Received: STI

AUG 12 1991

ANL/CP--72218

DE91 016516

RADIATION INDUCED GROWTH OF MICRO CRYSTALLITES

Dan Meisel

Chemistry Division
Argonne National Laboratory
Argonne, IL 60439

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

The submitted manuscript has been authored by a contract of the U. S. Government under contract No. W-31-109-ENG-38. Accordingly, the U. S. Government retains a nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or allow others to do so, for U. S. Government purposes.

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

RADIATION INDUCED GROWTH OF MICRO CRYSTALLITES

Dan Meisel

Chemistry Division, Argonne National Laboratory, Argonne, IL 60439

INTRODUCTION

Generation of colloidal particles during the radiolysis of aqueous solutions was already observed in the early days of radiation chemistry. Systematic studies using radiation chemistry techniques as synthetic tools in the preparation of colloidal particles, primarily metallic particles, were begun approximately a decade ago in conjunction since they were found to catalyze multi-electron redox processes. A large number of metallic colloidal particles were then synthesized, including silver (1,2), gold (3) platinum (4), iridium (5), nickel (6), cadmium (7) and others. More recently, attention has turned to semiconductor colloidal particles. The stimulus to these studies is the observation of quantum size effects in small semiconductor particles that exhibit hybrid properties between those of the molecular species and the solid state bulk material (8). In the following we discuss our own observations on the evolution of semiconductor particles whose growth has been initiated by pulse radiolysis.

For the initiation of semiconductor clusters growth, an organic precursor that contains the anionic moiety of the semiconductor material is released to the solution via reaction 1. If the solution contains the metal ion

component of the semiconductor material at concentrations exceeding the solubility limit of this material, particle growth will be initiated. When silver halides are the materials of interest the organic precursor could be an alkyl halide; when chalcogenides are to be studied thiolates could serve the same purpose.

The initiation process creates a super-saturated solution in the M(metal ion)-X material. Several pathways, shown in Scheme I for a monovalent ion, are now available to the components of the insoluble material. At early times the parent ions constitute the majority species. Their recombination reaction is nearly always diffusion controlled and thus equilibrium 2 will be rapidly established (often on the μs time scale). However, this equilibrium may be strongly shifted to the left even if the bulk material is highly insoluble (see below, silver-halides). Other equilibria may be available to the ionic components, such as acid-base equilibria (see below for CdS), and these will also affect the extent of the recombination reaction 2. As reaction 2 consumes

the ions, the concentration of the molecular species will concomitantly increase. Two new pathways will now interfere with reaction 2: molecule-molecule nucleation (reaction 3), whose role will increase as the concentration of the ionic components decrease; and ion-molecule complex formation. The latter is a well-known process in the growth of both metallic silver clusters and silver halide clusters.

SCHEME 1

When the concentration of nuclei increases due to reaction 3, molecule (or ions if one of them is in excess) - cluster growth, reaction 4, will become a major growth process. Observations by pulse radiolysis indicate that at this time the electrostatic surface potential of silver halide clusters is already fully developed. Soon thereafter cluster-cluster aggregation (reaction 5) becomes the dominant growth process. This process is believed to be diffusion controlled, albeit modified by the electrostatic effect of the ζ -potential at the particle interface. At the very long time regime, the classical Ostwald ripening mechanism will take over, but this process will not be discussed here.

Several detection techniques are available to study these processes. We have utilized absorption spectroscopy, conductivity and light scattering techniques in our own studies. A major deficiency, common to all of these techniques, is lack of specificity. Surface-enhanced Raman and resonance-Raman spectroscopies seem promising techniques that may allow better identification of clusters but have not been utilized for this purpose as of yet. The limiting factor in the study of these processes is clearly not time resolution but species identification.

SILVER HALIDES

Using pulse radiolysis, the evolution of silver iodide could be followed spectrometrically from the stage of single molecules (9,10). Reaction 1 was employed to release halide ions from alkyl halides. Even at relatively high silver halide concentrations, no restrictions on the analysis were imposed by instrumental time resolution.

To determine rate and equilibrium constants for reaction 2a, conductivity detection proved most useful, since the absorption spectra of the monomolecular species is inconveniently located in the far ultraviolet region. The decrease in the solution conductance allows determination of the forward and back rate constants as well as the equilibrium constant for the various molecules. Table 1 summarizes the constants collected for the three silver halides using this approach. It can be seen in Table 1 that the rate of reaction

Table 1: Stability and Rate Constants for the formation of AgX in aqueous solutions.

Halide	K, M ⁻¹	k _f , M ⁻¹ s ⁻¹	k _b , s ⁻¹ (a)
AgCl	2.0x10 ³	2.0x10 ¹⁰	9.1x10 ⁶
AgBr	2.9x10 ⁴	1.3x10 ¹⁰	4.6x10 ⁵
AgI	3.8x10 ⁶ (c)	8.1x10 ⁹	2.1x10 ³

a) Calculated from equilibrium constant and k_f.

of silver ions with all the halides is very close to the diffusion controlled limit. The differences in the stability of the molecules between the various halides are primarily due to the different rates of dissociation of the molecules. Importantly, the stability constants indicate relatively high solubility of the molecular species; orders of magnitude higher than those of the bulk material.

