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The growth of CdSe quantum dots on a single wall carbon nanotubes template without organic solvent and surfactant

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Abstract

A conventional synthesis of Cadmium selenide (CdSe) quantum dots (QDs) usually employs toxic organic solvents, and the synthesized CdSe QDs must be modified for dispersion in an aqueous solution. This modification often limits the application of CdSe QDs in biomedical fields. In this study, a simple method was developed to synthesize CdSe QDs on single wall carbon nanotubes (SWCNTs) employing the SWCNTs as a template to prevent the aggregation of the CdSe QDs in an aqueous solution without the addition of any organic reagent.

Our newly developed synthetic procedure included the formation of SWCNTs with carboxyl groups (SWCNT–COOHs) followed by mixing these with the precursors of Cd and Se to obtain SWCNT–CdSe QDs. The resulting SWCNT–CdSe QDs were analyzed using spectrophotometry, transmission electron microscopy (TEM) and X-ray diffraction (XRD).

Results showed that CdSe nanocrystals with a zinc blend structure could be synthesized on the SWCNT–COOHs. The average crystal size of the synthesized CdSe QDs was approximately 3 nm. The blue-shift of CdSe QDs powerfully emitted light at 550 nm as compared to the bulk CdSe at 730 nm. These CdSe QDs were synthesized in an aqueous environment without using toxic surfactants and are expected to have great potential as bio-labeling contrast agents in the future.

Keywords: SWCNTs; CdSe QDs; Bio-labeling contrast agent; Semiconductors

1. Introduction

Cadmium selenide (CdSe) quantum dots (QDs), nanoparticles of the group II–VI semiconductors, have attracted a great deal of attention over the past decades. Due to the quantum confinement effects, CdSe nanoparticles have strong size-dependent properties and unique photophysical characters, such as photostability, broad absorption profile and a narrow emission line width in photoluminescence (PL) spectra; thus, these nanoparticles are widely applied in biomedical applications [1]. In contrast with the limitation of traditional fluorophores, CdSe QDs reveal the superiority of cellular bio-labeling and have been used as contrast agents in animal experiments [2,3].

Varied methods to fabricate CdSe QDs have been reported for different purposes [4,5]. Colloid chemistry proposed by Peng and co-workers has been the most conventional method to synthesize CdSe QDs nanoparticles [6,7]. This process, however, used toxic components such as $Cd(OH)_2$ and trioctylphosphine oxide (TOPO). In addition, the synthesized CdSe nanoparticles have to be dispersed and preserved in non-polar organic solvents, making it inconvenient for further surface modification in the aqueous solutions required for biomedical applications [8]. Compared to the colloid method, co-precipitation synthesis of CdSe QDs in an aqueous phase is less toxic with lower cost, and is more convenient for further surface treatment. Nevertheless, the size of CdSe QDs, which are obtained by the co-precipitation method, cannot be controlled in a relatively narrow range and sometimes overgrowth to even sub-micro sizes. The overgrowth results in a loss of photoluminescence. Although methods to further screen or filter CdSe QDs has been applied to narrow down the size distribution, the results were

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not promising with low yields that ended up increasing the production cost.

Building blocks and templates have been applied in the synthesis of CdSe QDs to resolve the problem of overgrowth and to attain a more narrow-sized distribution. Some nano-scale templates were introduced to regulate the synthesis process to control the growth of CdSe QDs including PEO–PPO–PEO tri-block polymer, starch, apoferritin, and $Cd(OH)_2$ crystal [9–12]. However, the synthesized CdSe QDs are generally low in crystallinity, or even amorphous, because the templates employed have no structure of crystal lattice structure.

Carbon nanotubes (CNTs), including single-and multi-walled CNTs, have been used as a guiding template for nanoparticle growth [13–16]. Generally, CNTs provided nucleation sites on the surface, and then the CdSe QDs were precipitated in an organic solvent using the TOPO method. Although high-quality CdSe QDs have been obtained using this method, the use of toxic organic solvents and the surfactant TOPO is still needed. Furthermore, the length of the CNTs was sometimes longer than 10 μm and has to be cut down to an applicable length before further application. This method, unfortunately, is not optimal for medical uses.

