Synthesis and Characterization of Cadmium Phosphide Quantum Dots Emitting in the Visible Red to Near-Infrared

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Recently, the goal of obtaining materials whose emission wavelengths span the visible red through the near-infrared (NIR) spectral region has stimulated research interest, as this spectral region is potentially well-adapted for use in many applications, such as in vivo biological imaging,[1,2] solar-cell devices,[3] and electronic and photonic devices.[4] Nanocrystallites (NCs) or quantum dots (QDs), primarily because of their tunable band gaps, have demonstrated the possibility of fulfilling this aim in terms of improved luminescence quantum yields and increased fluorescence lifetimes, among other benefits.[5] In comparison to traditional organic fluorophores, NIR-emitting QDs should allow more sensitive bimolecular detection and multicolor optical imaging.[6−10] There are, however, very few materials presently available (molecular dyes, nanoparticles, or composites) that can readily be tuned to address the spectral region ranging from 600 to 1200 nm. For example InP, which is one of the most prominently investigated IR nanomaterials, possesses a bulk band gap of 1.35 eV and is therefore limited in a best-case scenario to 920 nm.[11] Cadmium phosphide, which features a small direct band gap (0.55 eV at 300 K),[12] a relatively high dielectric constant (5.8),[13] a large exciton Bohr radius,[14−16] and a small effective mass of the electron, is the most prominent of the II_3V_2 semiconductors and has been the subject of intensive interest, as it has the potential to address just this spectral region.[17] It also possesses a large number of atoms in its unit cell, which exhibits a remarkable stability.[18] Previous reports have also revealed that Cd_3P_2 NCs have the potential to be employed as lasers,[19] solarcells,[3] ultrasonic multipliers, telecommunications relays, and Hall generators.[20−22] To date, however, Cd_3P_2 has not successfully been synthesized in quantum-dot form to have high-quality optical properties and be monodisperse without the requirement of postpreparative size-selective techniques.

Hot-injection solvothermal methods have been widely employed in colloidal synthesis and have been demonstrated to yield superior-quality nanoparticles in terms of size control, monodispersity, and crystallinity;[23−25] they have been successfully employed to prepare III−V,[26,27] VIIIA−V,[28] IV−VI,[29] and doped QDs (d-dots).[30,31] Up to the present time, the synthesis of cadmium phosphide nanocrystallites has mainly been undertaken using colloidal routes such as phosphinolysis,[32−34] alcoholysis, and thermolysis[15,16,35−39] as well as reactions between cadmium alkoxides and tris(trimethylsilyl)phosphine ($(TMSi)_3P$).[40] A common difficulty has been in the scaling-up of the synthesis, which results from the fact that many of the precursors are extremely toxic, pyrophoric, or explosive and in addition that the procedures are generally laborious.[16] $(TMSi)_3P$ is a more user-friendly phosphorus source than PH_3 because it is a liquid at room temperature and has a good leaving group
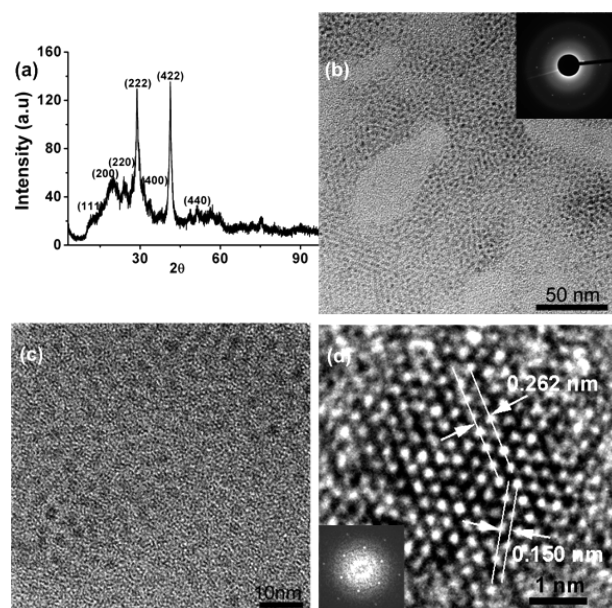

Figure 1. (a) XRD diffractogram, (b, c) TEM images, and (d) contrast-enhanced Fourier-filtered HRTEM images of Cd_3P_2 nanocrystals. The insets in (b) and (d) are the SAED pattern and the FFT pattern of the original HRTEM image, respectively.

