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Magic-Sized Cd_3P_2 II–V Nanoparticles Exhibiting Bandgap PhotoemissionRuibing Wang,[†] Christopher I. Ratcliffe,[†] Xiaohua Wu,[‡] Oleksandr Voznyy,[‡] Ye Tao,[‡] and Kui Yu^{*,†}*Steacie Institute for Molecular Sciences and Institute for Microstructural Sciences, National Research Council of Canada, Ottawa, Ontario K1A 0R6, Canada**Received: August 7, 2009; Revised Manuscript Received: September 9, 2009*

The very first single-sized Cd_3P_2 II–V nanoparticles were synthesized via a non-injection-based approach which was designed to be thermodynamically driven. The Cd_3P_2 nanoparticles were synthesized in a pure form and exhibited bright bandgap photoemission peaking at 455 nm with a full width at half-maximum (fwhm) of only 17 nm and narrow bandgap absorption peaking at 451 nm. Compared to those reported before with a fwhm of 50–150 nm, the newly developed Cd_3P_2 nanoparticles represent significant progress in synthesis with better design and control. Cadmium acetate dihydrate ($\text{Cd}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$) and tris(trimethylsilyl)phosphine ($(\text{TMS})_3\text{P}$) were used as Cd and P source compounds, respectively; the synthesis was carried out in 1-octadecene (ODE), a noncoordinating solvent. The novel Cd_3P_2 nanoparticles were further characterized by transmission electron microscopy (TEM), energy-dispersive X-ray spectroscopy (EDX), powder X-ray diffraction (PXRD), and ^{113}Cd and ^{31}P solid-state NMR. These single-sized Cd_3P_2 nanoparticles are the first example of class II–V magic-sized nanoparticles (MSNs).

Introduction

Bulk cadmium phosphide Cd_3P_2 , a typical type II–V semiconductor materials with a bandgap of 0.55 eV, has been explored for various applications including photodetectors, lasers, and photovoltaics.^{1–3} Meanwhile, with an excitonic radius of 18 nm, bandgap-engineered Cd_3P_2 nanoparticles should have potential in many areas such as optoelectronics. The colloidal photoluminescent (PL) Cd_3P_2 nanoparticles that have been reported so far are broad in size distribution. It has been acknowledged that PL colloidal semiconductor nanoparticles represent a new generation of leading-edge nanomaterials; they are also called quantum dots (QDs) when spherical in shape, whose syntheses have been recently advanced, particularly via hot-injection approaches.^{4–7} However, such synthetic efforts have been focused mainly on type II–VI, IV–VI, and III–V semiconductors, such as CdSe , PbSe , and InP QDs.^{4–9} Recently, single-sized II–VI and IV–VI nanocrystals with bandgap emission were also reported.^{10,11} It seems that much less attention has been directed toward the synthesis of type II–V semiconductor QDs; the lack of advances on the colloidal Cd_3P_2 nanoparticles may be related to the intrinsic complications of the synthesis and characterization, the difficulty of which has been well documented.^{12,13}

Among the limited body of literature on the colloidal Cd_3P_2 nanoparticles, Weller and co-workers reported one synthesis involving the injection of phosphine gas (PH_3) into a solution of a cadmium salt, such as cadmium propionate.^{13,14} The resulting nanoparticles exhibited broad absorption peaking from 300 to 800 nm, together with broad and asymmetric emission

