

New Transparent Chalcogenide Materials Using a Sol–Gel Process

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The inorganic sol–gel process is now well-known as a synthetic route for the preparation of oxide materials (SiO_2 , V_2O_5 , TiO_2 , etc.) starting from molecular precursors in solution.¹ Gels are either heated at several hundred degrees to make dense materials or dried at room temperature to form transparent matrixes (so-called xerogels) which may entrap organic or biological species.^{2,3} Final materials can be obtained in any desired shape, including thin films and coatings (0.1–10 μm thick) which present a large practical interest since they are easily deposited onto large substrates by spin- or dip-coating. A large variety of materials have been synthesized in this way, with current or potential applications in optical, electronic, protective, and sensor devices.^{2–4}

The oxide sol–gel synthesis proceeds from a polymerization reaction involving the hydrolysis of a molecular precursor followed by the condensation through the formation of metaloxane bonds. The detailed mechanisms have been investigated for silica which serves as a model system because its chemistry and structure are easily controlled, thus allowing the preparation of optically transparent amorphous materials.^{1,5} Further developments of the sol–gel method for non-oxide materials requires to find successive reactions which would ensure the bonding between monomers or elementary particles in a controlled way, similarly to the hydrolysis–condensation in the silica polymerization.

Here, we develop a scheme for the II–VI chalcogenide sol–gel synthesis, using cadmium sulfide as a model system. Referring to our previous work on colloidal chemistry of II–VI compounds,⁶ we find that it is possible to prepare a highly concentrated CdS sol and put it in suitable conditions for gelation. The destabilization of the sol, leading to aggregation and gelation is achieved by a progressive decomplexation of the particles. Furthermore, we show that this gel processing offers the possibility to prepare new transparent and

nanostructured materials at low temperature, with variable shapes, textures, and properties.

The colloidal synthesis of II–VI compounds has been the subject of extensive investigations in the past 10 years,^{7–12} motivated by the physical properties related to quantum confinement.¹³ Most synthesis procedures involve the stabilization of the particles through the complexation of their surface with a passivating agent, whose the chemical nature determines the solvent of dispersion. But the best results in terms of colloid concentration are obtained when the solvent is also the surface complexing agent of the nanoparticles, thus improving their passivation toward the aggregation.^{10–12} Consequently, the progressive decomplexation of the particles in this medium is not possible, and these sols cannot be considered as proper candidates for gelation.

We find that the use of the 4-fluorophenylthiol (FPhSH) as a strong surface complexing agent, instead of the phenylthiol,¹⁰ greatly improves the dispersion of the nanoparticles in organic solvents. Dispersion can be achieved in acetone, tetrahydrofuran (THF) or dimethylformamide at very high concentrations (at least 5 mol L⁻¹, i.e., a volumic fraction of about 15%), and to a smaller extent in ethanol and chloroform.

CdS nanocrystals were synthesized by precipitation in inverted micelles with different cadmium concentrations.^{7b} The average size of the particles (1–5 nm) was deduced from the absorption spectrum using previously published size/gap correlation curves¹⁴ (Figure 1). The excess hydrogen sulfide was eliminated by bubbling with nitrogen. FPhSH and TEA (triethylamine) were then added with a concentration equal to 5 times the initial cadmium concentration. The excess of thiol molecules and TEA to neutralize acidity from H₂S and thiol allowed a more efficient capping of the particles. The surface complexation of the particles induced the flocculation of the colloids which could then be recovered as a powder by centrifugation. After washing with heptane, the particles were dispersed in acetone with a tunable concentration up to 15% volume ratio. Previously reported ¹¹³Cd NMR and transmission electronic microscopy data have shown that these colloids consist of dense cubic blende CdS nanocrystals capped with a surface cadmium thiolate complex.⁶

In preliminary experiments, gelation was observed after a long exposure of the sol to the ambient air. It is well-known that thiols can be easily oxidized by various oxidizers such as oxygen from air, hydrogen peroxide or sodium periodate, to give either dithiol