In this study, a new approach was proposed to apply the single-walled carbon nanotubes (SWCNTs) as building blocks to synthesize CdSe QDs in the absence of an organic reagent. The *d*-spacing (0 0 2) of SWCNTs is very close to that of CdSe (1 1 1) which makes it feasible to precipitate CdSe on the SWCNTs. We report our newly developed procedure as well as the properties of these aqueously synthesized SWCNT–CdSe QDs. The SWCNTs could be treated with acid solution to reduce the length of SWCNTs to an applicable size and to create a –COOH functional group on the surface. The surface-treated SWCNTs with a negative charge at a neutral pH would attract the positively charged Cd^{2+} to the surface to increase the concentration of local ion species for nucleation and the subsequent build up (1 1 1) of CdSe QDs on (0 0 2) of SWCNT by an epitaxial mechanism. The preparation process was all conducted in an aqueous solution.

2. Materials and methods

2.1. Materials

Cadmium sulfate hydrate ($3CdSO_4{\cdot}8H_2O$), sodium sulfite (Na_2SO_3), selenium (Se) power, sulfuric acid (H_2SO_4) and nitric acid (HNO_3) were purchased from Sigma–Aldrich Co. SWCNT was kindly provided by Conyuan Biochemistry Technology Co. Ltd. The SWCNTs were synthesized through a high-pressure CO disproportionation process (HiPco type).

2.2. SWCNTs template preparation

Further treatment and purification was needed to remove the amorphous impurities from the SWCNTs before use. The procedure of purification is briefly described as follows: 20 mg of the SWCNTs was mixed with 20 ml of HNO_3 (65%) and then refluxed by stirring at 120 °C for 4 h. The precipitate was re-suspended in 20 ml of HNO_3 (65%) and then refluxed for another 2 h. The purified SWCNTs were centrifuged and stored for further use.

A sample of purified SWCNTs (20 mg) was further treated with a mixture of H_2SO_4/HNO_3 (3/1 volume ratio) at 45 °C for 2 h. The length of the SWCNTs was reduced through this process to obtain an appropriate size for biomedical application. In the meantime, the carboxyl group (–COOH) was attached to the surface of SWCNTs as a nucleation site for CdSe epitaxial growth [13,17]. The length-reduced and surface-modified SWCNTs (SWCNT–COOHs) were washed twice with DI water to remove the residual H_2SO_4 and HNO_3.

2.3. SWCNT–CdSe QDs synthesis

A sample of SWCNT–COOHs (5 mg) was well mixed with 146 mg of $3CdSO_4{\cdot}8H_2O$ in 30 ml of DI water (SWCNT–COOHs–Cd solution) for 2 h under N_2 flow to prevent any oxidation. A 63.2 mg sample of Se and a 252.1 mg sample of Na_2SO_3 were dissolved in 20 ml of DI water, and the solution was stirred for 2 h at 80 °C followed by filtration to prepare the Na_2SeSO_3 solution. This solution was adjusted to pH 9 and served as a Se precursor. The adjusted Na_2SeSO_3 solution was then mixed with the SWCNT–COOHs–Cd solution at room temperature and was allowed to react for 10 min. The final product (SWCNT–CdSe QDs) was centrifuged, collected, washed twice with DI water and dried using a freeze dryer (FDU-1200, EYELA, Japan).

2.4. Raman spectroscopy analysis

The bonding of the carbon structure of the SWCNTs was examined by Raman spectroscopy. The SWCNT powder was excited by a laser light at 632.8 nm using Raman spectroscopy (LabRAM HR, Horiba Jobin Yvon, Japan). The data were collected from 1000 to 1800 cm^{-1}, and the integral time was 10 s. The purified SWCNTs and the SWCNT–COOHs were tested using Raman spectroscopy in an identical process to the un-treated SWCNTs.

