process, controlled solely by the diffusion of the reacting species through the solvent.

Recently, Ranjani Viswanatha, Heinz Amenitsch and D. D. Sarma put to in-depth scrutiny several of these long-held notions using extensive time-resolved experiments involving SAXS beamline at Elettra and UV-visible absorption experiments at their Bangalore laboratory using the case of ZnO as the critical test-bed. They used Zinc acetate and sodium hydroxide as the sources of Zn^{2+} cations and $(OH)^-$ anions, forming $Zn(OH)_2$. However, the reaction medium, iso-propyl alcohol being very hygroscopic, readily extracts a molecule of water out from the zinc hydroxide, thereby forming ZnO nanocrystals, a reaction that has been well-known in the literature for a long time. Surprisingly, the growth kinetics of ZnO nanocrystals was found to deviate very strongly from the well-accepted Ostwald ripening process. In a more dramatic departure of the expected behaviour, it was found that the increase in one of the reactants, namely NaOH, beyond a critical concentration suppressed catastrophically the reaction rate. Thus the reactants that are supposed to propel the reaction forward vigorously virtually stopped the reaction, a sort of trusted-friend-turned-into-an-unexpected-enemy kind of situation.

Systematic experiments revealed the source of this unexpected result. The reactant, NaOH, is not only a source of $(\text{OH})^-$ ions, but also an equal number of counterions, namely Na^+ . One has long assumed that the presence of Na^+ has no effect on the chemical reactions forming ZnO. However, the present investigation suggests that the growing nanocrystal, particularly with $(\text{OH})^-$ ions attached to it, coulombically attract a charged cloud of Na^+ ions to form a virtual protective layer around the growing

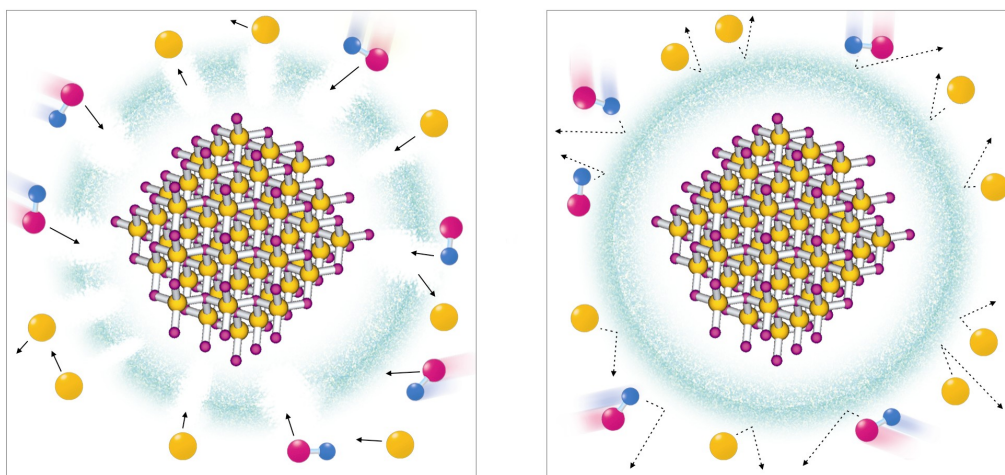


Figure caption: Yellow spheres represent Zn^{2+} and the blue-red dumbbells represent $(\text{OH})^-$ ions, trying to reach the surface of the growing nanocrystal for further reaction and incorporation, leading to the growth of the nanocrystal. The charge cloud of Na^+ ions are shown as the light blue halo around the nanocrystal. Left panel shows the low concentration of Na^+ scenario, while the right panel shows the formation of an effective capping layer of Na^+ charge cloud around the growing nanocrystal of ZnO.

nanocrystals. When the NaOH concentration is low, the Na^+ charged cloud around the growing nanocrystals is not complete and therefore, further increase in the NaOH concentration in this limit leads to the expected increase in the growth rate, since the reactants, namely Zn^{2+} and $(\text{OH})^-$ ions find their way to the nanocrystal surfaces (see the left panel in the above figure). When the reaction is attempted with a concentration of NaOH that can provide enough Na^+ ions to form a complete protective layer, as in the right frame in the above picture, the growth stops completely, as the reactants cannot reach the ZnO nanocrystal surface.

Details of this work can be found in *J. Am. Chem. Soc.*, **129**, 4470 (2007) DOI: 10.1021/j068161b.