Supporting Informations for the paper

Multigram Scale, Solventless and Diffusion-Controlled Route to Highly Monodisperse PbS Nanocrystals

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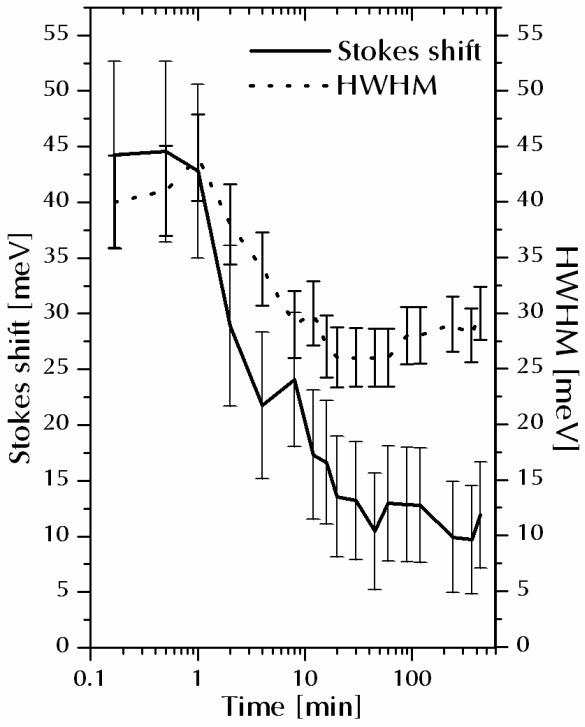
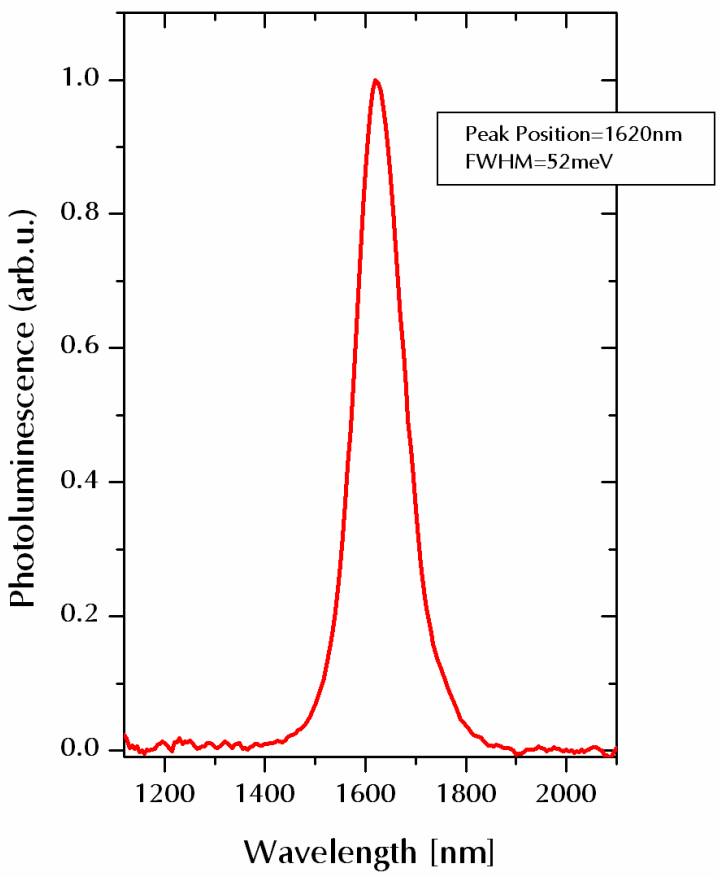
Experimental Details:

