# MATERIALS CHEMISTRY COMMUNICATION

## Sol–gel transition in CdS colloids

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We report the preparation of transparent gels from concentrated sols of CdS nanocrystals. The principles of our method can be applied to other systems, enlarging the domain of the inorganic sol–gel process which so far has been restricted mainly to oxides.

A gel is an open three-dimensional skeleton of aggregated particles, with solvent trapped in its pore network. The formation of an inorganic gel usually requires a well controlled colloidal synthesis, and the successive stabilization and slow destabilization of nanoparticles. The first step, the preparation of a stable colloid,[1] can be achieved by the limited growth of the particles in solution while preventing their agglomeration due to van der Waals interactions. In dielectric solvents, particles having surface charges offer repulsive forces which counterbalance the van der Waals interactions. When this electrostatic repulsion between the particles is absent or too weak, their aggregation has to be limited by the presence of molecules which either provide steric hindrance between the particles or passivate their surface. In any case, the conditions of the stability of colloids give upper limits for the particle size and their concentration in the synthesis medium. The second step is the further evolution of the colloid into a gel instead of a precipitate. Gelation requires the formation of aggregates with an open structure and only occurs when the number and/or the reactivity of the bonding sites at the surface of the particles is low, thus preventing the formation of dense aggregates.[2] This can be induced by addition of a chemical agent to the colloid which slowly increases the reactivity of the particles.

So far, the inorganic sol–gel process has been restricted to oxide systems.[3] We here report the preparation of non-oxide concentrated colloids, sols and gels of II–VI semiconductor chalcogenides such as CdS. The elementary CdS particles are either nanocrystals resulting from controlled growth in inverted micelles or small clusters prepared in the presence of complexing molecules. In both cases, stable and concentrated colloids are obtained by surface complexation of the elementary particles with 4-fluorophenylthiol. The destabilization of these colloids, leading to aggregation and gelation, is achieved by progressive decomplexation of the particles.

The first step is the synthesis of colloidal II–VI compounds. This problem has been the subject of extensive investigations,[4–8] motivated by the physical properties related to quantum confinement.[9] Many synthesis procedures have been developed, which all used the stabilization of the nanoparticles with a complexing agent, *e.g.* thiol, phosphine, phosphate. The highest colloid concentrations are obtained when the solvent used for the dispersion can also complex the surface of the particles, thus improving their passivation towards aggregation.[6,8] Such passivation prevents gelation. In this work, we looked for both efficient complexation and dispersion in common solvents, together with the possibility of controlled depassivation. We find that 4-fluorophenylthiol (FPhSH), used as a strong surface complexing agent, allows the dispersion of the particles in various solvents such as acetone, tetrahydrofuran (THF) and dimethylformamide, with very high concentrations (at least 5 mol $l^{-1}$, *i.e.* volumic fraction ca. 15%). Two methods have been adapted from previous studies[4,8] for the synthesis of such concentrated colloids.

(1) Colloids from the P-I process were prepared by the growth of particles directly in the presence of FPhSH. A solution of deaerated acetone containing $H_2S$ ($5\times10^{-3}$ mol $l^{-1}$), FPhSH ($1\times10^{-2}$ mol $l^{-1}$) and triethylamine (TEA; $2\times10^{-2}$ mol $l^{-1}$) was added dropwise into the same volume of a stirred solution of acetone containing $4\times10^{-3}$ mol $l^{-1}$ of $Cd(NO_3)_2$. The use of TEA ensured the neutralization of the acidity from $H_2S$ and FPhSH. The average size of the particles (*ca.* 1 nm) was deduced from the absorption spectrum using previously published size–gap correlation curves.[10] The small size is a consequence of the high thiol content needed to stabilize the particles. The flocculation of the particles resulting from complete evaporation of the solvent and subsequent washing with ethanol led to a powder which was dispersed in fresh acetone with a molar concentration.