with a full width at half-maximum (fwhm) larger than 100 nm at room temperature; some emission consisted of multiple emission bands. These optical properties suggest that a broad size distribution, together with defects, resulted from fast growth after nucleation. Later, O'Brien and co-workers reported the growth of Cd_3P_2 nanoparticles in tri-*n*-octylphosphine oxide (TOPO) or 4-ethylpyridine via the thermolysis of single-source precursors such as cadmium diorganophosphide $[\text{MeCd}(\text{P}^i\text{Bu}_2)_2]_3$.^{15,16} The synthesis of the single-source molecules, however, required special synthetic expertise, and the resulting Cd_3P_2 nanoparticles exhibited broad absorption peaking from 400 to 500 nm and emission with a fwhm larger than 60 nm; similar to the report by Weller's research group, the nanoparticles were very much polydispersed in size. Recently, small Cd_3P_2 nanoparticles were synthesized inside the pores of MCM-41 silica modified with functional groups containing ethylenediamine; after the incorporation of Cd^{2+} into the pore channels, phosphine gas was applied for the formation of the nanoparticles.¹⁷ The resulting nanoparticles exhibited a broad absorption peaking at ~ 380 nm, and a weak and broad emission peaking at ~ 456 nm with a fwhm of ~ 100 nm. Obviously, the synthesis of high quality Cd_3P_2 regular quantum dots (RQDs) with narrow size distribution and bright bandgap emission still remains a challenge, not to mention the synthesis of Cd_3P_2 single-sized nanoparticles, also called magic-sized nanoparticles (MSNs).

Here, we report the very first work on the thermodynamically driven formation of single-sized Cd_3P_2 nanoparticles. The as-synthesized Cd_3P_2 nanoparticles exhibited bright bandgap absorption peaking at ~ 451 nm and bright bandgap emission peaking at ~ 455 nm with a fwhm of only ~ 17 nm. These MSNs were synthesized via a facile non-injection-based approach which was designed to be thermodynamically driven and lead to the formation of magic-sized nanoparticles, without

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subsequent growth. The thermodynamically driven synthesis was carried out in 1-octadecene (ODE), a commonly used noncoordinating solvent, with cadmium acetate dihydrate ($\text{Cd}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$) and tris(trimethylsilyl)phosphine ($(\text{TMS})_3\text{P}$) as Cd and P source compounds, respectively. It was realized mainly with the presence of the Cd precursor cadmium acetate oleate ($\text{Cd}(\text{OAc})(\text{OA})$), formed in ODE with a molar feed ratio of oleic acid (OA) to $\text{Cd}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ around 2 and smaller, together with low reaction temperature (80–140 °C). Our synthetic formulation and reaction conditions favored slow kinetics leading to the thermodynamic product, magic-sized nanoparticles without further growth. The nanoparticles were characterized by energy-dispersive X-ray spectroscopy (EDX), which suggested a stoichiometry of Cd_3P_2 , and by ^{113}Cd and ^{31}P solid-state NMR. High resolution transmission electron microscopy (HRTEM) observations of some of the particles showed lattice fringes, suggesting a regular atomic array, but powder X-ray diffraction (PXRD) results did not indicate a crystalline material. The single-sized Cd_3P_2 nanoparticles that we synthesized, to the best of our knowledge, are the very first example of type II–V MSNs.

Results and Discussion

In a typical synthesis, 0.2 mmol of $\text{Cd}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$, 0.2 mmol of oleic acid (OA), and 4 g of ODE were loaded in a three-neck reaction flask at room temperature. A Cd precursor, $\text{Cd}(\text{OAc})(\text{OA})$, was freshly synthesized at 120 °C under a vacuum for 2 h. Subsequently, this Cd precursor solution was cooled down to ~40 °C under argon. Meanwhile, 0.05 mmol of $(\text{TMS})_3\text{P}$ was mixed with 1 g of ODE and purged by ultrapure nitrogen (N_2). The $(\text{TMS})_3\text{P}$ solution was added into the freshly prepared $\text{Cd}(\text{OAc})(\text{OA})$ solution with stirring, followed by degassing and heating under N_2 at a rate of ~10 °C every 5 min to 240 °C. Aliquots were taken at each increase of 20 °C of the reaction temperature. The formation kinetics of the nanoparticles was monitored by the temporal evolution of their optical properties. Note that the present approach is non-injection-based, with the use of $\text{Cd}(\text{OAc})(\text{OA})$ instead of $\text{Cd}(\text{OA})_2$ as the Cd precursor and with the relatively slow increase of the reaction temperature from 40 °C. Such an approach ensured the existence of a limited amount of Cd^{2+} , released from the Cd precursor, together with a thereafter slow reaction kinetics leading to the presence of the magic-sized Cd_3P_2 nanoparticles, whose formation was most probably driven thermodynamically, as shown in eqs 1–4.