All chemicals were purchased from Aldrich unless otherwise stated.
1g $PbCl_2$ (98%) and 1.93g of technical grade oleylamine (OLA) (1:2 molar ratio) are magnetically stirred under N_2 flow in a round-bottom flask and heated to 100 °C when the flask is sealed and degassed under vacuum for 5 minutes. The flask is then reopened and the N_2 flux is restored while the temperature is increased to 120°C and left there for 30 minutes.
In a separate vial 0.0115g of elemental sulfur is dissolved in 0.2g of OLA (0.1:0.2 molar ratio with respect to the $PbCl_2$ suspension) by using first sonication and heating at 80°C for 30 minutes.
During this time the $PbCl_2$ suspension becomes homogeneous and highly viscous (higher $PbCl_2$:OLA ratios induce gelling of the suspension at ~120°C).
The sulfur solution is then quickly injected in the PbCl2-OLA solution via a syringe. As a consequence of the injection the temperature drops and it is allowed to stabilize at 100°C where it is then kept for the growth of the nanocrystals.
Once the desired size is achieved the reaction is quenched by pouring the product in cold hexane. The solution is centrifuged to precipitate excess $PbCl_2$ while the supernatant is transferred to a separate test tube. The nanocrystals are precipitated from the supernatant by adding minimum amount of ethanol. The turbid solution is centrifuged for 1 minute at 3000rpm, the supernatant is removed and the precipitates is solubilized in hexane. In order to remove the excess sulfur precursor still present in the solution we added to the nanocrystal solution enough oleic acid to make the solution turbid and we let it sit for 5 minutes. After this is time has passed the solution is centrifuged, the supernatant containing the sulfur precursor is removed and the precipitate is redispersed in hexane. At this stage, if the solution looks turbid (usually because of insoluble $PbCl_2$

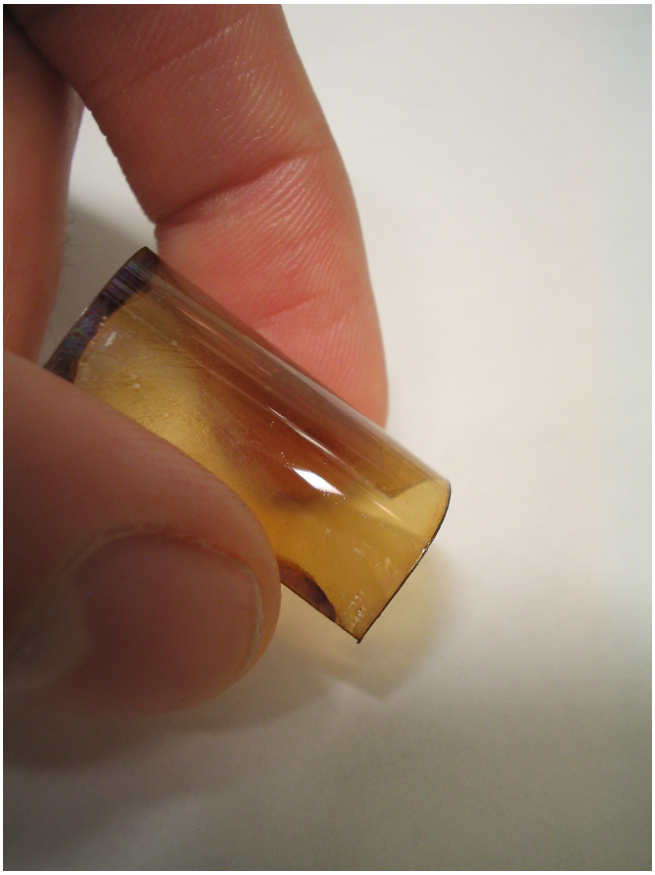
still present), it might be necessary to centrifuge to remove the excess $PbCl_2$ precursor made insoluble by exposure to oleic acid.
After these steps are completed the nanocrystal solution can be precipitated with ethanol and redispersed in hexane or other apolar solvents 2 or 3 times in order to completely remove residual traces of oleic acid and oleylamine. This additional washing do not compromise the colloidal stability of photoluminescence of the nanocrystals (unless consistent amount of water is present in the ethanol used for precipitation or too much ethanol is used for precipitation)



