



Article A Novel and Cost-Effective CsVO₃ Quantum Dots for Optoelectronic and Display Applications

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Abstract: Quantum dots (QDs) have an unparalleled ability to mimic true colors due to their sizetunable optical and electronic properties, which make them the most promising nanoparticles in various fields. Currently, the majority of QDs available in the market are cadmium, indium, and lead-based materials but the toxicity and unstable nature of these QDs restricts their industrial and practical applications. To avoid using heavy metal ions, especially cadmium, the current research is focused on the fabrication of perovskite and vanadate QDs. Herein, we report the facile synthesis of a novel and cost-effective CsVO₃ QDs for the first time. The sizes of the CsVO₃ QDs produced were tuned from 2 to 10 nm by varying the reaction temperature from 140 to 190 °C. On increasing QD size, a continuous red shift was observed in absorption and emission spectra, signifying the presence of quantum confinement. In addition, along with CsVO₃ QDs, the CsVO₃ manosheets self-assembled microflower-like particles were found as residue after the centrifugation; the X-ray diffraction indicated an orthorhombic structure. Under 365 nm excitation, these CsVO₃ microflowerlike particles exhibited broad emission with CIE coordinates in the white emission region. The acquired results suggest that CsVO₃ QDs may represent a new class of cadmium-free materials for optoelectronic and biomedical applications.

Keywords: CsVO3 quantum dots; hotplate synthesis; quantum confinement effect; tunable emissions

1. Introduction

Research on semiconductor nanocrystals, also called colloidal quantum dots (QDs), has dominated the field of nanoscience because of their ability to tune optical and electronic properties through size control [1–3]. Ever since, Colvin et al. [4] described the CdSe QD-based light-emitting diodes (QLEDs) in 1994, several QDs such as CdS, CdTe, PbSe, PbS, and InP@ZnSeS have been produced as potential materials for QLEDs, solar cells, display devices, photodetectors, fluorescent probes, and various biomedical diagnostics [5–8]. However, some drawbacks such as self-aggregation, toxicity, and heavy metal content are mostly limiting their practical applications [9].

In many regions of the world, the use of heavy metals in many household goods is restricted, and thus, most of the cadmium-based quantum dots are unfeasible for indoor applications [10,11]. In addition, the studies on QD toxicity have focused on cadmium and lead-containing particles, as CdSe QDs release free cadmium when irradiated with ultraviolet (UV) light or oxidized by air [12–14]. In the absence of UV light, QDs coated with a stable polymer are essentially non-toxic. However, though surface coatings like ZnS and bovine serum albumin (BSA), which are used to reduce surface oxidation by



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Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). preventing the self-aggregation of QDs and enhance quantum yield and stability, reduce concerns of toxicity, they do not wholly eliminate the cytotoxicity [15,16], and thus there is a need for the development of non-toxic and cost effective QDs.

In order to address this toxicity issue, we selected self-activated CsVO₃ as a host material in which vanadium exists in the '5+' oxidation state, as in this form vanadium is non-toxic, stable, and cheaper than cadmium and lead-containing raw materials. In addition, the vanadate cluster $[VO_4]^{3-}$, in which the central metal ion is coordinated by four oxygen ions in tetrahedral (T_d) symmetry, serves as an efficient luminescent center and exhibits excellent quantum efficiency [17–19]. From the biological viewpoint, only the higher oxidation states (4+ and 5+) of vanadium are given importance in biomedical research due to the ability of vanadium in these states to participate in redox reactions when coordinated with its ligands, which is a remarkable property well utilized in drug design. Furthermore, vanadate has numerous biological activities, not the least of which is its ability to inhibit many enzymes [20,21]. Therefore, to avoid the above-mentioned limitations of Cd and Pb-containing QDs, we undertook the development of CsVO₃ QDs for various optoelectronic and biomedical applications.

In this study, we synthesized novel cadmium-free CsVO₃ QDs using a simple hotplatebased method for the first time. The sizes of the CsVO₃ QDs produced were tuned from 2 to 10 nm by varying the reaction temperature from 140 to 190 °C. Band gap energies were calculated from absorption spectra. The existence of the quantum confinement effect was established using absorption and photoluminescence (PL) studies. In addition, CsVO₃ nanosheets self-assembled microflower-like particles were obtained as residue after centrifuging the reaction mixture. Morphological studies were conducted on these nanosheets using scanning and transmission electron microscopy (SEM and TEM), and their crystalline nature was examined by energy-dispersive X-ray spectroscopy (EDX) and X-ray diffraction (XRD). The PL properties of CsVO₃ QDs and the microflower-like particles were studied using an excitation wavelength of 365 nm.

