Metallic nanoparticles enhanced the spontaneous emission of semiconductor nanocrystals embedded in nanoimprinted photonic crystals

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Supporting information available:

To synthetize 9.6 x 34 nm Au NPs in according to Jana's procedure (reference 19), 2g $HAuCl_4 \cdot 3H_2O$ were dissolved in 50 mL deionized water. Next, 3.64 g solid cetyltrimetylammonium bromide (CTAB) and 1 mL AgNO3 (1 M) was added and sonicated for 5 min to create a suspension. Next, 1.76 g ascorbic acid (dissolved in 10 mL water) was mixed and vortexed for a few minutes until the emulsion colour changed from orange to white. Finally, an appropriate amount of $NaBH_4$ (0.01M) was added. The solution colour changed to deep brown within a few minutes. The resulting solution of Au NPs was centrifuged to remove the excess of surfactant. The Au NPs were then re-dispersed in deionized water. In the next step, a phase transfer in organic solvent was carried out on the water soluble mercaptosuccinic acid (MSA)-functionalized Au NPs conferring them a negative charge at high pH. Thus, Au NPs were quickly transferred into toluene phase by electrostatic interactions between MSA and positively charged tetraoctylammonium bromide (TOAB) dissolved in toluene [39]. TEM image was performed on the solution containing the Au NPs drop cast on a TEM grid (Figure 10).

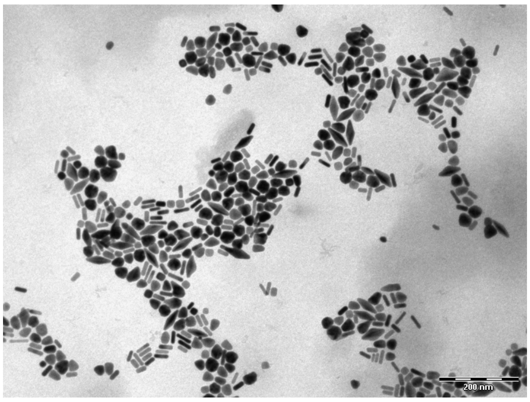

Figure 10: TEM image of the toluene solution containing the Au NPs.

The synthesis of (CdSe)ZnS NCs was carried out in the presence of size-regulating agents by reacting the atomic precursors [40]. In a typical synthesis, CdO was dissolved at 120°C in a 3-necked flask connected to a nitrogen-vacuum line, with trioctylphosphine oxide (TOPO, 99%), hexadecylamine (HDA, 99%) and tert-butyl phosphonic acid (TBPA, 98%). The resulting mixture was heated at 290°C, and 2 ml of tributylphosphine (TBP, 99%) were added in the reaction vessel. As the temperature reaches 300°C, the Se precursor solution, consisting in Se dissolved in TBP, was quickly injected into the hot solution, in order to initiate the NC nucleation. The NC growth was performed at 270°C for a variable reaction time, as a function of the desired NC dimensions. The reaction was monitored by taking aliquots during the growth, diluting them in chloroform and recording their UV-vis absorption spectra. Typically the reaction, carried out for 3min, generates CdSe NCs of 3.5-4 nm in size. The synthesis can be stopped whenever the first exciton peak in the absorption spectrum reached a desired value, by rapidly cooling the flask.

To physically and chemically protect the CdSe nanocrystal core from the external environment and to induce a better electronic confinement, a shell of ZnS was grown on CdSe NC surface. The ZnS shell growth was carried out directly on the original CdSe NC solution. After an annealing step at 110°C for one hour, the CdSe NC solution was heated at 155°C. A stock solution for the ZnS growth was freshly prepared by dissolving a solution of diethylzinc ($Zn(C_2H_5)_2$, 1.0 M solution in heptane) and of hexamethyldisilathiane (HMDS, synthesis grade) in TBP. The injections were done drop-wise, to allow a slow and uniform shell growth and to prevent the nucleation of ZnS crystals. The shell growth was controlled by monitoring UV-Vis absorption and PL spectra on aliquots of the solution. The reaction was stopped soon after the maximum of the PL was observed. After completing the injection, the solution was cooled to 60 °C and butanol was added in order to avoid solidification and to quench the residual unreacted chemicals. Emission and absorption spectra were measured using an F-2500 fluorescence spectrophotometer under unpolarized light.

Silicon stamps with two-dimensional photonic crystals were produced by electron beam lithography (*Jeol 6000*) with a dose of 130 μC / cm^2 under a beam current of 100 pA on single layer of a *ZEP* 520 resist (from *Zeon*) - 150 nm thick. The 30 s development is carried out in a solution of ZED N50. The silicon is etched with a depth of 300-350 nm by wet-etching. The stamp is treated with an anti-adhesive layer (tridecafluor-1, 1, 2, 2-tetrahydrooctyl trichlorosilan) deposited in vapour phase, which results in a very low surface energy. This treatment is very important in order to avoid sticking of the polymer to the stamp during the imprinting process and to facilitate demolding.

References

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