Atomic Ligand Passivation of Colloidal Nanocrystal Films via their Reaction with Propyltrichlorosilane

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Supporting Information

Materials and method

Chemicals: Cadmium oxide (99.999%), sulfur powder (99.9%, 100mesh), selenium powder (99.9%, 100mesh), tellurium powder (99.8%, 200mesh), 1-octadecene (ODE 90%), Hexadecanediol, Gold(III)chloride, Oleic acid, Oleylamine, (TMS)_2S, Tetrakis(acetonitrile)copper(I) hexafluorophosphate (97%), dodecyldimethylammonium bromide (DDAB), Ammonium bromide, o-dichlorobenzene (ODCB) and water free toluene, methanol, acetonitrile (MeCN) and ethanol were purchased from Sigma while trioctylphosphine (TOP, 97%), Lead acetate trihydrate, Platinum chloride, Trioctylphosphine oxide (TOPO, 99%), Tributylphosphine, (TBP, 97%), were purchased from Strem. Octadecylphosphonic acid (ODPA, 99%) and Hexylphosphonic acid (HPA, 99%) and Octylphosphonic acid (OPA, 99%) were purchased from Polycarbon Industries. Propyltrichlorosilane (PTCS, 97%) and Hydrazine monohydrate (98%) were purchased from Alpha Aesar. Ammonium hydroxide (33%) was purchased from J.T. Baker. All the chemicals were used as shipped.

CdSe, CdS, CdSe/CdS core/shell rods and dots were synthesized following already reported procedures\textsuperscript{[1]} with slight modifications.

Synthesis of CdSe dots

TOPO (3.0g), ODPA (0.280g) and CdO (0.060g) were mixed in a 50mL flask, heated to 120°C and put under vacuum for about 1 hour. Then, under nitrogen, the solution was heated to 300-350°C to dissolve the CdO until it turned optically clear and colorless. At this point, 1.5g of TOP was injected in the flask.
and the temperature was allowed to recover to 370°C and the Se:TOP solution (0.058g Se + 0.360g TOP) was injected. The reaction was stopped after 3 minutes removing the mantle. After the synthesis, the nanocrystals were precipitated with methanol, they were washed with repeated re-dissolution in toluene and precipitation with methanol, and they are finally dissolved in toluene or TOP according with the next step.

**Synthesis of CdSe/CdS nanodots and CdSe/CdS nanorods**

In a typical synthesis of CdSe/CdS nanodots *via* seeded growth, CdO (60mg) is mixed in a flask together with TOPO (3g), ODPA (290mg). After pumping the vacuum in the flask for about 1 hour at 120°C, the resulting solution is heated to 350°C under nitrogen till the solution turned colorless. After this point the solution of sulphur precursor and nanocrystals was injected and the shell was left growing for about 5min after which the heating mantle was removed. Particles were washed 3 times with toluene and methanol and redispersed in fresh toluene.

For the growth of a rod like shell the protocol is similar but HPA is added to the flask along with the CdO, TOPO and ODPA.

**Synthesis of CdTe dots and rods**

For the synthesis of CdTe nanocrystals TOPO (3g), ODPA (0.315g), and CdO (60mg) were loaded into a 50mL threeneck flask and degassed for 1h at 120 °C. Next, under nitrogen flow, the mixture was heated to 380°C and held at that temperature until the solution turned clear. At this point, 1.5g of TOP was added, and the temperature was allowed to recover to 380°C, after which 0.780g of the 10 wt % Te/TOP stock solution was quickly injected. The heating mantle was removed immediately after the injection.

For the synthesis of the CdTe rods a similar protocol was used: ODPA (800mg), OPA (315mg), TOPO (3g), and CdO (200mg) were degassed at 120°C for 1h in a 50ml three-neck flask. Then, the solution was heated at 320°C under nitrogen till the solution turned clear and colorless. Next, 60mg of tellurium dissolved in 560mg of TOP were rapidly injected to the vigorously stirring precursors and particles were allowed to grow for 5 minutes before the mantle was removed to stop the reaction. After cooling down, the solution was washed with methanol and toluene.
Synthesis of PbSe NCs

For the synthesis of PbSe nanocrystals, 2g of lead acetate trihydrate and 7mL of oleic acid were dissolved in 40mL of octadecene. The mixture was heated to 100°C for 1.5h under vaccum to form lead oleate and removing the water. Next, the lead oleate solution was heated to 175°C and 18mL 1M solution of Se in TOP were injected under vigorous stirring. The reaction mixture was kept at 155-160°C for 6min and then cooled to room temperature. Nanocrystals were precipitated with ethanol and re-dispersed in toluene.