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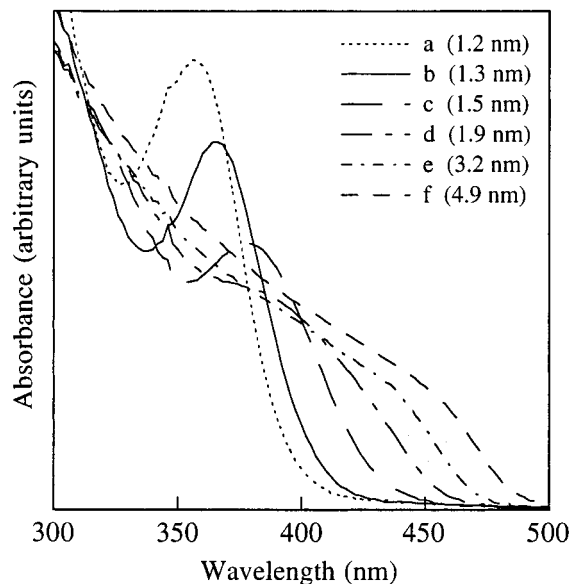


Figure 1. Absorption spectra of CdS colloids obtained by precipitation in inverted micelles. All spectra were normalized for the total Cd concentration. In all experiments, the concentrations of AOT (AOT stands for the di-2-ethylhexyl sulfosuccinate sodium salt surfactant) and water in heptane were kept constant equal to 0.5 and 2.5 mol L⁻¹, respectively. The CdS colloids were obtained after injection of H₂S in excess. The average size of the particles varied from 1 to 5 nm, starting from cadmium concentrations in the water droplets ranging from 0.01 to 0.15 mol L⁻¹.

(FPh-S-S-PhF) or sulfonate (FPh-SO₃⁻), depending on the experimental procedure.¹⁵ As these compounds are no longer bonded to the surface of the particles, they leave reactive sites at the surface and thus permit the aggregation. Since the surface of the particles is slowly activated, random aggregation occurs leading to lacunar aggregates and thus making the sol-gel transition possible. In that sense, chalcogenide II-VI colloids complexed with FPhSH and dispersed in weakly complexing solvents (acetone, THF, etc.) present a unique opportunity to observe gelation.

Gelation was then studied in controlled conditions by using addition of H₂O₂ to the deaerated CdS sol. This was performed at low temperature (0 °C), under vigorous stirring in order to allow an homogeneous dispersion of the oxidant in the solution before it started to react. After a few minutes, the solution was stored at room temperature. For example, transparent stiff gels were obtained within a few minutes for 1-nm crystallites occupying a volume fraction of 1% treated with 0.3 equiv of hydrogen peroxide (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.

The kinetics of the gelation process and the further aging of the gels are obviously influenced by several parameters. A specific parameter for the CdS gelation is the oxidized thiol fraction ($x = 2[\text{H}_2\text{O}_2]/[\text{FPhSH}]$) which controls the number of active surface sites in a starting sol for which the size (d) and the volumic fraction (v) of particles are given. The gelation time (t_g) decreases with increasing x ratio. For example, t_g shifts from one week for $x = 30\%$ to 4 weeks for $x = 10\%$, keeping the other parameters constant ($v = 0.1\%$ and $d = 1$ nm). For higher amounts of H₂O₂ ($x > 30\%$),