$[−Si(CH_3)_3]$.[15] Its use in organometallic routes for the synthesis of phosphide semiconductors has been motivated primarily by its easier handling and less elaborate laboratory workup procedures. We therefore used a cadmium alkylcarboxylate as the Lewis base and $(TMSi)_3P$ as the Lewis acid in order to effect an electron transfer reaction to synthesize the cadmium phosphide, similar to the case of InP.[41,42] It was found that high-boiling point alkenes [e.g., n-octadecene (ODE)] can act as good solvents for cadmium carboxylates and control the nucleation process.[41−44] In this work, efforts were focused on synthesizing cadmium phosphide nanocrystallites using cadmium oleate, into which $(TMSi)_3P$ was injected. The influence of a number of factors, including time of growth, reaction temperature, ligand type [fatty acids, amines, and trioctylphosphine (TOP)], and concentration, on the synthesis of the cadmium phosphide QDs were studied and the optical properties [absorption and photoluminescence (PL)] investigated. The results indicate that high-quality cadmium phosphide QDs can be obtained with a 6:1 cadmium/phosphorus molar ratio and that PL emission spanning from red to NIR wavelengths (650−1200 nm) can be obtained by controlling the synthesis parameters. In addition, via photoelectrochemical measurements, the photocurrent response was evaluated by exposing a cadmium phosphide-derivatized indium tin oxide (ITO) electrode to supra-band-gap illumination.
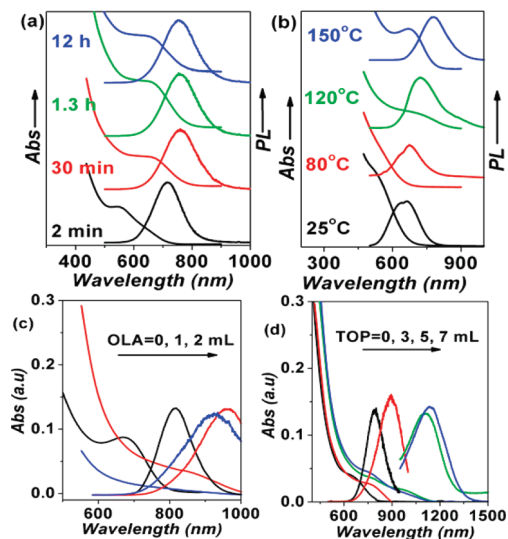
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Figure 2. Influence of (a) reaction time, (b) temperature, (c) amount of oleylamine, and (d) amount of trioctylphosphine on the absorption and PL properties of Cd_3P_2 NCs. For wavelengths below 1000 nm, the spectra were recorded using toluene as the solvent, while for longer wavelengths, tetrachloroethylene was employed.

Details of a typical synthesis are provided in the Supporting Information. The X-ray diffraction (XRD) pattern of an as-prepared sample synthesized at 80 °C (Figure 1a) shows the peak broadening characteristic of a nanocrystalline material and exhibits a number of well-resolved peaks that can be indexed to the (200), (220), (222), and (422) planes of cubic cadmium phosphide (JCPDS 22-0126).[45] This is, to our knowledge, the first time that the crystalline structure of this nanomaterial has been unambiguously assigned to be cubic; all other references known to us have only commented on the material being crystalline, and it is of interest to note that no XRD pattern was presented for any of the Cd_3P_2 nanoparticles reported to date.[25] Energy-dispersive X-ray analysis (EDAX) linked with scanning electron microscopy (SEM) confirmed cadmium and phosphorus to be the main elements present, but there was also a small amount of silicon (~2.0 wt %) (Figure S1 in the Supporting Information). Low-magnification transmission electron microscopy (TEM) images using a wide field of view (Figure 1b,c) showed that the sample contained nearly monodisperse crystals in the size range of 3.5 to ~4.5 nm, and the NCs were observed to self-assemble into monolayers on the TEM grid. The low contrast observed in the TEM images appears to be a material property and was evidenced in all previous reports. The clear selected-area electron diffraction (SAED) pattern (Figure 1b inset) indicated that the particles were indeed crystalline in nature and confirmed their cubic symmetry.[46] The high-resolution TEM (HRTEM) image together with the fast Fourier transform (FFT) pattern (Figure 1d plus inset) revealed the nanocrystals to be spherical with resolved lattice fringes, which is a further demonstration of the crystallinity. The lattice fringes are separated by distances of 0.26 and 0.15 nm, corresponding to the (400) and (444) lattice spacings of face-centered cadmium phosphide.

