Quantum-Dot Synthesis

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Room-Temperature Synthesis of Air-Stable and Size-Tunable Luminescent ZnS-Coated Cd_3P_2 Nanocrystals with High Quantum Yields**

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Among nanoscale semiconductor materials, those whose emission wavelengths span a large spectral region (from the visible red to the near-infrared), are highly desired by virtue of the wide-range of applications for which they might be suitable, such as tunable emitters for bio-labeling, lasers, light emitting diodes, or solar cells.[1,2] Cadmium phosphide, in particular, has a great potential with a band gap of 0.55 eV and a large excitonic radius of 18 nm.[3] Surprisingly little research on synthetic strategies has been performed, leading, until recently, to limited sized nanocrystals (NCs; 2 to 3 nm) and incomplete optical characterizations or poor properties.[4–7] In 2010, both Peng et al.[8] and Hickey et al.,[9] successfully obtained Cd_3P_2 NCs of controllable sizes spanning the spectral range between 500 and 1500 nm. In both cases, the synthesis relies on the same system of reactants (CdO, oleic acid (OA) and tris(trimethylsilyl)phosphine ($(TMS)_3P$) in the presence or not of additional surfactants (oleylamine and trioctylphosphine), in octadecene (ODE). High temperatures are required, either for the formation of the Cd_3P_2 NCs (250 °C for Peng et al.[8]), or for the solubilization of the cadmium precursor (270 °C for Hickey et al.[9]). Nearly monodisperse, the obtained NCs present good quality optical properties with quantum yields (QYs) $\geq 30\,\%$ in most cases. However, further developments and applications of quantum dots (QDs) in general, require the implementation of simple "routine" synthesis methods to ensure run-to-run reproducibility, automation possibilities, and standardization of the nanomaterials.[1] In this context, the high temperatures required for these synthesis are a major drawback,[10,11] which, beyond obvious energetic concerns, imposes in addition the use of high-boiling-point solvents. Then, strenuous purification procedures are required and residual solvent cannot be totally removed, resulting in high carbon contents.[12] In addition, Cd_3P_2 NCs, being oxygen sensitive, precludes any application in open air in the absence of a protective shell around the NCs.

We present, here, a room-temperature process (synthesis of Cd_3P_2 QDs and subsequent Zn-S coating) leading to size-tunable and air-stable Cd_3P_2/ZnS QDs of high optical quality (QYs higher than 50 %).

The formation of Cd_3P_2 QDs at room temperature encounters a major blocking point, the lack of solubility of the cadmium precursors which have been chosen to date (mainly CdO or $Cd(OAc)_2$). Yu et al. mentioned this issue in 2009,[7] when preparing the more soluble Cd(OAc)(OA) at 120 °C as a precursor of Cd_3P_2 NCs, unfortunately the as-prepared QDs showed very poor QYs.[7] The design of highly soluble precursors appears thus to be of central importance. Therefore, we have prepared, at room temperature, a new and straightforward Cd precursor, $Cd(OAc)_2(OAm)_2$ (Octylamine = OAm), which meets the reactivity and the solubility requirements (highly soluble in apolar solvents such as toluene). This complex was fully characterized using a combination of techniques (in particular IR, 1D and 2D solution nuclear magnetic resonance (NMR) spectroscopy).

In a typical experiment, $(TMS)_3P$ is injected in a solution of $Cd(OAc)_2(OAm)_2$ (in excess, 3:1 Cd:P ratio, and in the presence of 1 equiv of OAm) in toluene at 30 °C. This method is efficient at 20 °C but, for sake of accurate control of temperature, we have chosen to set the reaction temperature at 30 °C. Transmission electron microscopy (TEM) image of the sample obtained after 24 h of reaction is shown in Figure 1. No size separation techniques are applied. The mean diameter of the roughly spherical particles is centered around 4.1 ($\pm$0.7) nm with a relatively narrow size distribution. The energy-dispersive X-ray emission (EDX) spectrum shows Cd and P to be the main constitutive elements.