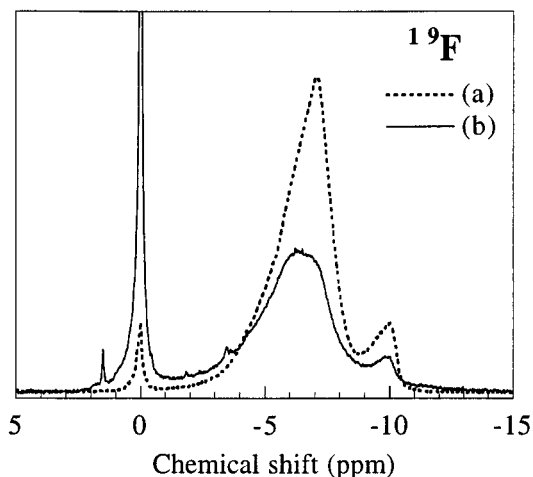


Figure 2. ¹⁹F NMR spectra of a partially oxidized sol prepared with 1 nm crystallites. Chemical shifts are given relatively to the FPhS-SPhF resonance, whose signal stands at -113 ppm from the standard reference Freon 11 (CFCl₃). (a) The spectrum recorded before oxidation shows two large dissymmetric bands peaking at about -7 and -10 ppm which we attribute to ⁴SPhF and ¹SPhF groups, respectively. A small amount of disulfide (FPhS-SPhF, 0 ppm) is observed due to oxidation from residual air. (b) The treatment with 0.3 equiv of hydrogen peroxide (relative to the thiol concentration) leads to a progressive oxidation of thiol species into the corresponding disulfide and, to a much lower extent, the sulfonate derivative (FPhSO₃⁻, -1.5 ppm).¹⁵

there is an excess of reactive sites so that new bonds may be formed after gelation, leading to a shrinkage of the solid network and expulsion of the liquid from the pores (syneresis). Starting from diluted sols, the syneresis shrinkage can be as high as 90%. Finally, when x is beyond 100%, there is a total decomplexation of the colloids and a precipitate is observed.

Concerning the aggregation mechanism, let us first state that it does not proceed from reversible physical interactions between particles since the solvent addition or temperature rise do not affect the gel. To characterize the aggregation and the gelation processes, ¹⁹F NMR spectroscopy was performed on a sol formed of 1 nm crystallites. The addition of 0.3 equiv of hydrogen peroxide led to a progressive oxidation of the thiolate species to form the disulfide (Figure 2). The concentration measurements performed on the liquid resulting from the syneresis revealed that it contained almost all the products of the thiol oxidation. This clearly suggests that thiol and disulfide molecules do not directly participate in the establishment of the chemical bonding between the particles. As gelation by direct oxidation of the thiol in air was observed (i.e., without addition of H₂O₂), the link between the particles was neither achieved by the H₂O₂ molecules.¹⁶ At last, we observed gelation for sols in various solvents. This excludes the participation of acetone in the formation of links, as has been previously observed for Hg and Cd polynuclear complexes.¹⁷ We therefore conclude that the aggregation between the particles occurs through the direct contact of the CdS particles with no organic link.

As has already been shown for silica gels, scattering techniques are the most appropriate way to study the

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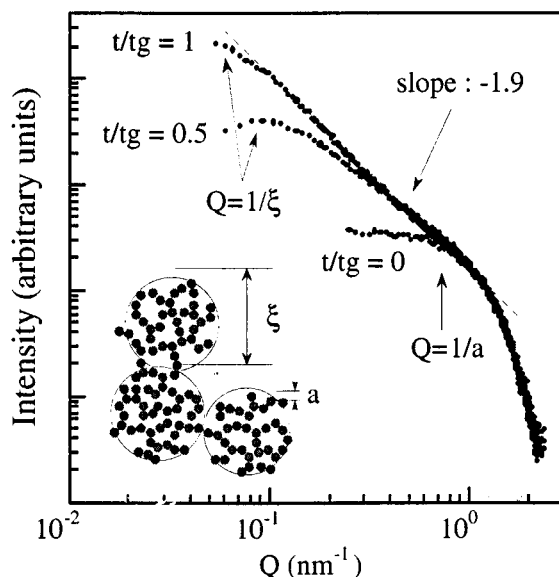


Figure 3. Small-angle X-ray scattering (SAXS) curves¹⁹ in a Q range extended from 5×10^{-2} to 2 nm^{-1} showing the time evolution of the structure for 2 nm CdS colloids (volume fraction of 0.6%) after adding H_2O_2 . CdS crystallites progressively arrange themselves in a fractal way with a dimension of about $D = 1.9$. The fractal range increases in size with increasing time, up to 18 nm at the gelation time t_g . It is consistent with the schematic structural illustration displaying the two sizes (a and ξ) which limit the fractal range.