2.5. FT-IR analysis

FT-IR was applied to analyze the functional groups of the synthesized products. The powder of the un-treated SWCNTs, the purified SWCNTs and the SWCNT–COOHs were individually well mixed with potassium bromide (KBr) before the FT-IR analysis. The specimens were scanned in transmission mode on a 410-JASCO in the range of 400–4000 cm^{-1}.

2.6. HR-TEM analysis

HR-TEM was used to examine the morphology and to identify the crystal structure of the synthesized CdSde QDs. The SWCNTs, the SWCNT–COOHs and the synthesized SWCNT–CdSe QDs were suspended and well dispersed in 95% ethanol under ultrasonic vibration for 30 min. A sample of the well-dispersed solution (10 μl) was discharged on the carbon-coated copper grid and dried at room temperature overnight. The sample-mounted copper grid was carefully placed in the sample holder for morphological examination and to identify the crystal structure of the synthesized CdSde QDs by HR-TEM (Tecnai G2, FEI, USA) using the double-tilt mode at 200 keV. The CdSe for comparison with SWCNT–CdSe QDs were synthesized as described in Section 2.3, but without the use of SWCNT–COOHs.

2.7. XRD analysis

The crystal structure of synthesized SWCNT–CdSe QDs was inspected using a XRD (Geigerflex, Rigaku, USA). The sample was scanned within a 2θ range of 15°–55° by Cu Kα (λ = 1.5406 Å) radiation with scanning speed of 4° min^{-1} using 30 keV and 20 A m.

2.8. PL spectra analysis and UV–Vis analysis

The optical properties of the SWCNT–CdSe QDs in aqueous solutions were identified by PL spectra (F-4500, Hitachi, Japan) and UV–Vis spectra (DU 800, Beckman Coulter, USA). The blank solution of UV–Vis spectra was DI water. The CdSe aqueous solution for comparison with SWCNT–CdSe QDs in PL spectra was synthesized according to the method described in Section 2.3, only without the use of SWCNT–COOHs.

3. Results

3.1. Analysis of the Raman spectra

The Raman spectra of the un-treated SWCNTs, the purified SWCNTs and the SWCNT–COOHs are shown in Fig. 1. Raman spectrophotometry is a common method used to analyze the structure of the carbon nanotubes. Two characteristic peaks were observed in the spectra known as the G band and the D band. The G band at 1570 cm^{-1} harmonizes with the energy mode of graphite, indicating the existence of sp^2 bonds between carbon atoms along the SWCNTs axis. The amorphous carbon (impurities) and defects of the SWCNTs contribute to the D band at 1370 cm^{-1} [18]. The ratio of the area under the line of the D (I_D) band and the G (I_G) band corresponds to the impurity and structural integrity of the SWCNTs. The I_G/I_D ratios of the SWCNTs, the purified SWCNTs and the SWCNT–COOH are calculated as 7.35, 2.51 and 19.36, respectively.

3.2. Analysis of the FT-IR spectra

Fig. 2 shows the FT-IR spectra of the purified SWCNTs and the SWCNT–COOHs with three major absorption bands. They are the C–O stretching, C=O vibration and –OH stretching vibration at the wave numbers of 1056 cm^{-1}, 1717 cm^{-1} and 3446 cm^{-1}, respectively [19]. The C=O vibration was found in the SWCNT–COOHs' spectrum, but it was not detected in the spectrum of the purified SWCNTs. The area of –OH stretching vibration in the purified SWCNTs was much smaller than that of SWCNTs–COOH. The surface of the SWCNTs became hydrophilic and attracted the water from the air to the surface.