(2) In the case of colloids from process P-II, CdS nanoparticles were synthesized within water droplets from a water (2.5 mol $l^{-1}$)–AOT (0.5 mol $l^{-1}$)–heptane emulsion [AOT = sodium di-(2-ethylhexyl)sulfosuccinate surfactant].[7] The average size of the particles (1–5 nm) was controlled by the initial cadmium concentration in water (0.01–0.15 mol $l^{-1}$). Excess $H_2S$ was eliminated by $N_2$ bubbling. Addition of FPhSH and TEA with a concentration equal to 5 times the initial Cd concentration induces flocculation of the particles which can then be recovered as a powder by centrifugation. After washing, the particles were dispersed in acetone with a molar concentration.

$^{113}$Cd NMR spectroscopy was used to study the structure and the surface complexation of CdS particles (Fig. 1). Following Dance and co-workers,[11] the various $CdS_x(SPhF)_{4-x}$ contributions ($0\leqslant x\leqslant4$) can be determined, together with the coordination of the thiolate ligands (either bridging, $^{\mu}$SPhF, or terminal, $^{t}$SPhF). The signals are rather large, which severely limits spectral interpretation. This broadening arises from a distribution of Cd chemical shifts corresponding to some variations in the S—Cd—S bond lengths and angles.

For the particles prepared by process P-I, we observed a

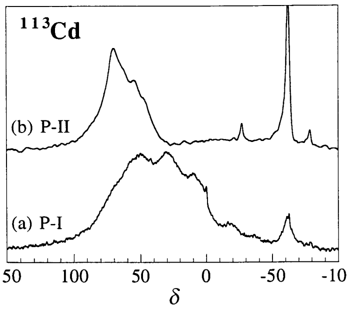

**Fig. 1** $^{113}$Cd NMR spectra performed on CdS concentrated sols in acetone. Chemical shifts are given with reference to $Cd(CH_3)_2$. (a) Typical spectrum for 1 nm particles prepared by the P-I process. (b) Spectrum for 3.4 nm particles obtained by the P-II process.

large distribution of Cd environments. The broad bands at $\delta$ 70 and 50 reveal $CdS_4$ sites, in cubic, zinc-blende-type and hexagonal, wurtzite-type fragments, respectively. The band at $\delta$ $-62$ corresponds to $Cd(^{\mu}FPhS)_3(^{t}FPhS)_1$, *i.e.* Cd complexed with four thiolate ligands, and is relatively narrow as the thiolate groups rotate freely around the Cd ion. The bands at $\delta$ $+30$, $+10$ and $-20$ probably correspond to the three other environments: $CdS_3(SPhF)_1$, $CdS_2(SPhF)_2$ and $CdS(SPhF)_3$ groups, respectively. This large distribution is obviously related to the competition between precipitation and complexation reactions which is inherent to this process. The partial substitution of the tetrahedrally coordinated sulfurs of the zinc blende structure by bridging or terminal thiol groups limits the particle growth. Thiolate species appear as inhibitors for the precipitation and lead to small polymeric particles, *i.e.* clusters of size 1 nm.

For the nanoparticles obtained by the inverted micelle technique (P-II) and complexed by thiolate species, the $^{113}Cd$ NMR spectrum revealed the presence of $CdS_4$ in a cubic, zinc blende lattice, $CdS_3(SPhF)$ and $Cd(SPhF)_4$ groups. The $Cd(SPhF)_4$ groups give the sharp line located at $\delta$ $-62$ and form a complexing shell around the particles. No other cadmium environment was detected in these samples, which suggested that these colloids were formed by dense CdS nanoparticles capped with a surface cadmium thiolate complex.

It is well known that thiols can be oxidized easily by various oxidizers such as $O_2$ from air, hydrogen peroxide or sodium periodate, to give either dithiol (FPh—S—S—PhF) or sulfonate (FPh—$SO_{3-}$), depending on the experimental procedure.[12] As these compounds are no longer bonded to the surface of the particles, they leave reactive sites at the surface and thus permit aggregation. Since the particle surface is slowly activated, random aggregation occurs leading to lacunar aggregates and thus making the sol–gel transition possible. In this sense, chalcogenide II–VI colloids complexed with FPhSH and dispersed in weakly complexing solvents (*e.g.* acetone, THF) present a unique opportunity to observe gelation.