Synthesis of Au NCs

For the synthesis of Au NCs 35mg of AuCl₃ was dissolved in 10mL of toluene with 92mg of dodecylidomethylammonium bromide (DDAB). 40µL of 9.4M aqueous solution of NaBH₄ was added dropwise to the solution of metal salt under vigorous stirring. After few minutes the solution turned dark purple. After 20min of vigorous stirring, 1mL of oleylamine was injected and the solution was left stirring for 5 more minutes. NCs were washed with ethanol and toluene. After the redispersion of the precipitate in toluene the solution was centrifuged without ethanol addition in order to separate the unstable parts. The supernatant was made of Au NCs of 4-5nm of diameter. This recipe provides oleylamine passivated NCs. In order to obtain thiol passivated particles 1ml of dodecanethiol was added to a solution of oleylamine passivated Au NPs, and the solution was stirred for 5 minutes before washing with ethanol and toluene. The high affinity between thiols and Au NCs allows the ligand exchange. The passivation with thiols can even be achieved adding 0.8ml of dodecanethiol at the place of oleylamine after the NCs synthesis and before the washing procedure.

Synthesis of Pt NCs

Platinum nanocrystals synthesized by the injection of a solution of 0.15g of platinum acetylacetonate in 5ml of o-dichlorobenzene into a refluxing bath of 10ml of o-dichlorobenzene containing 0.3g of 1,2-hexadecanediol, 0.1ml of oleic acid, 0.1ml of oleylamine, and 0.06ml of TOP. The solution was heated for 120min before cooling and washing with ethanol and toluene.

Ammonia solution treatment on Pt NCs film

After the treatment con PTCS the film of Pt NCs was left overnight dipped in an ammonium hydroxide solution. Before further characterization the film was copiously rinsed with Millipore water.
Synthesis of Cu$_2$Se NCs

Cu2Se NCs were synthesized exchanging the Cd cations with the Cu cations in the CdSe NCs following
the cation exchange procedure of Sadtler et al.\textsuperscript{[2]}

Ligand exchange on films made of NCs with different composition, shape and surfactancts

\begin{scheme}
\textbf{Scheme S1:} General scheme of the reaction between NCs passivated with different types of surfactants and PTCS in acetonitrile. From top: phosphonic acids, amines, carboxylic acids and thiols. In most cases, Cl atoms are left of the surface of the NCs; In the case of Au NCs, however (bottom), their surface is left unpassivated.
\end{scheme}
**Figure S1:** SEM images of films of CdSe/CdS core/shell NCs drop-cast on interdigitated electrodes used for the conductivity characterization. a-b) film before the treatment with PTCS and c-d) film after the treatment with PTCS.

**Figure S2:** HRTEM images of a-b) CdSe/CdS core/shell NCs and c) Au NCs after PTCS treatment.
CdSe/CdS rods

Figure S3: Top view of vertically aligned CdSe/CdS nanorods before a) and after b) PTCS. c) FTIR d) XRD and e) XPS spectra of not assembled CdSe/CdS rods before (black) and after (red) the reaction with PTCS solution. In c) the blue curve represents the transmittance of ODPA.

Figure S4: XPS spectra of CdSe/CdS rods films treated with PTCS around Cd 3d 5/2 a) and Cl 2p b) peaks, before (black) and (after) annealing. XRD c) and FTIR d) spectra of CdSe/CdS rods films before (black) and after (red) annealing. Annealing was performed under inert atmosphere at 180°C for 20min.
Figure S5: a) I-V curves on CdSe/CdS nanorods at 15K. Photo (red) and dark (black) current and their ratio (empty circles) are shown for a) as deposited film; b) film treated with PTCS. Both samples were annealed at 180°C for 20min.
CdTe NCs

Figure S6: TEM images of CdTe NCs before a) and after b) PTCS treatment. TEM images of CdTe film before c) and after d) PTCS treatment. FTIR e), XRD f) and XPS g) spectra of CdTe NCs film before (black) and after (red) PTCS treatment. In f) XRD spectra are compared with the chart 00-019-0193 of wurtzite (blue) and 00-015-0770 of zinc blende (green) CdTe and the broad peak around 30 degrees, present in both spectra is due to the Si substrate.

Figure S7: CdTe nanorods before a) and after b) PTCS treatment.
PbSe NCs

Figure S8: a-b) TEM images of PbSe NCs before (a) and after treatment with PTCS (b); c) FTIR, d) XRD and e) XPS spectra of PbSe NCs before (black) and after (red) the reaction with PTCS solution in MeCN. In d) spectra are compared with the chart 01-077-0245 of cubic PbSe, in e) XPS spectra, around the peaks of Cl2p, before and after PTCS, are shown.

Cu$_2$Se and CuInS$_2$ NCs

Figure S9: a) FTIR spectra of Cu$_2$Se NCs (passivated with TOPO and ODPA) before (black) and after (red) the treatment with PTCS. The blue spectrum is the transmittance of the glass slide on which the particles were drop-casted. b) FTIR spectra of CuInS$_2$ NCs (passivated with oleic acid and oleylamine) before (black) and after (red) the treatment with PTCS.
Au NCs

Figure S10: a) and b) TEM image of a 3D assembly of gold NCs after the treatment with PTCS. b) zoom-in of the area inside the orange frame of a). FTIR c) and XRD d) spectra of gold NCs film before (black) and after (red) PTCS treatment. e) top, XPS spectra of a film of gold NCs passivated with oleylamine before (black) and after (red) PTCS treatment.; e) bottom, XPS spectra of a film of gold NCs passivated with dodecanethiol before (black) and after (red) PTCS treatment.
Figure S11: a) top, film of Au NCs on glass after few minutes in few milliliters of pure PTCS. Bottom, film of Au NCs treated for 10s in a solution of PTCS in acetonitrile. The treated film is immersed in few milliliters of toluene. b) PTCS extracted from the vial on the top of Figure a). c) The same solution of b) after about 10h.