3.3. The analysis of HR-TEM

No apparent morphological difference between the un-treated SWCNTs, the purified SWCNTs and the SWCNTs–COOHs could be found when examined under HR-TEM. They all were maintained as individual or separate tubes, except that the untreated SWCNTs had more amorphous carbons in between the individual SWCNTs than that of the purified SWCNTs.

Fig. 3 shows the morphology of CdSe and of epitaxially grown CdSe QDs on SWCNT templates. The particle size of CdSe, shown in Fig. 3(a), was about 50 nm in diameter, and attempted aggregate. In Fig. 3(b), the length of individual CdSe

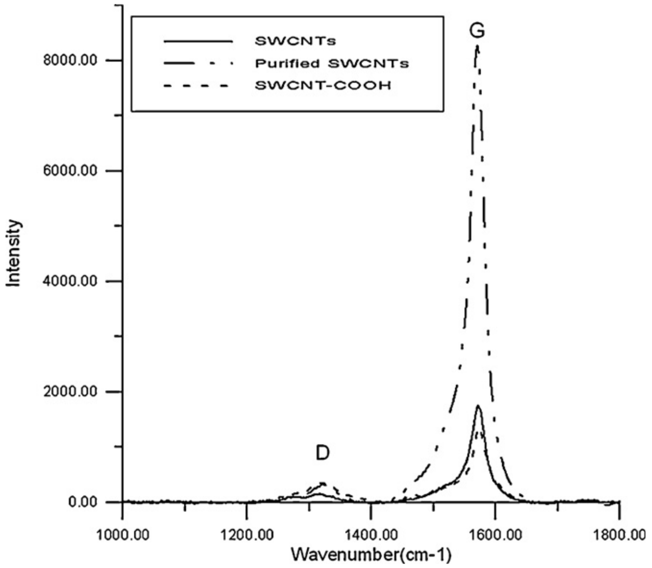

Fig. 1. Raman spectra of untreated SWCNTs, purified-SWCNTs and SWCNT–COOHs.

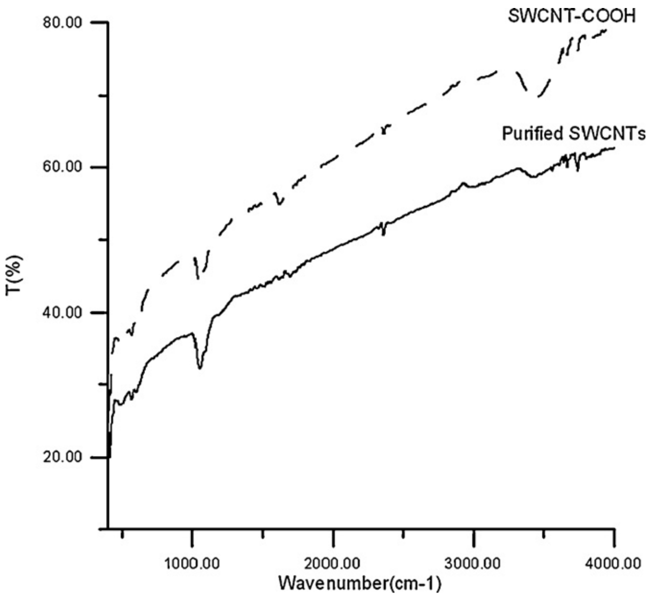

Fig. 2. FT-IR spectra of purified SWCNTs and SWCNT–COOHs.