Gelation was studied in controlled conditions by adding $H_2O_2$ to the deaerated CdS sol. This was performed at 0 °C under vigorous stirring in order to allow a homogeneous dispersion of the oxidant in the solution before reaction. After a few minutes, the solution was stored at room temperature. For example, transparent stiff gels (Fig. 2) were obtained within a few minutes for 2 nm crystallites occupying a volume fraction of 5% treated with 0.3 equiv. $H_2O_2$ (relative to the thiol concentration). We note that such optically transparent gels are obtained for CdS volume fractions higher than 1%, and light scattering is increasingly observed as the CdS particle concentration is decreased.

Concerning the aggregation mechanism, $^{19}F$ NMR experiments[13] have recently shown that thiol and disulfide molecules do not participate directly in the establishment of chemical bonding between the particles. This suggests that aggregation between the particles occurs through direct contact between CdS particles with no organic link.

As has already been shown for silica gels, scattering techniques are the most appropriate way to study the fractal structures of aggregates and to determine their fractal dimension, $D$, which is related to the aggregation mechanism.[14] X-Ray scattering experiments were carried out using synchrotron radiation at LURE (Orsay, France). For a CdS gel resulting from oxidation of P-I process sol (small polymeric units), the scattering curve between $Q = 2 \times 10^{-2}$ and $5 \times 10^{-1}$ nm$^{-1}$ exhibits a power law corresponding to a fractal dimension of 1.9. As observed for silica gels, this value is consistent with the fractal dimension of lacunar objects resulting from the cluster–cluster aggregation model.[14]

In conclusion, we have reported the preparation of transparent gels of CdS. The specific case of chalcogenides (CdS, ZnS, CdSe) is an immediate extension of this work. The general scheme of the synthesis is based on the following steps: (i) synthesis of the colloid; (ii) preparation of a concentrated sol consisting of particles complexed by an organic molecule and dispersed in a neutral solvent; (iii) controlled aggregation and gelation through slow depassivation of the surface of the particles. The gels may be further processed as transparent nanostructured monoliths or thin films, the properties of which are under investigation.

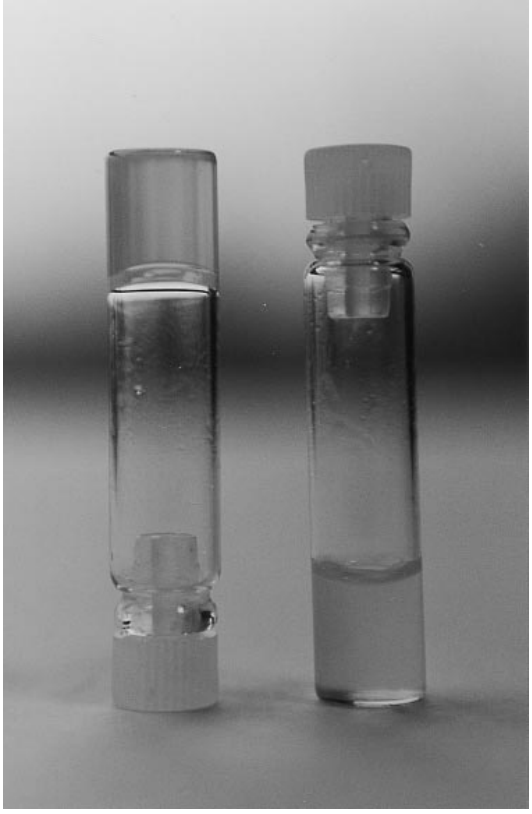

**Fig. 2** Sol–gel transition performed by thiol oxidation at the surface of 2 nm CdS crystallites dispersed in acetone (CdS volumic fraction 5%)

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