Please note that in eqs 1–3, for simplification purposes, we employed “ Cd^{2+} ” and “ P^{3-} ” to represent the Cd-associated and P-associated reactants, respectively; they react with each other, leading to the formation of monomers, oligomers, and eventually nanoparticles. The investigation on the reactants leading to the formation of nanocrystals such as CdSe and PbSe can be found elsewhere.^{18–20} It is easy to understand that, in ODE, the Cd and P monomers, oligomers, and nanoparticles are “stabilized” by a number of ligands present throughout the reaction.

Figure 1. Temporal evolution of the absorbance (offset) of the as-synthesized Cd_3P_2 nanoparticle samples from one synthetic batch with feed molar ratios of 4OA-4Cd-1P and [P] of 10 mmol/kg. With a nonstop heating pattern and a heating rate of ~10 °C every 5 min, the reaction was heated up from 60 °C up to 240 °C. The 10 nanoparticle ensembles were sampled at 60 °C (1), 80 °C (2), 100 °C (3), 120 °C (4), 140 °C (5), 160 °C (6), 180 °C (7), 200 °C (8), 220 °C (9), and 240 °C (10); they were dispersed in toluene, with a concentration of 10 $\mu\text{L}/\text{mL}$. Note that, usually, MSNs are easy to aggregate; meanwhile, such physical aggregation can be readily broken via gentle shaking.

Figure 1 shows the temporal evolution of the optical properties of the as-prepared Cd_3P_2 nanoparticles sampled from one synthetic batch with the feed molar ratio of 4OA-4Cd-1P and the concentration of $(\text{TMS})_3\text{P}$ of 10 mmol/kg in 5 g of ODE. Ten nanoparticle samples were taken when the reaction temperature was increased from 60 to 240 °C. In the early stage of the reaction, at ~80 °C, both $\text{Cd}(\text{OAc})(\text{OA})$ and $(\text{TMS})_3\text{P}$ were soluble in ODE. The resulting Cd^{2+} and P^{3-} , as represented by eqs 1 and 2, were reactive, as shown by eq 3, leading to the formation of one nanoparticle ensemble (curve 2) which exhibited bandgap absorption peaking at ~450 nm.

When the reaction temperature was increased to the range of 100–140 °C (curves 3–5), the formation of single-sized Cd_3P_2 nanoparticles (shown by eq 4) was very clearly evidenced. These magic-sized nanoparticles ($(\text{Cd}_3\text{P}_2)_n$) in a pure form, exhibiting a sharp and persistent bandgap absorption peaking at ~451 nm, should have a precise atomic composition with a unique structure.^{10,11} It is necessary to emphasize that the persistency of the bandgap absorption peaking at ~451 nm during the reaction between 80 and 140 °C suggested the absence of growth in size of the MSNs: once they were developed, there was little growth in size at higher reaction temperature and/or with longer reaction periods. These MSNs were magic-sized nuclei ($(\text{Cd}_3\text{P}_2)_n$) which were virtually thermodynamically stable without further growth. Indeed, a balanced nucleation and growth (BNG) model predicted, under certain circumstances, the presence of stable nuclei as a final product, without further growth.²¹ In contrast, regular nuclei resulting from $(\text{Cd}_3\text{P}_2)_x$ (soluble, $x \neq n$) grow in size. Because of their thermodynamic stability, MSNs produced through eq 4 are the major product under our synthetic conditions.

It seemed that the process leading to the formation of the soluble magic-sized $(\text{Cd}_3\text{P}_2)_n$ started at ~60 °C. For these magic-sized nuclei with little aggregation, it seems reasonable that the carboxylate ligands were interacting with their surface atoms

Figure 2. Emission (thick line, right y axis) and absorbance (thin line, left y axis) spectra of the as-synthesized Cd_3P_2 sample (also shown in Figure 1, curve 5, whose reaction temperature was 140 °C). The fwhm is ~ 17 nm, and the QY is $\sim 3\%$ (estimated with an excitation wavelength of 400 nm^{10d-s}). Note that the bandgap emission at 455 nm of the as-synthesized Cd_3P_2 sample is very bright with its narrow bandwidth. The storage stability is shown in Figure S1 of the Supporting Information.

and thus providing colloidal stability.¹⁰ During the increase of the reaction temperature from 60 to 120 °C, the yield of the Cd_3P_2 MSNs in pure form was enhanced significantly (as evidenced by the optical density shown in Figure 1, curves 2–4). During the increase of the reaction temperature from 120 to 140 °C (curve 5), the MSN yield decreased; thus, the Cd_3P_2 MSNs might become thermally unstable from ~ 120 °C and up under our experimental conditions.