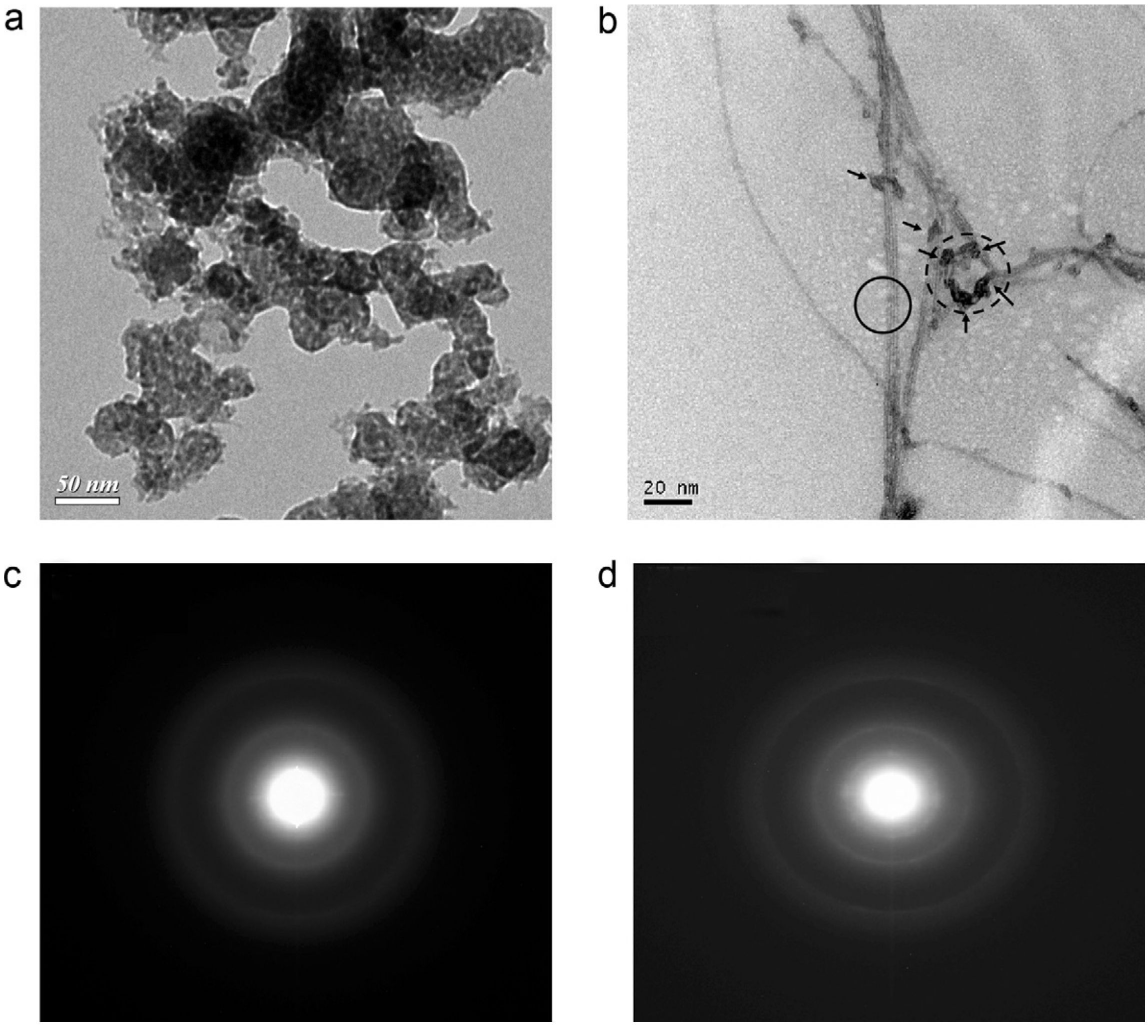

Fig. 3. HR-TEM of CdSe QDs and SWCNT–CdSe (a) CdSe QDs; (b) SWCNT–CdSe; (c) SAED pattern of solid-lined circle and (d) SAED pattern of dashed-lined circle.

crystals (shown by arrows in the TEM picture) was about 3 nm. The CdSe crystals were generally epitaxially grown on the SWCNT sidewalls especially on the rough surface created by the oxidation process.

Panels (c) and (d) in Fig. 3 are the selected areas of electronic diffraction (SAED) patterns for the SWCNTs, as indicated by the solid-lined circle and dashed-lined circle in the TEM picture. Fig. 3(c) shows two very light and blurry rings on the SAED pattern identified as (0 0 2) and (1 0 0) of the SWCNTs.