fractal structure of aggregates and to determine their fractal dimension D , which is related to the aggregation mechanism. The scattering law is given by $I(Q) \propto Q^{-D}$, where Q is the magnitude of the scattering vector and $1 < D < 3$ for a volume fractal object. Figure 3 shows an example of X-ray scattering data for the CdS gelation. The scattering curves shows a progressive growth of fractal particles characterized by 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.¹⁸ Besides, absorption spectra of transparent gels are not drastically modified compared to the ones recorded on the starting colloids. This shows that CdS gels exhibit quantum confinement as expected for an open fractal structure with a low connectivity between elementary units. Note that this fractal structure can also account for the observed light scattering in diluted gels.²⁰

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(19) Preliminary SAXS experiments were carried out using synchrotron radiation at LURE (Orsay, France). The white beam from the storage ring was monochromatized by a double-crystal monochromator of Si tuned for 8.5 keV ($\lambda = 0.15216 \text{ nm}$). A one-dimensional position-sensitive detector was used to record the scattered X-ray intensity from the CdS polymeric sol placed in a capillary tube. The parasitic scattering from air, slits, and sample holder was subtracted from the experimental SAXS intensity using standard methods.

(20) In a simple model of homogeneously packed fractal aggregates, light scattering is expected if the size ξ of the fractal domains is in the same range as the light wavelength, i.e., a few hundred of nanometers. The volumic fraction v of nanocrystals is given by $v = (\xi/a)^{D-3}$, where a is the size of the primary units, and D the fractal dimension ($D = 1.9$).²³ Therefore, optical transparency should be observed for volumic fractions higher than about 1%.

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Non-oxide gels developed here in the case of CdS lead to dried materials similar to those already known for silica: bulk monoliths, thin films, and eventually aerogels. Bulk monoliths are usually obtained after a careful drying of the gels. This step is often complicated by strong stresses within the solid network of the gel, arising from the removal of the solvent from the pores. This can be avoided to some extent by drying the gels slowly enough so that densification and strengthening of the solid network through rearrangement of the aggregates occur concomitantly to the solvent evacuation. Optically transparent CdS monoliths were obtained in this way, with dimensions (a few millimeters) limited by the small quantity of starting nanoparticles.

Thin films were easily deposited on usual glass slides or silicon wafers by spin coating from a partially oxidized CdS sol. The thickness was controlled through the viscosity of the sol, by modifying the colloid concentration or the advance of the aggregation. For instance, CdS thin films with no cracks were spin-coated at 2000 rpm onto glass substrates. Characterization by ellipsometry evidenced a thickness of $0.1 \mu\text{m}$ and an optical index of 1.9 at 600 nm.

This new sol-gel processing should offer large opportunities for further developments. A first class of potential applications concerns the use of the xerogels as nanostructured dielectric matrixes with a high index of refraction. As the concentrated CdS sols are prepared in standard organic solvents, we are able to make transparent semiconductor thin films or monoliths homogeneously doped with optically active organic molecules or biological species. This results in new hybrid organic-inorganic materials whose properties and practical interest are to be investigated.

A second class of applications is related to the optical properties of bulk and quantum-sized semiconductors such as photoconduction,²¹ electroluminescence,²² and optical nonlinearities.²³ We want to put special emphasis on the ability of this synthesis method to control the texture of the final film, through the mild oxidation step. A texture with a low connectivity between semiconductor nanocrystals could be expected with a weak amount of the oxidant while a high concentration of the oxidant should lead to high connectivity. In addition to the chemical nature and size of the initial particles, this offers an additional optimization parameter which can be adjusted according to the desired application.

In conclusion, we have reported the first extension of the sol-gel process on the preparation of transparent gels, thin films and monoliths of CdS. The specific case of chalcogenides (CdS, ZnS, CdSe, etc.) is an immediate extension of this work, but we believe that this process, described here in the case of the CdS model system, establishes the general principles which should allow future developments of the sol-gel technique to other non-oxide materials.

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