Figure S12: FTIR spectra of Au NCs film of different thickness, before (black) and after (red) PTCS treatment. In a), the average film thickness was about 120nm while in b) and c) it was respectively about 200 and 500nm. Films with a thickness between 50 and 200nm (as those used for this report) show that almost all the natural ligands have been removed after the treatment. Films with higher thickness still present a high percentage of native ligand trapped in it after the exchange.
Pt NCs

Figure S13: TEM images of Pt NCs before a) and after b) PTCS treatment and after c) PTCS and NH$_4$OH solution treatment. FTIR d), XRD e) and XPS f) spectra of a film of Pt NCs before (black) and after (red) PTCS treatment. g) XPS spectra in the area around the Cl 2p peaks before (black) and after (red) PTCS treatment and after the rinsing of the NCs film in ammonium hydroxide solution (blue). h) XPS spectra around N 1s peak before (black) and after the treatment with PTCS and ammonium hydroxide (blue).
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*Table S1:* Average NC size before and after ligand exchange

**Electrodes Fabrication**

We used the common top down electron beam lithography (EBL) process to fabricate ours interdigitated electrodes on SiO$_2$/Si++ substrates (oxide thickness of 300nm, heavily p doped silicon).

Briefly, we exposed our sample primarily covered with a thin layer of Poly(methyl methacrylate) (PMMA) as resist (130nm) to the electron flow of the electron beam (Raith 150H2, 10kV) following the pattern of the electrodes. Then we removed the PMMA exposed areas with a solution of 1:3 Methyl isobutyl ketone (MIBK) and Isopropanol. Next, we deposited 5nm of Titanium as adhesion layer with the help of an e-beam evaporator following by the deposition of 100 nm of gold using an high temperature evaporator (Kurt J Lesker evaporator PVD 75). We finally got our electrodes after a subsequent lift-off.
Nuclear Magnetic Resonance (NMR) Spectroscopy

NMR characterization: The $^1$H and $^{13}$C NMR spectra were recorded on a Bruker DRX 400 spectrometer at 298K. $d_3$-acetonitrile and $d_8$-toluene were used as deuterated solvents.

In order to clarify the mechanism and to assess whether acetonitrile is involved in it, we performed some NMR measurements to see if acetonitrile binds to propyltrichlorosilane (PTCS) or it acts only as assistance in the ligand exchange procedure. First, we compared the NMR spectra of PTCS in $d_8$-toluene (Figure S13-S14) and $d_3$-acetonitrile (Figure S15-S16): $^1$H NMR (400 MHz, toluene-$d_8$): $\delta$ (ppm) 1.32-1.22 (m, CH$_2$), 0.86-0.82 (m, CH$_2$), 0.70 (t, $J = 7.3$ Hz, CH$_3$) and $^{13}$C NMR (100 MHz, toluene-$d_8$): $\delta$ (ppm) 25.8, 15.9, 15.8. Results were compared with a solution prepared by adding a droplet (10-20µl) of acetonitrile to the $d_8$-toluene solution (Figure S17-S18). The $^1$H NMR and $^{13}$C NMR spectra do not show any significant change in the chemical shifts of PTCS indicating that probably acetonitrile does not bind to the silane. In order to state that acetonitrile plays simply a role of assistant in the ligand exchange reaction it would be necessary to perform some more measurements at low temperature which we cannot currently perform with our setup.

Figure S14: $^1$H 400 MHz spectrum of PTCS in $d_8$-toluene. Inset: Zoom in of the region between 0.5 and 1.4 ppm.
Figure S15: $^{13}$C 100 MHz spectrum of PTCS in d8-toluene. Inset: Zoom in of the region between 14 and 27ppm.

Figure S16: $^1$H 400 MHz spectrum of PTCS in d3-acetonitrile. Inset: Zoom in of the region between 1 and 2.2ppm.
**Figure S17:** $^{13}$C 100 MHz spectrum of PTCS in d3-acetonitrile. Inset: Zoom in of the region between 0 and 30ppm.

**Figure S18:** $^1$H 400 MHz spectrum of PTCS in d8-toluene after the injection of 20µl of acetonitrile. Inset: Zoom in of the region between 0.5 and 1.5ppm.
Figure S19: $^{13}$C 100 MHz spectrum of PTCS in d8-toluene after the injection of 20µl of acetonitrile. Inset: Zoom in of the region between -2 and 30ppm.

Additional References