Fig. 3(d) shows the SAED pattern of SWCNT–CdSe as indicated by the white circle in the picture. There are two rings on the SAED patterns. Among those, (0 0 2) of SWCNT is more clear than the SAED pattern of the upper left corner of the picture. The (0 0 2) ring almost overlaps the (1 1 1) of CdSe, this phenomenon may contribute to the close *d*-spacing for the CdSe expitaxial growth. The second ring is the (1 0 0) of the SWCNTs.

3.4. Analysis of the XRD

Fig. 4 shows the XRD patterns of SWCNTs and the synthesized SWCNT–CdSe QDs. The dashed line shows the pattern of SWCNTs where the broaden peak at 24.9° corresponds to (0 0 2) of the SWCNTs.

The solid line shows the XRD pattern from the SWCNT–CdSe QDs developed in this study. The three reflection peaks at 25.3°, 42.8° and 48.7° are identified as (1 1 1), (2 2 0) and (3 1 1), respectively, of the CdSe. The strongest and broadest peak at 25.3° is attributed to the reflection of (0 0 2) of SWCNTs and (1 1 1) of CdSe. From JCPDS No. 19-191, the crystal structure of CdSe QDs grown on SWCNTs is similar to that of zinc blend structure.

The (1 1 1) peak can be used to calculate the crystal size of CdSe QDs by the Scherrer equation, given in Eq. (1):

$$d = \frac{K\lambda}{B\cos\theta} \tag{1}$$

d is the mean dimension, *K* is the shape factor, λ is the wavelength of the X-rays, *B* is the broadening of the full width at half maximum (FWHM) in radians, and θ is Bragg's diffraction angle.

The calculated crystal size of prepared CdSe QDs is about 3.2 nm in line with the result of the TEM.

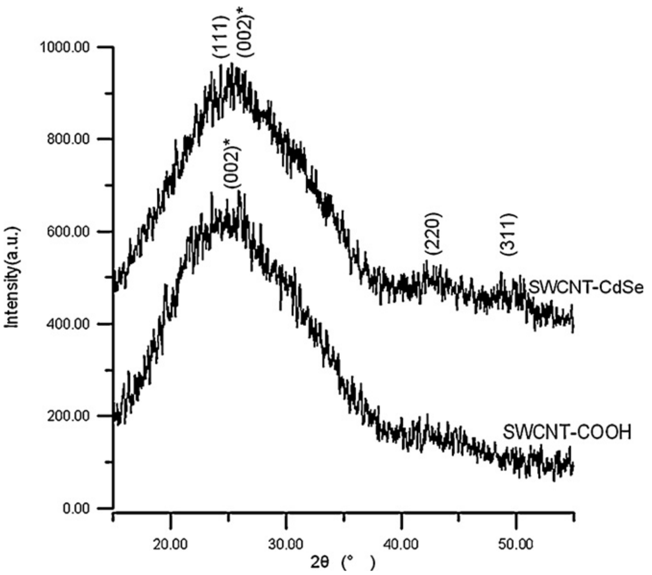

Fig. 4. XRD of SWCNT–COOHs and SWCNT–CdSe; ()*: plane for SWCNT–COOH; (): plane for CdSe.

3.5. Analysis of the UV–Vis and the PL spectra

Fig. 5 indicates the optical properties of the prepared SWCNT–CdSe. The solid curve is the PL spectra of SWCNT–CdSe excited at 400 nm. It shows strong emission light at 550 nm and this strength is different from the emission of the bulk CdSe, which emits at 730 nm, due to the blue shift.

The dashed line shows the UV–Vis spectra of SWCNT–CdSe. The strong absorption band at 517 nm differed from the expected absorption of the bulk CdSe (716 nm), which is also attributed to the blue shift [20].