2. Materials and Methods

2.1. Materials

Cesium nitrate [CsNO₃] (Sigma-Aldrich, Seoul, South Korea; high purity grade), ammonium metavanadate [NH₄VO₃] (Sigma-Aldrich, high purity grade), 1-octadecene [CH₃(CH₂)₁₅CH=CH₂] (Sigma-Aldrich; technical grade, 90%), oleylamine [CH₃(CH₂)₇CH=CH(CH₂)₇CH₂NH₂] (Sigma-Aldrich; technical grade, 70%), oleic acid [CH₃(CH₂)₇CH=CH(CH₂)₇COOH] (Daejung, Sinan, South Korea; extra pure), ammonium hydroxide solution [NH₄OH] (Sigma-Aldrich; ~25% NH₃ basis), and acetone [CH₃COCH₃] were of analytical grade. Triple-distilled de-ionized (DI) water was used to dissolve the CsNO₃. All the above-mentioned reagents were used without additional purification.

2.2. Synthesis of CsVO₃ QDs

The required amount of CsNO₃ was dissolved in 10 mL of DI water in a beaker. Separately, NH₄VO₃ was dissolved in a solvent mixture (15 mL octadecene, 3 mL oleylamine, and 1.5 mL oleic acid) in another beaker, placed on a hot plate set at 50 °C, and stirred for 1 h. The Cs solution was added dropwise under continuous magnetic stirring, and then the hot plate temperature was increased to 170 °C. After 1 h, 1 mL of NH₄OH was added to the mixture and stirred for 2 h. The reaction mixture was then cooled to room temperature, and 20 mL of acetone was added to precipitate the CsVO₃ QDs. The CsVO₃ nanosheets self-assembled microflower-like particles were obtained by centrifugation at 10,000 rpm for 15 min. The residue was again washed with acetone and then dried under ambient conditions for 8 h. The experiment was repeated at different reaction temperatures of 140, 150, 160, 180, and 190 °C to achieve color tunability of CsVO₃ QDs. Details of the characterization techniques used are provided in the Supplementary Materials.

3. Results and Discussion

Highly stable and cost-effective CsVO₃ QDs were produced by facile hotplate synthesis. The spherical-shaped CsVO₃ QDs were precipitated using acetone and separated from the solvent (as supernatant) after centrifugation for 15 min at 10,000 rpm. The $CsVO_3$ nanosheets self-assembled microflower-like particles were found as residue after centrifugation and the resultant SEM and TEM images are presented in Figure 1a,b. The selected area (electron) diffraction pattern of CsVO3 nanosheets displayed a ring pattern with bright spots overlaid on it (Figure 1c), indicating the nanocrystalline nature of the particles. The obtained d-spacings of 2.87, 4.93, 1.43, 1.64, and 2.45 corresponded to the (0 0 2), (1 1 0), (3 3 2), (3 3 0), and (2 2 0) planes of orthorhombic CsVO₃ matrix (JCPDS No. 070-0680). The chemical compositions of CsVO₃ QDs and the microflower-like particles (synthesized at 170 °C) were examined by EDX analysis; the resultant EDX spectra of CsVO₃ QDs and the microflower-like particles are presented in Figure 1d-g. The atomic and weight percentages of Cs, V, and O elements in CsVO₃ QDs and microflower-like particles are displayed as insets in Figure 1d, f, respectively. The position of X-ray peaks in both spectra showed 'V' and 'O' ions occupied the K-shell, and that 'Cs' ions occupied the L-shell of the energy spectrum at 4.949, 0.525, and 4.286 eV, respectively. Elemental mapping of the microflower-like particle confirmed that Cs, V, and O were homogeneously distributed within the particle (Figure 1h–j).



Figure 1. (**a**–**c**) SEM and TEM images and SAED pattern of CsVO₃ nanosheets self-assembled microflower-like particles. (**d**,**e**) EDX spectrum and the corresponding TEM image of CsVO₃ QDs. (**f**–**j**) EDS spectrum, SEM image, and the elemental mapping of a CsVO₃ microflower-like particle.

The TEM images of CsVO₃ QDs synthesized at 140 °C (blue), 170 °C (green), and 190 °C (red) are shown in Figure 2a–c, and TEM images of CsVO₃ QDs synthesized at 150 °C (sky blue), 160 °C (cyan), and 180 °C (yellow) are presented in Figure S1. The size