When the reaction temperature reached 160 °C and higher (curves 6–10), the Cd_3P_2 MSNs disappeared almost completely; the nanoparticles might have dissolved back into soluble species (such as monomers). Meanwhile, it seems that RQDs showed up; it is worth mentioning that these RQDs exhibit photoemission. Note that the present study addresses the formation of the II–V Cd_3P_2 MSNs instead of RQDs.

For the cadmium precursor with the right solubility to dissociate at low temperature such as 60 °C, the oleate group of $\text{Cd}(\text{OAc})(\text{OA})$ seemed to play an important role; the resulting Cd^{2+} with a limited concentration in the reaction medium led to the formation of the MSNs (at ~ 60 °C with their thermal stability around ~ 120 °C). Under the same reaction conditions, when oleic acid was replaced by myristic acid (MA), then the Cd precursor became $\text{Cd}(\text{OAc})(\text{MA})$. The solubility of $\text{Cd}(\text{OAc})(\text{MA})$ is relatively low in ODE, as compared to that of $\text{Cd}(\text{OAc})(\text{OA})$; for example, a $\text{Cd}(\text{OAc})(\text{MA})$ ODE solution becomes cloudy at ~ 70 °C when it is decreased from ~ 120 °C. Therefore, few MSNs were formed from the synthetic batch when MA was used.

The formation of the Cd_3P_2 MSNs seems to be thermodynamically driven, a concept which is revolutionary and is being investigated and demonstrated in our laboratories currently with a model CdSe system. Most importantly, these Cd_3P_2 MSNs exhibited bright bandgap emission, as shown in Figure 2. Figure 2 shows the emission (thick line) and UV–visible absorption (thin line) spectra of the as-synthesized Cd_3P_2 nanoparticles sampled at 140 °C (curve 5 in Figure 1). The Cd_3P_2 nanoparticle ensemble exhibited bandgap absorption peaking at 451 nm and bandgap emission peaking at 455 nm with a fwhm of only 17

Figure 3. Energy-dispersive X-ray (EDX) emission spectrum of the Cd_3P_2 ensemble (whose optical properties are shown in Figure 1, curve 5, and Figure 2). The result of the elemental analysis indicates a 3Cd:2P atomic ratio (averaged from multiple scans, as shown in Table S1 of the Supporting Information).

nm. Thus, this ensemble can be termed as Cd_3P_2 MSN family 451. This narrow bandwidth attests to the very limited size distribution of the particles. The small fwhm value of the bandgap emission of the present MSN ensemble has never been achieved before and is drastically smaller than those reported of 50–150 nm.^{13–17} The photoluminescent (PL) quantum yield (QY) of the bandgap emission of the fresh sample was estimated to be $\sim 3\%$, and interestingly, the aged sample (4.5 months old) gave a QY of 7.2%. The highest QY of the Cd_3P_2 RQDs was reported to be 15%, but that was from both bandgap emission and trap emission; the latter was broad and intense.¹³ The present Cd_3P_2 MSNs exhibited only bandgap emission with little trap emission. The emission peak position of the MSNs, similar to their absorption, was independent of the reaction periods and temperature; the MSNs are stable and are believed to be molecular-like with a fixed atomic composition together with a unique structure.^{10,11}

The detailed structural nature of the single-sized nanoparticles still remains an open question, with no one technique giving a definitive answer. A model consistent with the information from several different characterization techniques is still being sought: Figure 3 shows a typical energy-dispersive X-ray emission (EDX) spectrum for the exploration of the elemental composition of the single-sized Cd_3P_2 nanoparticles. The EDX spectrum was obtained at 0–10 kV, along with peaks assigned only for the elements of Cd, P, C, and Cu; elements C and Cu were from the carbon-coated copper grid. After the integration of the peak areas of Cd-L and P-K, the X-ray counts were converted into the elemental weight percentage, with quantification software, namely, the Oxford Instrument INCA Energy TEM 200 system. Six scans of different areas of the TEM sample (as shown in Figure 4 and Table S1 and Figure S5 of the Supporting Information) gave an average stoichiometry of Cd_3P_2 .