Figure 2a shows the UV–vis–NIR absorption and PL spectra of cadmium phosphide QDs taken at different time intervals during a reaction at 80 °C. The cadmium phosphide was synthesized in the presence of excess cadmium precursor (6:1 Cd/P ratio), and no size-selective techniques were performed on any of the samples prior to recording their spectra. Cadmium phosphide NCs from a typical synthesis (~4 nm by TEM) possess a well-defined emission peak at ~760 nm, and the emission profile possesses a full width

at half-maximum (fwhm) of ~120 nm (0.26 eV) and a Stokes shift of 0.1 eV. This is in accordance with previously reported results for cadmium phosphide thin films[47] and cadmium phosphide nanoparticles synthesized using cadmium propionate and PH_3.[34] Photoluminescence excitation (PLE) spectra (Figure S2) were found to mirror the UV–vis absorption spectrum reasonably well. By careful comparison with rhodamine 6G and rhodamaine 101, the quantum yield of the as-prepared cadmium phosphide QDs was evaluated to be 38%. Figure 2a presents the particles' growth with time, where it may be seen that the growth mainly takes place within the first 30 min after the injection of $(TMSi)_3P$. Figure 2b displays the dependence of the optical spectra on the injection/reaction temperature. As the reaction temperature increases from 25 to 150 °C, both the onset of absorption and the emission-peak maximum shift toward longer wavelengths, indicating that the mean size of the cadmium phosphide NCs is larger at higher synthesis temperatures. It is worth noting that an intense absorption peak at ~450 nm, which has been ascribed to very small crystal seeds of cadmium phosphide, was observed when the injection was undertaken at room temperature.[25] However, this peak was not present when higher injection temperatures were employed. It was also observed that when the synthesis was carried out at temperatures greater than 150 °C, the particles aggregated, resulting in cadmium phosphide with bulklike properties. Injecting a stoichiometric or larger ratio of $(TMSi)_3P$ into the cadmium carboxylate produced a material with lower optical quality that was observed to give only a weak PL signal, clearly indicating that the use of lower ratios of $(TMSi)_3P$ favor the formation of emitting cadmium phosphide QDs. This may be due to the fact that more Si species are expected to be present on the NC surface when a larger amount of $(TMSi)_3P$ is used, as the presence of this surface Si species could dramatically decrease the emission intensity.[48,49] Using an excess amount of oleic acid (OA) (e.g., Cd/OA = 1:3) resulted in a slight decrease in the mean size of the cadmium phosphide nanoparticles. However, when greater amounts of OA (Cd/OA = 1:9) were added, the reaction yielding cadmium phosphide was prevented from occurring. The reason for this is likely to lie in the fact that upon the addition of $(TMSi)_3P$, the acid environment favors the release of P^{3-} or the in situ creation of PH_3, and in the presence of excess OA, the reaction between P^{3-} that is formed during the reaction and the cadmium is prevented by side reactions with the carboxylic acid functionality.[11]