High-resolution transmission electron microscopy (HRTEM) together with the fast Fourier transform (FFT) pattern revealed lattice fringes separated by distances of 0.217 nm and 0.294 nm, corresponding respectively to the (400) and (203) lattice spacings of tetragonal cadmium phosphide (Figure 1 b, Supporting Information, Figure S1). This structure is confirmed by X-rays diffraction (XRD) (Figure 2) measured on the air-stable version of these QDs after Zn-S coating as described below. The XRD pattern shows relatively well resolved peaks (given the usual broadening associated with the nanoscale of the crystals) which can be indexed to the (004) and (400) planes of tetragonal Cd_3P_2 (space group *P42/nmc*, $a = 0.872$ nm, $c = 1.234$ nm) in accord-

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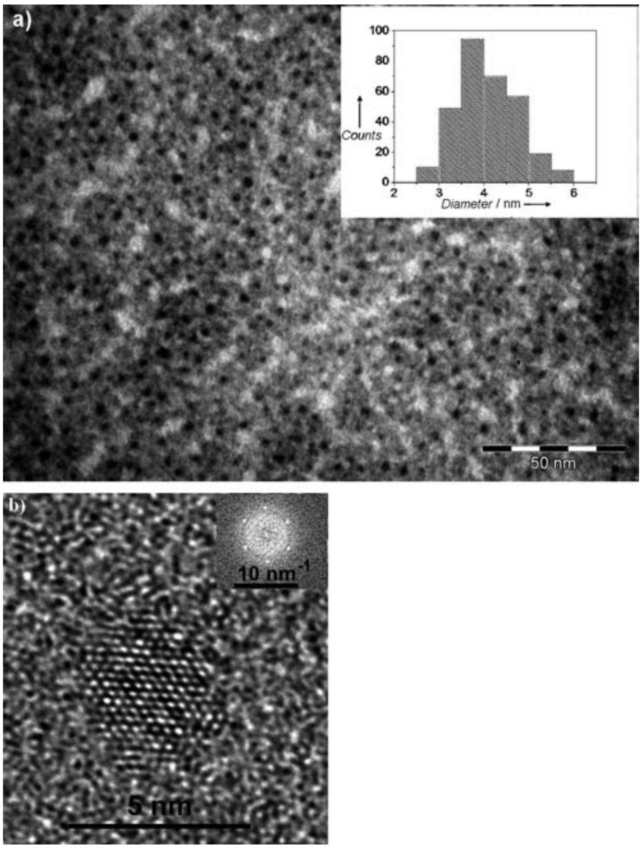

Figure 1. a) TEM image of a typical sample of Cd_3P_2 nanoparticles prepared at 30 °C with $(TMS)_3P$ (0.1 mol L^{-1}). Inset: size distribution, mean diameter centered around 4.1 nm. b) HRTEM image of a typical sample of Cd_3P_2 NCs prepared at 30 °C with $(TMS)_3P$ (0.1 mol L^{-1}). Inset: its FFT pattern.

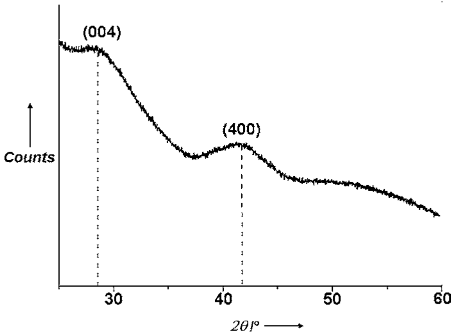

Figure 2. X-ray diffraction pattern of Cd_3P_2@ZnS ((004) and (400) planes of tetragonal cadmium phosphide).

ance with the structure recently described by Peng et al. for Cd_3P_2 NCs.[8]

Using the NMR spectroscopy techniques available for QDs analysis (advanced ^1H, ^{13}C, and ^{31}P solution and solid-state NMR studies), a detailed description of the core and coordination sphere can be gained. The sole broad resonance at $\delta = -263$ ppm observed in the $^{31}P\{^1H\}$ magic-angle spinning (MAS) NMR spectrum (Supporting Information Figure S2) lies in the upfield range typically found for nanoparticles of metal phosphides[12] and supports the formation of Cd_3P_2 as the only phosphorus-based material. The cross-polarization (CP) ^1H-^{13}C MAS NMR spectrum (Supporting Information, Figure S3) indicates acetate ($\delta = 179.5$ and 22.6 ppm respectively for carbonyl and methyl carbon atoms) and octylamine ($\delta = 43.1$ for the carbon atom located α to the amine function) as ligands of the QDs. Diffusion ordered spectroscopy (DOSY) (Supporting Information, Figure S4) unambiguously confirms that acetate is tightly bound to the NCs surface, whereas the amine is involved in fast exchange, between a QD-associated and a free state as observed in the case of CdSe QDs or ZnO NCs stabilized by octylamine.[13,14]

The as-prepared Cd_3P_2 NCs present a well-defined emission peak at 779 nm (Figure 3) with a full width at half-maximum (fwhm) of 89 nm. The photoluminescence (PL) quantum yield (QY) of 58 % is comparable with the highest QYs described in the literature for Cd_3P_2 QDs prepared at high temperature.[8,9]