Fig. 6 is the PL of CdSe QDs synthesized with or without SWCNTs. It reveals an obvious blue shift of the SWCNT–CdSe' emission spectrum, which is probably due to the smaller crystal size of SWCNT–CdSe QDs than of CdSe QDs in aqueous solution.

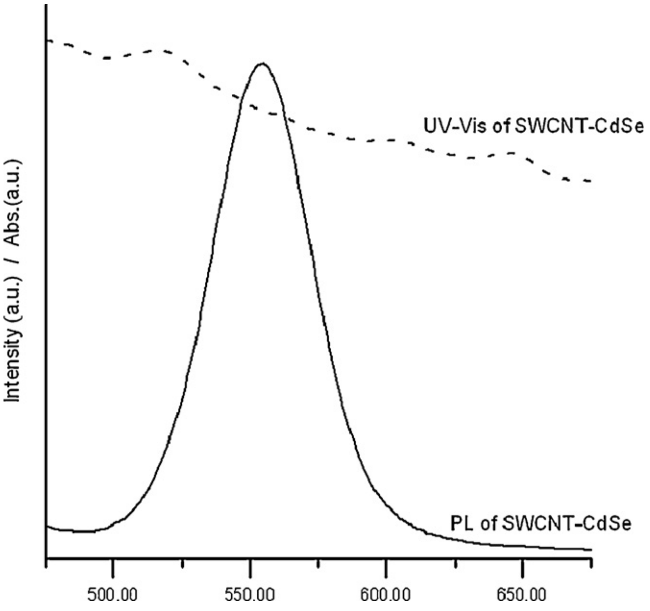

Fig. 5. PL spectra and UV–Vis spectra of SWCNT–CdSe.

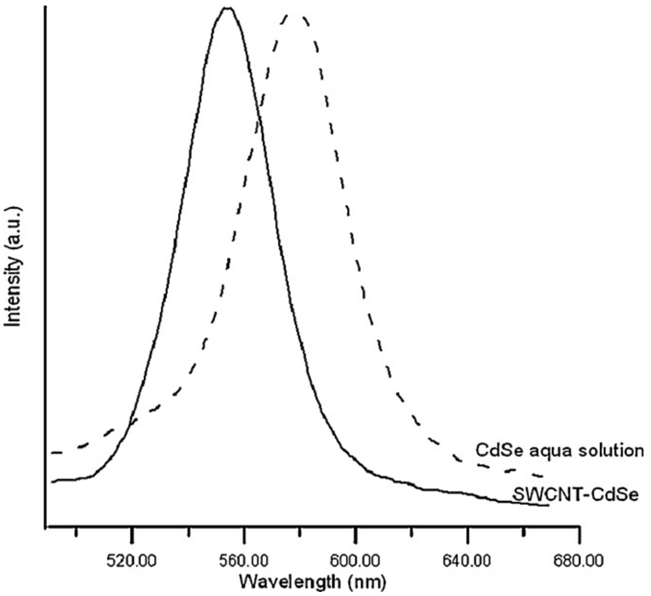

Fig. 6. PL spectra of SWCNT–CdSe and CdSe in aqueous solution.

4. Discussion

The steps of purification and oxidation were applied to prepare SWCNT–COOHs. During the purification process, the HNO_3 removed the amorphous carbon from the SWCNTs' base material. The I_G/I_D ratio, therefore, decreased from 7.35 to 2.51. Concurrently, the purified SWCNTs were oxidized by the mixing the strong acids H_2SO_4 and HNO_3, and the –COOH functional groups were created on the surface of the purified SWCNTs. The density of the surface defects on the purified SWCNTs increased significantly because of acid etching and led to a sharp increase of the I_G/I_D ratio from 2.51 to 19.36.