of the QDs increased monotonically by increasing the reaction temperature from 140 to 190 °C as shown in Figure 2a–c, confirming the existence of the quantum confinement effect. According to the literature, the quantum confinement effect alters the optical and electrical properties of semiconductor nanocrystals (2 to 10 nm), and causes sizedependent changes in fluorescence wavelengths [1]. At a reaction temperature of 140 °C, particle sizes of 2–3 nm were obtained, which fluoresced blue, whereas at temperatures of 170 and 190 $^{\circ}$ C, CsVO₃ QDs with particle sizes of 5–6 and 8–10 nm were obtained that fluoresced green and red, respectively. A plot of emission versus size of $C_{s}VO_{3}$ QDs was presented in supplementary information Figure S2. Digital photographs of CsVO₃ QDs and the microflower-like particles (synthesized at 170 °C) under daylight and UV-light (365 nm) are shown in Figure 2d,e, respectively. As can be seen from the figure, the CsVO₃ QDs and microflower-like particles exhibited green and white emission, respectively. In order to determine the crystalline phase of QDs, the XRD patterns were recorded for the corresponding powder samples. Figure 2f shows the XRD patterns of CsVO₃ microflowerlike particles at reaction temperatures from 140 to 190 °C; corresponding SEM images are presented in Figure 2f(i–vi), respectively. Up to 160 °C, the obtained diffraction patterns were indexed to the orthorhombic phase of $Cs_2V_4O_{11}$ with space group Cmm2 (JCPDS No. 088-0705) and some cesium impurity peaks, whereas the XRD patterns of samples synthesized at 170, 180, and 190 °C were well matched with the orthorhombic phase of CsVO₃ with space group Pbcm(57) (JCPDS No. 070-0680). Figure 2g shows the reference patterns of $Cs_2V_4O_{11}$ and $CsVO_3$ and the diffraction patterns obtained for $CsVO_3$ powder samples synthesized at 160 and 170 °C. On raising the reaction temperature from 170 to 190 °C, the relative intensities of XRD peaks located at 29°, 30°, and 33° corresponding to the (0 4 0), (0 0 2) and (0 4 1) planes altered (Figure 2f), which was attributed to a change in nanocrystal orientation, as it is well-established that the preferred orientations depend on the nanoparticle size and shape [17,22]. As can be seen from the figure, the nanosheets that self-assembled as microflower-like particles (Figure 2f(iv)) became rod-like particles (Figure 2f(vi)) on increasing the reaction temperature from 170 to 190 °C, and the preferred orientation of rod-like particles is mostly in one direction. Therefore, as a result of preferential orientation, the intensities of (0 4 0), (0 0 2), and (0 4 1) planes altered in the XRD pattern. Furthermore, the average crystallite size (D) of the microflower-like particles was calculated using the well-known Scherrerer equation ($D_{hkl} = \kappa \lambda / \beta \cos \theta$, [23,24] where k is scherrer constant, λ is x-ray beam wavelength, θ is diffraction angle, and β represents the full width at half maximum of the diffraction peak. The average crystallite size was calculated to be 57.6 nm.

The absorption spectra of CsVO₃ QDs synthesized at different reaction temperatures are presented in Figure 2h. All spectra displayed a strong absorption band between 320 to 620 nm, which suggested that the CsVO₃ QDs are suitable for near-UV and visible excitation-based QLEDs. As the reaction temperature was increased from 140 to 190 °C, the broadness of the absorption band increased and the band maxima redshifted from 354 to 480 nm, which confirmed an increase in CsVO₃ QD size. The optical band gap energies (*E*_g) of CsVO₃ QDs synthesized at different reaction temperatures were estimated using Tauc's relation [25,26]:

$$\alpha hv = B\left(hv - E_g\right)^n \tag{1}$$

where α represents the absorption coefficient, B is the proportionality constant, photon energy is represented by hv, and n adopts values 1/2, 2, 3/2, or 3 depending on the type of transition. According to Tauc's relation, n takes the value of 1/2 and 2 for direct and indirect allowed transitions, whereas the value of n becomes 3/2 and 3 for direct and indirect forbidden transitions, respectively. Straight line plots were obtained for $(\alpha hv)^2$ versus (hv) signifying the direct allowed transitions. The E_g values of CsVO₃ QDs were evaluated by extrapolating the linear regions onto the energy axis, as shown in Figure 2i. Estimated E_g values of CsVO₃ QDs synthesized at temperatures of 140, 150, 160, 170, 180, and 190 °C were 3.17, 2.83, 2.72, 2.63, 2.47, and 2.31 eV, respectively. As expected, E_g values decreased with increasing QD size, which confirmed the presence of quantum confinement effect. For CsVO₃ QDs, the band gap of 2–3 nm sized QDs was 3.17 eV, whereas the band gap of 8–10 nm sized QDs was 2.31 eV, which means the red QDs (8–10 nm) need less energy than blue QDs (2–3 nm) to reach the conduction band and thus release less energy when they return to the ground state. A schematic illustration of the quantum confinement effect is provided in Figure 3a. Digital photographs of CsVO₃ QDs in the absence and presence of UV-light are shown in Figure 3b,c, respectively.