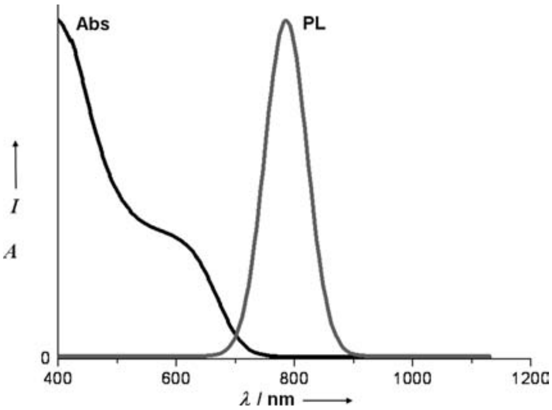

Figure 3. UV/Vis absorption and PL emission of a typical sample of Cd_3P_2 QDs prepared at 30 °C with $(TMS)_3P$ (0.1 mol L^{-1}).

Remarkably, the sizes of Cd_3P_2 NCs can be finely controlled by varying the temperature of reaction and the concentrations of the reactants. Thus, their emission peaks positions can be tuned in the range 616–976 nm.[15] Figure 4 illustrates the evolution of the optical properties (all the PL intensities were normalized) under different concentrations at 30 °C and at 90 °C, the increase of temperature and/or concentration producing the same general trend with a shift of the emission peak towards the highest wavelengths. As example, at 90 °C with a concentration of $(TMS)_3P$ of 0.1 mol L^{-1}, the emission peak reaches 976 nm (fwhm of 60 nm) with a mean diameter of 7.0 (± 1.0) nm (Figure 5). Whatever the concentration used, no more temporal evolution (Supporting Information, Figure S5) of the optical properties (PL emissivity wavelength and intensity) of the Cd_3P_2 NCs is observed after 24 h at 30 °C, and after 2 h at 90 °C (excepted in the case of the highest concentration at 90 °C for which 24 h are necessary). The smallest NCs can be obtained at 30 °C with a concentration of $(TMS)_3P$ of 1.25×10^{-3} mol L^{-1} which is the minimal concentration required to ensure the formation of NCs.

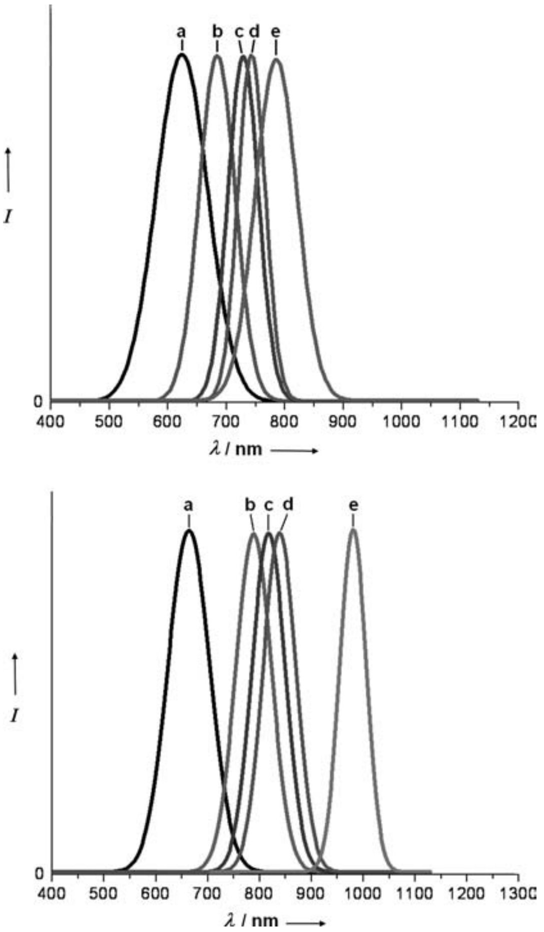

Figure 4. Concentration effect on the PL emission at 30 °C (top) and 90 °C (bottom). The varied $(TMS)_3P$ concentrations values are a) 1.25 mmol L^{-1}, b) 10 mmol L^{-1}, c) 20 mmol L^{-1}, d) 40 mmol L^{-1}, e) 0.1 mol/L, all the experiments are performed with constant molar ratios (3:1 Cd:P). Variations of the PL line widths are not discussed as they remain within the error of particle size distribution.