The absorption spectra of the growing clusters can also be monitored, although the assignment of a spectrum to particular species becomes intractable. At early stages the absorption of monomeric species can be extracted, but as the clusters evolve, generalized approaches must be assumed (10). For that purpose Brus's theory seems most appropriate (8). The spectral evolution of growing silver iodide particles in water is shown in fig. 1. Good agreement has been obtained between sizes calculated from the absorption edge of these particles and sizes determined from light scattering measurements when the latter technique could be utilized. A transition from cluster-cluster to ion-cluster growth mechanisms was observed when comparing the behavior of AgI and AgBr to that of AgCl and was attributed to the differences in stability constants of the corresponding molecules. In the former cases, the concentration of ions is decreased in the initial stage to such low levels that a cluster-cluster growth mechanism dominates. For AgCl, however, only a small fraction of the ions is depleted in the initial step of reaction 2a. An even smaller fraction of the molecules (below the detection limit of any of our techniques) proceeds to form growth nuclei which, following an induction period, proceed to grow via an ion-cluster mechanism. For the AgCl system,

the rate of disappearance of ions from the solution, as measured by conductivity, is identical to the rate of appearance of relatively large particles as measured by light scattering. Furthermore, in this system the well-resolved absorption bands of small particles could not be detected prior to the appearance of large particles.

Figure 1: Spectral evolution of growing AgI particles in solutions containing $[Ag^+]_0=0.1$ mM and $[I^-]_0=0.2$ mM. The initial spectrum at $6 \mu s$ is attributed to molecular AgI.

CHALCOGENIDE PARTICLES

Many semiconductor materials, notably II-VI chalcogenides, are of great interest in energy conversion systems, in particular at the very small size regime. A similar approach to the one described above for silver halides was utilized to study the growth of CdS (11,12). Hydrogen sulfide is released from a parent thiol via reaction 1a and the ensuing reaction of Cd^{2+} with the released sulfide ions was then followed by absorption spectroscopy and via

conductivity. In this system, the acid-base equilibrium of the sulfide ions (reaction 8, with $pK_a=7.0$) has a pronounced effect on the rate and

mechanism of particle growth as mentioned above. The evolution of the spectrum of CdS particles as a function of time is shown for two pH's in fig. 2. It can be noted in fig. 2 that the smallest particles observed at pH 4.1 are relatively large. An ion-cluster growth mechanism could thus be inferred.

Figure 2: The absorption spectra of growing CdS particles at pH 4.1 and 7.1. Both contain 1×10^{-4} M Cd^{2+} ions and 0.01 M 3-mercapto propanediol. Initial $[\text{H}_2\text{S}] = 7.5 \times 10^{-5}$ M for pH 4.1 and 1.5×10^{-4} M for pH 7.1. No particles of smaller sizes than those shown for pH 4.1 could be observed.

The most pronounced effect in this system, however, is the control of the size by the thiol. It was found that the thiolate form, RS^- , provides an unexpected size control of the particle and allows an *a priori* design of essentially any predetermined particle size. This, of course, occurs whether the reaction is initiated chemically or radiolytically (13). In any of these syntheses, the final size of the particles decreases as the concentration of the thiolate increases, the concentration of H_2S decreases, the pH increases, or the concentration of Cd^{2+} increases. All these effects are commensurate with a mechanism in which RS^- competes with HS^- for Cd^{2+} ions. When the size

dependent steady state concentration of sulfide in the solution drops to a level at which RS^- complexation at the surface dominates, the growth process terminates.

The ability to systematically control the size of the particles via surface modifications opens up avenues for further control of the particles properties. Using such surface modification and size control, the particles may be rendered highly hydrophobic and thus, their dispersion in organic solvents may be easily achieved. Furthermore, due to the presence of ready electron donors at the particle surface (RS moieties), many of the pre-existing surface trapping states may be eliminated. The presence of the thiolate moieties at the surface enhances significantly the quantum yield for radiative charge recombination (11). The ease with which the thiols bind to the particles surface can be further utilized to bind various other functionalities to the particles.

ACKNOWLEDGMENT

Work performed under the auspices of the Office of Basic Energy Sciences, Division of Chemical Science, US-DOE under contract number W-31-109-ENG-38.

REFERENCES

1. A. Henglein, *Angew. Chem., Int. Ed. Engl.* 18, 41 (1979).
2. M. Mostafavi, J. L. Marignier, J. Amblard, J. Belloni, *Rad. Phys. Chem.* 34, 605-17 (1989).
3. D. Meisel, *J. Am. Chem. Soc.* 101, 6133-5 (1979).
4. M. O. Delcourt, N. Kéghouche, J. Belloni, *Nouv. J. Chim.* 7, 131-6 (1983).
5. M. O. Delcourt, J. Belloni, In *Proc. Fifth Tihany Symposium on Radiation Chemistry*; Akad. Kiado: Budapest, 1983; Vol. 1; pp 319-24.
6. J.-L. Marignier, J. Belloni, *J. Chim. Phys. Phys.-Chim. Biol.* 85, 21-8 (1988).
7. A. Henglein, J. Lilie, *J. Phys. Chem.* 85 1246-51 (1981).
8. L. Brus, *J. Phys. Chem.* 90, 2555-2560 (1986).
9. K. H. Schmidt, R. Patel, R.; D. Meisel, *J. Am. Chem. Soc.* 110, 4882-4 (1988).
10. D. Hayes, K. H. Schmidt, D. Meisel, *J. Phys. Chem.* 93, 6100-9 (1989).
11. D. Hayes, O. I. Micic, M. T. Nenadovic, V. Swayambunathan, D. Meisel, *J. Phys. Chem.* 93, 4603-8 (1989).
12. V. Swayambunathan, D. Hayes, K. H. Schmidt, Y. X. Liao, D. Meisel, *J. Am. Chem. Soc.* 112, 3831-7 (1990).
13. Y. Nosaka, K. Yamaguchi, H. Miyama, H. Hayashi, *H. Chem. Lett.*, 605-8 (1988).