Figure 2. (**a**–**c**) TEM images of CsVO₃ QDs synthesized at 140, 170, and 190 °C, respectively. (**d**,**e**) Digital photos of QDs and microflower-like particles under day light and UV light. (**f**,**g**) XRD patterns of CsVO₃ powder samples at different reaction temperatures and (**f**)(i–vi) the corresponding SEM images of the CsVO₃ samples. (**h**,**i**) Absorption spectra and corresponding Tauc plots of CsVO₃ QDs synthesized at different temperatures.

Figure 4a shows the PL spectra of CsVO₃ QDs synthesized at different reaction temperatures. As the reaction temperature increased from 140 to 190 °C, the emission band maxima shifted from 434 to 618 nm, as shown in Figure 4a. Usually, the emission wavelength of QDs is proportional to its size, and hence the emission wavelengths are redshifted along with the growing size of CsVO₃ QDs [27]. Full width at half maxima (FWHMs) of emission spectra were found to be 30, 36, 44, 45, 68, and 53 nm for CsVO₃ QDs synthesized at 140 (blue), 150 (sky blue), 160 (cyan), 170 (green), 180 (yellow), and 190 °C (red), respectively. The narrow emission bands of blue and green QDs and lower FWHM values indicated that the yellow and red QDs were not uniform in size. Figure 4b shows the PL emission spectrum of CsVO₃ microflower-like particles excited at 365 nm. The acquired emission spectrum covered the whole visible area (between 420 and 750 nm) with a band maximum at 526 nm, as shown in Figure 4b. Usually, the transfer of charge from a 2p orbital of O^{2-} to a 3d orbital of V^{5+} in VO_4^{3-} group with tetrahedral symmetry leads to the broad band emission of self-activated vanadate phosphors [28], which is perfectly suitable



for near-UV based white-LEDs (WLEDs). These CsVO₃ microflower-like particles could potentially replace the conventional rare earth-based WLEDs in the lighting industry.

Figure 3. (a) Schematic illustration of quantum confinement effect in CsVO₃ QDs, (b,c) digital photographs of CsVO₃ QDs synthesized at different reaction temperatures in the absence and presence of UV light.

Commission International De I'Eclairage (CIE) coordinates were calculated for different colored CsVO₃ QDs and are displayed in Figure 4c. All QDs have excellent chromaticity coordinates in their respective emission regions. CsVO₃ QDs synthesized at 140, 150, 160, 170, 180, and 190 °C had CIE chromaticity coordinates in the blue (0.148, 0.112), bluish green (0.166, 0.402), yellowish green (0.342, 0.622), yellow green (0.387, 0.584), yellow (0.522, 0.472), and reddish orange (0.623, 0.376) regions, respectively. On the other hand, CsVO₃ microflower-like particles showed excellent chromaticity coordinates in the white emission region (0.341, 0.402). Furthermore, the acquired CIE coordinates of blue and red QDs were close to the National Television System Committee (NTSC colorimetry (1953)) approved standard blue (0.14, 0.08) and red (0.67, 0.33) coordinates. Nonetheless, further studies are required to optimize the performances of the CsVO₃ QDs, whereas microflower-like CsVO₃ appear to be eminently suitable for use in solid-state lighting applications.



Figure 4. (a) Luminescence spectra of CsVO₃ QDs synthesized at different reaction temperatures from 140 to 190 °C, (b) PL emission spectrum of microflower-like CsVO₃ particles excited at 365 nm, and (c) CIE chromaticity coordinates of CsVO₃ QDs and microflower-like particles ((1–6) CsVO₃ QDs and (7) CsVO₃ microflower-like particles).

4. Conclusions

In this study, we synthesized novel cadmium-free CsVO₃ QDs by facile hotplate synthesis for the first time. The sizes of the QDs were controlled from 2 to 10 nm by increasing the reaction temperature from 140 to 190 °C, which resulted in a band gap reduction from 3.17 to 2.31 eV and red-shifting of the PL emission spectra, demonstrating the presence of quantum confinement effect. Estimated FWHM values indicated that blue and green QDs were more homogeneous than yellow and red QDs. Furthermore, the CsVO₃ nanosheets self-assembled microflower-like particles were obtained as residue at a reaction temperature of 170 °C. The obtained (as-synthesized) microflower-like particles were well crystallized in the orthorhombic phase and exhibited broad emission from 420 to 750 nm under 365 nm excitation. The calculated CIE coordinates of blue and red QDs were close to the NTSC colorimetry (1953) approved standard blue and red color coordinates, and CIE coordinates of the CsVO₃ microflower-like particles were in the warm white emission region.

Supplementary Materials: The following supporting information can be downloaded at: https: //www.mdpi.com/article/10.3390/nano12162864/s1, Figure S1: TEM images of CsVO₃ QDs synthesized at 150, 160, and 180 °C, and the video clip of CsVO₃ QDs in the absence and presence of UV light, Figure S2: Emission wavelength versus CsVO₃ QDs size.

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