The –COOH functional groups on the SWCNTs were verified by the FT-IR spectrum as shown in Fig. 2 where the absorption bands of the –COOH were observed. The results showed that the SWCNT–COOHs were successfully prepared for the CdSe growth. The –COOH would have potentially dissociated to a negatively charged ($–COO^-$) group at a neutral pH, thus attracting Cd^{+2} to the $–COO^-$-rich areas as the nucleation site for the growth of CdSe [18–20]. As shown in the HR-TEM image (Fig. 3), the CdSe crystal was generally on the rough-surface areas of the SWCNT, where the SWCNT was strongly etched by the acid due to oxidation, and more –COOH groups were created.

Fig. 3 exhibited that the mean particle size of the CdSe was larger than crystal size and proposed polycrystal structure. The CdSe also aggregated due to the high surface energy of the QDs. However, the SWCNT–CdSe had smaller particle size in line with crystal size calculated from Scherrer equation and monodisperse. Using the SWCNTs as a template not only worked as a building block but also acted as a steric obstacle to influence the grain growth of CdSe QDs.

In this study, CdSe nanocrystalline was epitaxially synthesized on the SWCNTs at the room temperature with SWCNT–COOH as a template without using organic solvents and a chemical linker. The precipitated CdSe nanoparticles were of a zinc blend structure, as shown in Fig. 4. The crystal size of synthesized CdSe QDs was about 3 nm examined under HR-TEM and is in agreement with the calculated result from the Scherrer equation.

Bulk CdSe belongs to the groups of II–VI of the semiconductors. Because of the infinite atoms of the CdSe lattices, there is a periodic interaction between the free electrons. When a semiconductor crystal is excited by photons, the energy absorption of the material results in the excitation of an electron from the valence to the conduction band and forms an electron–hole pair. The electron–hole pair is as so-called 'exciton', and the spatial separation of the exciton is described by the Bohr radius. In nanoparticles with sizes similar or smaller than that of the Bohr radius, the spatial confinement is truncated at the boundary, which is known as the quantum effect. As a result, the discrete band structure develops, and the energy gap of electric promotion is not only larger than that of bulk CdSe but is also strongly size-tunable. That is, in the optical spectrum, CdSe nanoparticles have blue shift as compared with that of bulk CdSe. In line with this concept, Fig. 5 shows a strong emission light at 550 nm, which was different than the bulk CdSe at 730 nm. The strong absorption band of UV–Vis spectra of SWCNT–CdSe at 517 nm did not match the 716 nm absorption band of the bulk CdSe either. These two results can be explained by the quantum effect resulting in the blue shift of the synthesized CdSe.

As mentioned previously, the optical absorption of a material is dependent on the exciton and the energy gap, which is strongly affected by the size of nanoparticle.

Therefore, the crystal size could be further determined by energy gap examination using the Brus-equation, Eq. (2).

$$\Delta E_g = \frac{h^2}{8a^2}\left(\frac{1}{m_e} + \frac{1}{m_h}\right) \tag{2}$$

ΔE_g is band gap; h is Planck's constant; m_e and m_h are the effective electron mass and hole mass, respectively, which are the reduced mass of exciton; and a is the crystal size to be calculated.

The absorption band at 517 nm shown in the UV–Vis spectra (Fig. 5) harmonized to the band gap of 1.9 eV that was used to evaluate crystal size of the synthesized CdSe. The crystal size of about 3.5 nm is in agreement with the result of the HR-TEM measurement (3 nm) and the theoretical value from the Scherrer equation, Eq. (1), (3.2 nm).

The SWCNT–COOH could play an important role as a template for the CdSe QDs epitaxial growth. The nano-sized CdSe crystals ($\sim$3 nm) have blue shift compared to the bulk CdSe in optical spectra.

5. Conclusion

In the study, CdSe nanocrystalline was epitaxially synthesized on SWCNTs at room temperature with SWCNT–COOH as a template in the absence of an organic solvent and a chemical linker. The precipitated CdSe nanoparticles had a zinc blend structure with crystal size about 3 nm when examined under HR-TEM. The monodispersed CdSe QDs that were synthesized in an aqueous environment have great potential for use in biomedical application.

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