Characterization by solid-state ^{13}C , ^{113}Cd , and ^{31}P MAS NMR confirmed the presence of both Cd and P and the organic oleate capping groups in the nanoparticles (see Figures S2 and S3 of the Supporting Information). The ^{31}P NMR spectrum clearly indicates that the nanoparticles are quite different from bulk tetragonal Cd_3P_2 .²² The PXRD results (see Figure S4 of the Supporting Information) also are incompatible with the bulk tetragonal Cd_3P_2 structure even when allowance is made for very small nanoparticles with resultant broadening of the diffraction lines according to the Scherrer equation. In fact, the

Figure 4. TEM image of the Cd_3P_2 nanoparticles (shown in Figure 1, curve 5, and Figures 2 and 3); the scale bar is 10 nm. The image reveals an average nanoparticle size of ~ 3 nm. The inset is a HRTEM image showing a crystal lattice, with a scale bar of 2.5 nm. See also Figure S5 of the Supporting Information.

PXRD pattern does not appear to represent a 3D crystalline structure. In this regard, it is interesting to note that no XRD pattern was presented for any of the previously reported Cd_3P_2 nanoparticles and other II–V nanomaterials.^{13–17}

Figure 4 shows a TEM image of the purified Cd_3P_2 MSNs. The nanoparticles are ~ 3 nm in diameter. The TEM size of 3 nm does not represent the exact size of the Cd_3P_2 MSNs synthesized; it has been acknowledged that a certain degree of aggregation/self-assembly of nearly all MSNs can occur during the TEM sample preparation including sample purification and solvent evaporation.^{10,11} The aggregation sometimes is useful; i.e., the aggregation of the CdSe MSNs was reported to engineer the formation of quantum wires.²³ In HRTEM images (e.g., Figure 4, inset), some of the particles show well-resolved fringes, with d -spacing values close to 2.5, 2.9, and 3.6 Å (also see Figure S5 of the Supporting Information), indicating ordered arrays within the nanoparticles. This might be taken as an indication of a certain degree of crystallinity. One speculative structure might be a very thin sheet-like or disk-like material with a regular 2D array, which might be sufficient to give rise to fringes in the HRTEM but not to produce a crystalline PXRD pattern. Alternatively, it is possible that the HRTEM is observing nanoparticles which are not representative of the bulk of the material.

Conclusions

Single-sized Cd_3P_2 nanoparticles exhibiting bandgap absorption peaking at 451 nm and narrow bandgap emission peaking at 455 nm with a fwhm of only 17 nm were successfully developed via a facile thermodynamically driven approach. This approach was non-injection-based, using cadmium acetate dihydrate ($\text{Cd}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$) and tris(trimethylsilyl)phosphine ($(\text{TMS})_3\text{P}$) as Cd and P source compounds, respectively. The thermodynamically driven formation of the MSNs was realized in 1-octadecene (ODE) as the reaction medium, with the

relatively low temperature ranging from 60 to 140 °C to slow down the reaction kinetics. The as-synthesized Cd_3P_2 MSNs were in pure form, exhibiting bright bandgap emission and little trap emission, and characterized by various techniques including TEM, EDX, XRD, and NMR. The Cd_3P_2 MSNs represent the highest quality of the Cd_3P_2 nanoparticles ever obtained, in terms of the absorption and emission bandwidth, and size distribution.

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Supporting Information Available: The storage stability of the Cd_3P_2 nanoparticles, solid-state ^{13}C , ^{113}Cd , and ^{31}P NMR, PXRD pattern, TEM images, and EDX elemental analysis table. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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