It has been reported that the addition of amine can activate the carboxylate precursor and thereby result in a higher yield of nanocrystals.[42,44] Therefore, in this study, different amounts of oleylamine (OLA) were added to the cadmium oleate/ODE system before injection. For the NCs so obtained, a red shift of the absorption onset and emission peak were observed (Figure 2c). By variation of the amount of OLA added, emission maxima from 800 to 1000 nm could be realized. In addition to this, the influence of the coordinating agent TOP on the optical properties was investigated. A series of syntheses whereby different amounts of TOP were injected was also undertaken, and the emission peak of the cadmium phosphide QDs was found to extend into the NIR (~1140 nm) as the amount of TOP injected was increased to 7 mL (Figure 2d). However, this was accompanied by a decrease in the PL intensity. When ODE as noncoordinating solvent was completely replaced by TOP, large particulate material without emission resulted (Figure S3). The PL decay was obtained using time-correlated single-photon counting (TCSPC). Fluorescence decay curves of cadmium phosphide QDs with maximum emission at 760, 800, and 900 nm are provided in Figure 3a. The observed lifetimes were relatively long (~250 ns) and tended to increase with increasing emission wavelength. This long lifetime of Cd_3P_2 permits
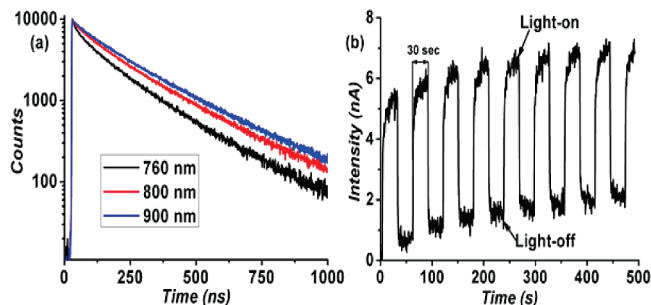
Figure 3. (a) Time-resolved fluorescence decay curves of three different sizes of Cd_3P_2 QDs measured at emission-peak maxima of 760, 800, and 900 nm. (b) Photoresponse of Cd_3P_2 QDs (emission band ∼800 nm) on an ITO substrate at an applied potential of −0.5 V vs a platinum pseudoreference.

an increased possibility of charge carrier extraction in solar cells or optoelectronic applications, lending it a wide potential applicability, and is an observation which has yet to be fully understood and explained.

To assess the suitability of the nanoparticles as optically active centers with a view to their incorporation into optoelectronic devices, a layer of cadmium phosphide QDs was deposited onto mercaptopropionic acid (MPA)-derived ITO substrates, and their photoelectrochemical response was studied both in organic and aqueous electrolytes by irradiation using a narrow-emission-band blue LED (λ_{peak} = 470 nm). The cyclic voltammograms of cadmium phosphide QD (emission ∼800 nm)-derivatized ITO electrodes displayed no redox peaks in the potential range −0.6 to 0.3 V with or without irradiation (Figure S5a,b), indicating that this is a stable working potential window. Figure 3b presents light-induced "ON"/"OFF" switchable photocurrents at an applied potential of −0.5 V versus a platinum pseudoreference in tetrabutylammonium perchlorate (TBAP)/actonitrile electrolyte. As can be seen, upon illumination, the photocurrent was observed to quickly increase and remain relatively constant during the illumination time (30 s), and when the illumination was switched off, the current returned to its preillumination value. This photocurrent response profile was reproducible over many cycles. By comparison to the blank sample (Figure S6a), an average photocurrent for a number of similarly prepared electrodes yielded values of ∼5 nA cm^{-2}. Cadmium phosphide QDs whose emission maxima were around 1000 and 1200 nm were also measured (Figure S6b,c). The differences in the photocurrent density may be ascribed to differences in particle surface densities and/or differences in absorbance at 470 nm.[4] Further studies of the photocurrent response of the cadmium phosphide QDs are presently underway.

In summary, for the first time, high-quality cadmium phosphide nanocrystals with emission bridging the gap between the visible red and the NIR (∼650 to 1200 nm) and high quantum yields (38%) have been readily synthesized. The results illustrate that the nucleation and growth linked with optical properties can be controlled by temperature, growth time, and the addition of ligands such as OLA and TOP. A long lifetime for the exciton decay that increased with increasing nanocrystal volume was observed. The ability to link the cadmium phosphide QDs to conducting substrates and probe their optoelectronic response has also been demonstrated.

Supporting Information Available: Experimental procedures, structural characterizations, and spectral data for the prepared samples. This material is available free of charge via the Internet at http://pubs.acs.org.

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