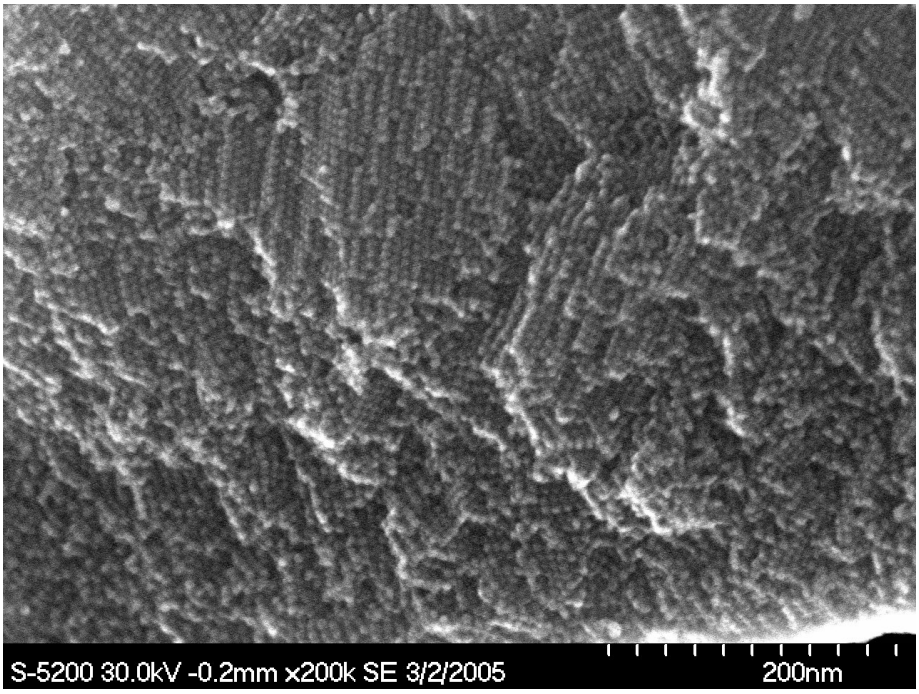
Supporting Figure 1. The Stokes shift and the half-width at half-maximum (HWHM) of the first exciton peak on the red side of the absorption spectrum is monitored during the reaction ($PbCl_2$:S:OLA=0.5:0.05:1). The abscissa is on a logarithmic scale and the lines are guide to the eye. The trend in the HWHM confirms the trend in the FWHM of the PL peak.



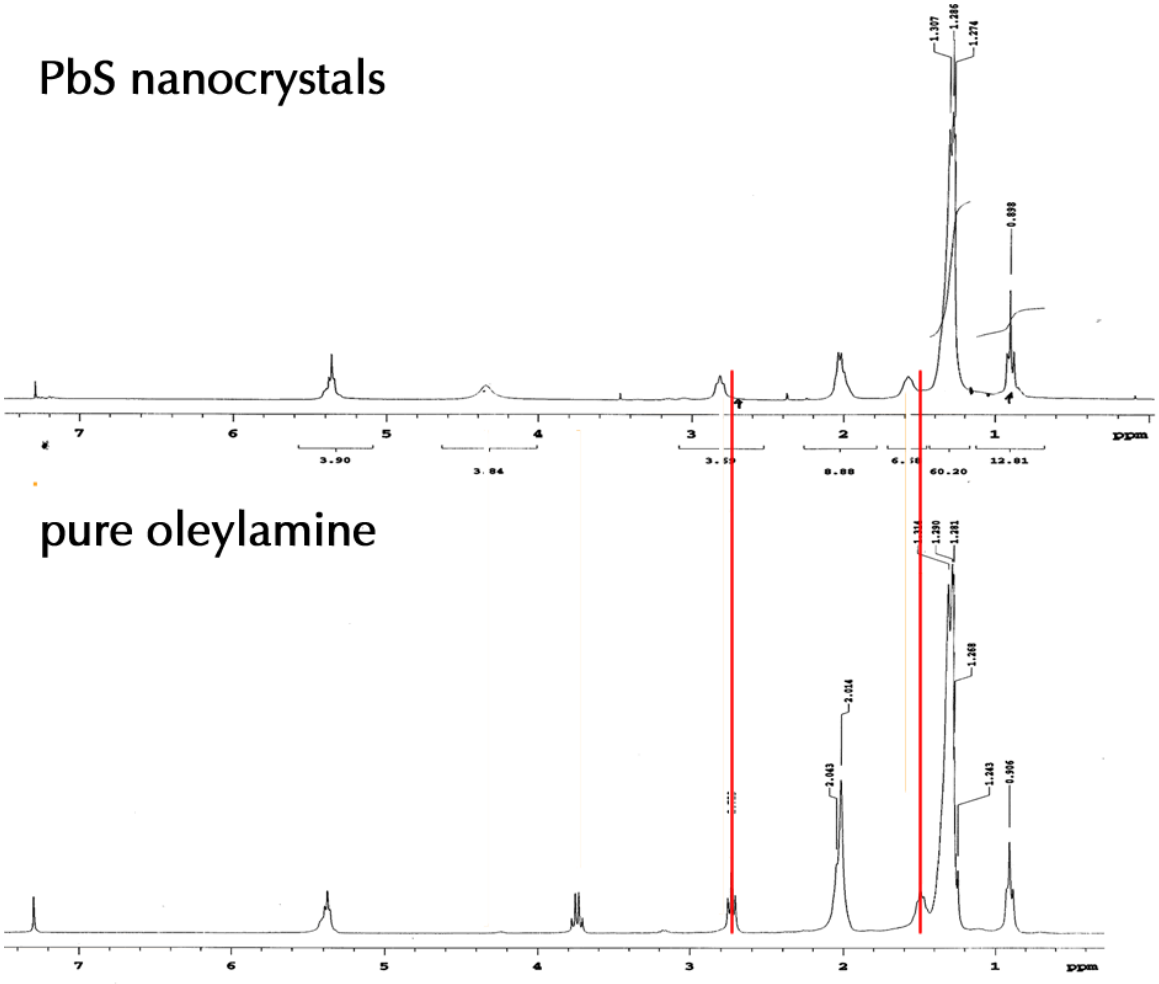
Supporting Figure 2. PL peak of a very monodisperse sample of PbS nanocrystals obtained by following the described procedure. Extra care was taken to exclude self-absorption and solvent absorption.