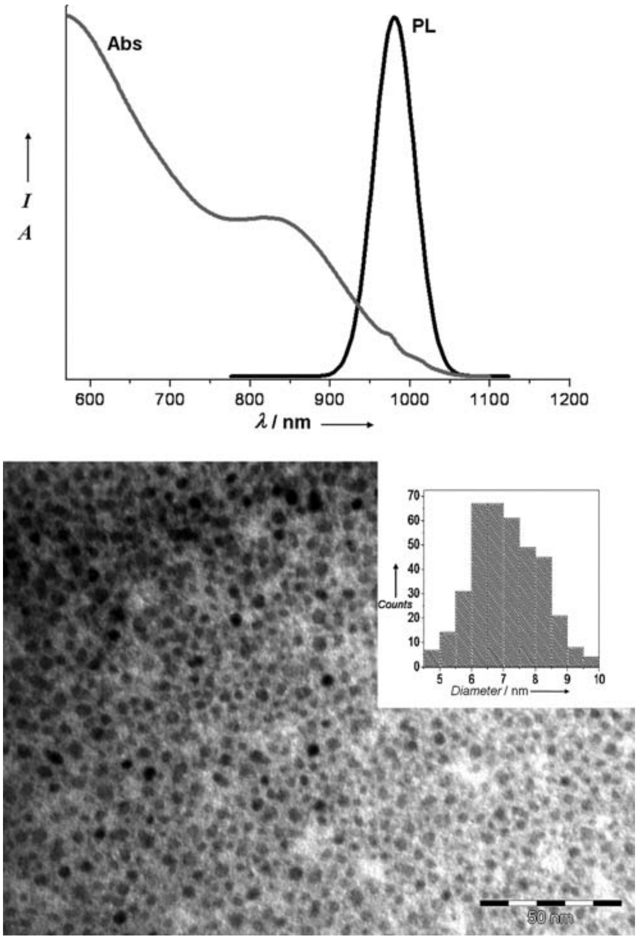

Figure 5. UV/Vis absorption and PL emission (top) and TEM image (bottom) of Cd_3P_2 NCs prepared at 90 °C with $(TMS)_3P$ (0.1 mol L^{-1}), inset: size distribution, mean diameter centered around 7 nm.

Exposure to air causes important damages to the QDs leading to a total loss of emissivity. The solution turns gradually from khaki to colorless (going through red then yellow) which can be attributed to a progressive decrease of the diameter of the emitting core. To circumvent this major drawback, we developed a novel room-temperature process for coating these Cd_3P_2 cores by a protective Zn-S based layer. Indeed, a recent study showed that shell depositing ZnS or CdZnS on CdSe cores could be carried out at temperatures much lower (65 °C) than those usually required (> 200 °C) if beforehand the precursors ($Zn(OAc)_2$ and $Cd(OAc)_2$) were made soluble by heating at 200 °C in ODE in presence of TOP/TOPO.[11] Then, following a similar strategy to the one developed for the cadmium precursor, we have prepared at room temperature a highly soluble Zn precursor ($Zn(OAc)_2$-$(OAm)_2$), and chose ethylene sulfide (C_2H_4S) as the sulfur precursor which is known for its easy desulfurization[16] and high solubility. Both precursors are added at 30 °C to the Cd_3P_2 NCs solution, to obtain, after 1.5 h, coated NCs easily dispersible in solvents, such as chloroform or toluene. In the case of the coating of Cd_3P_2 NCs prepared at 30 °C ($[(TMS)_3P] = 0.1\,\text{M}$), the mean diameter of the roughly spherical particles increased from 4.1 (± 0.7) nm to 4.6 (± 0.7) nm (Figure 6). HRTEM and XRD confirm the tetragonal Cd_3P_2 structure (Figure 6b, Figure S6, and Figure 2), EDX analysis gives Cd, P, Zn and S as main constitutive elements (Supporting Information, Figure S7).

When analyzing the isolated Cd_3P_2/ZnS QDs by ^{31}P MAS NMR spectroscopy, the $^{31}P\{^1H\}$ NMR spectrum (Supporting Information, Figure S8) shows, in addition to the signal of the Cd_3P_2 core, an extra resonance at $\delta = 8$ ppm. This signal is assigned to PO_4[17] and demonstrates that passivation with Zn-S occurs with minor oxidation (15 %) at the Cd_3P_2/ZnS interface. Similarly to the spectrum of the Cd_3P_2 nanoparticles, the CP ^1H-^{13}C MAS NMR spectrum displays characteristic resonances for coordinated acetate and octylamine (Supporting Information, Figure S9). However, for the coated NPs, the DOSY experiment (Figure S10) demonstrates that both ligands are tightly bound.