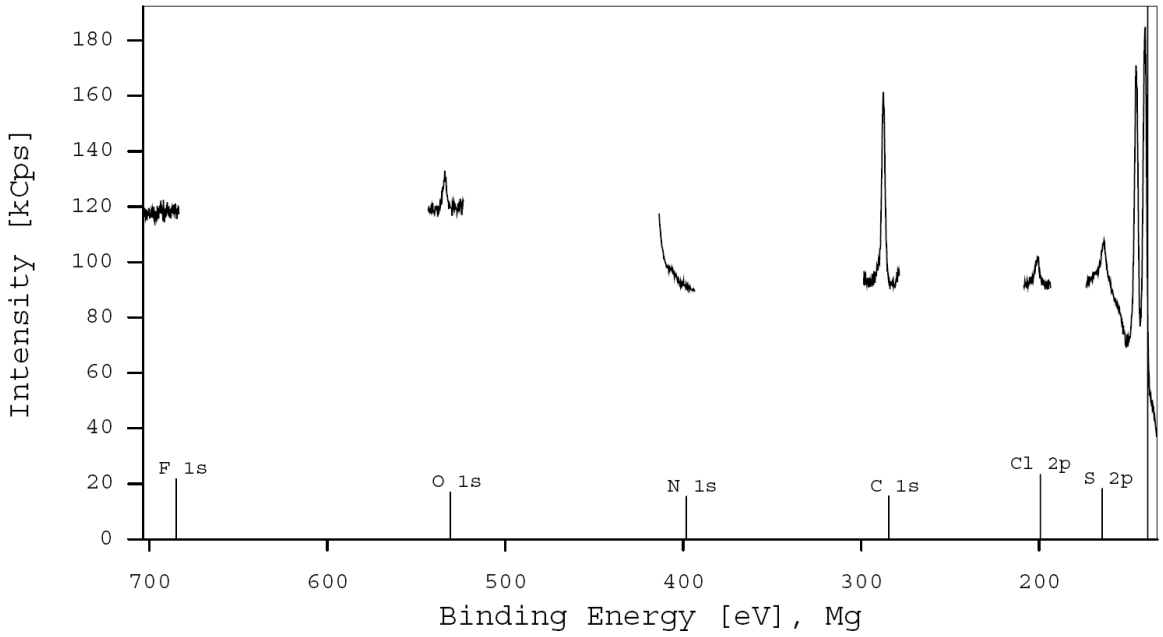
Supporting Figure 3. Photo of a flexible PbS nanocrystal solid obtained by nanocrystal-plasma-polymerization



Supporting Figure 4. SEM from a flexible PbS nanocrystal solid obtained by nanocrystal-plasma-polymerization



Supporting Figure 5. 1H-NMR of PbS nanocrystals (upper panel) and the ligand (tech, grade oleylamine – lower panel). The red lines mark the shifts induced by coordination to the surface of the amine group in the neighboring H atoms



Supporting Figure 6. XPS of a highly purified sample of PbS nanocrystals

Element	Atom %	Orbital
C	74.8	1s
N	0.1	1s
O	5.2	1s
F	0.2	1s
S	6.0	2p
Cl	4.5	2p
Pb	9.2	4f

Supporting Figure 7. XPS compositional analysis; O is coming from surface oxidation upon air exposure.