The as-prepared Cd_3P_2/ZnS NCs give a well defined emission peak at 780 nm (fwhm of 88 nm; Figure 7) and a QY estimated to 52 %. Remarkably, when exposed to air, their photoluminescence properties remain stable (Supporting Information, Figure S11).

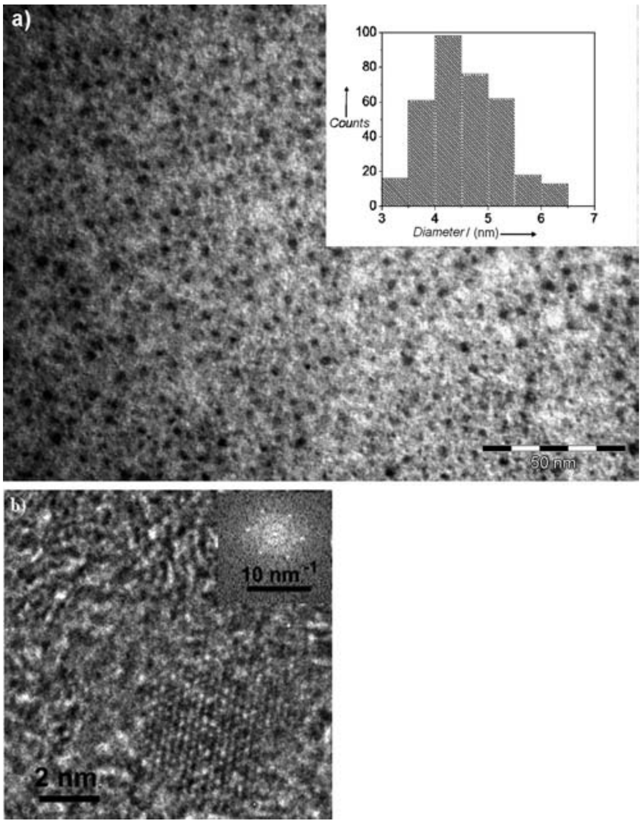

Figure 6. a) TEM image of a typical sample of Cd_3P_2/ZnS nanoparticles : Cd_3P_2 cores are prepared at 30 °C with $(TMS)_3P$ (0.1 mol L^{-1}); $Zn(OAc)_2(OAm)_2$ and C_2H_4S are then added to the solution at 30 °C to form a Zn-S layer. Inset: size distribution, mean diameter centered around 4.6 nm. b) HRTEM image of a typical sample of Cd_3P_2/ZnS QDs (prepared at 30 °C), inset: its FFT pattern showing lattice fringes separated by 0.219 nm and 0.298 nm, corresponding, respectively, to the (400) and (203) lattice spacings of tetragonal cadmium phosphide.

In conclusion, we have described an unprecedented room-temperature synthesis of air stable and high-quality Cd_3P_2/ZnS NCs emitting from the visible red to the near infrared. These NCs are size-tunable and exhibit an intense PL emissivity (QY > 50 %) which can be easily modulated from 616 nm to 976 nm (by varying the reaction temperature between 30 °C and 90 °C and the concentration of reactants). This novel approach relies on the design of highly soluble and reactive metallic precursors ($M(OAc)_2(OAm)_2$ with M = Zn, Cd), associated with a careful choice of phosphorus and sulfur sources ($(TMS)_3P$ and C_2H_4S). This work, provides a significant breakthrough in the search for straightforward and reliable routes to coated-QDs, and thus, opens up new perspectives for the development of room-temperature QDs core and/or shell preparations.

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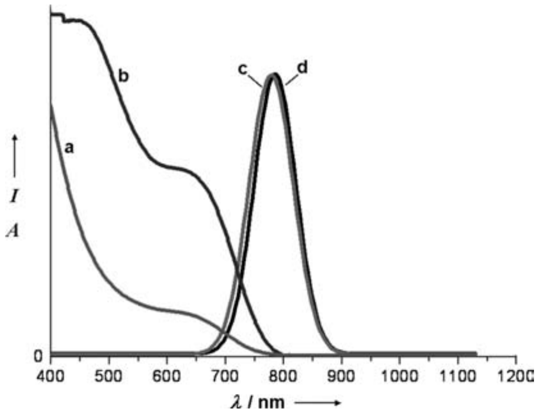

Figure 7. UV absorption (a,b) and PL emission (c,d) of a typical sample of Cd_3P_2 NCs before (a,d) and after (b,c) Zn-S coating (cores and protective layers prepared at 30 °C).

Keywords: cadmium · luminescence · nanomaterials · quantum dots · zinc

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