

Accepted Manuscript

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PII: S0925-8388(19)30128-8

DOI: <https://doi.org/10.1016/j.jallcom.2019.01.120>

Reference: JALCOM 49158

To appear in: *Journal of Alloys and Compounds*

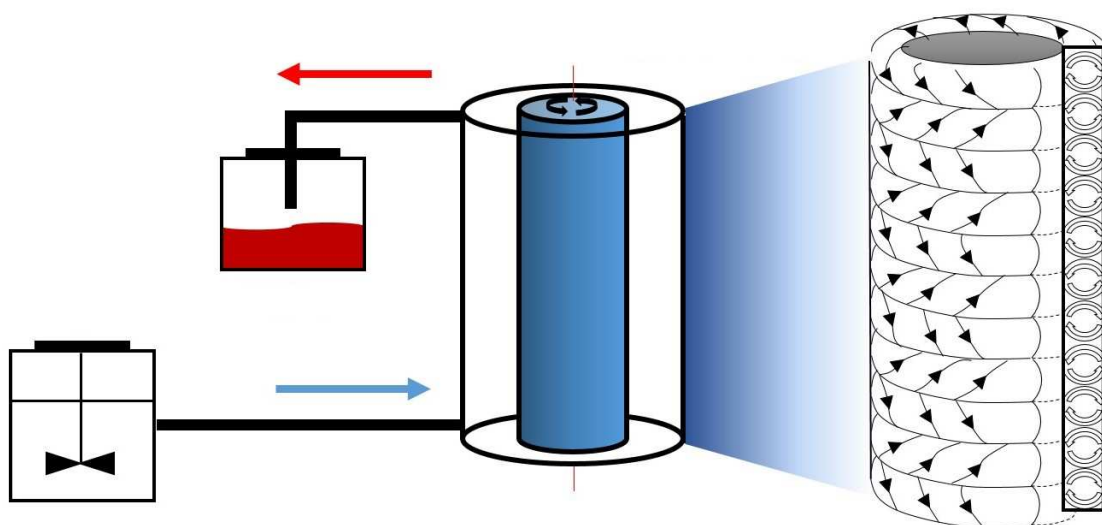
Received Date: 4 October 2018

Revised Date: 8 January 2019

Accepted Date: 10 January 2019

Please cite this article as: J.-Y. Jung, J.-G. Lee, Y.-K. Baek, Y.-D. Kim, J.-P. Hong, Y.-K. Kim, High throughput process for the continuous preparation of quantum dots using fluid dynamically controlled reactor, *Journal of Alloys and Compounds* (2019), doi: <https://doi.org/10.1016/j.jallcom.2019.01.120>.

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ACCEPTED MANUSCRIPT

High throughput process for the continuous preparation of quantum dots using fluid dynamically controlled reactor

Jae-Yong Jung^{a,b}, Jung-Goo Lee^a, Youn-Kyung Baek^a, Yang-Do Kim^b, Jong-Pal Hong^c and Young-Kuk Kim^{a*}

^a Powder & Ceramics Division, Korea Institute of Materials Science, 797 Changwondaero, Changwon, 51508, Korea

^b School of Materials Science and Engineering, Pusan National University, Jangjeon 2-dong, Geumjeong-gu, Busan, 46241, Korea

^c Laminar Co., Ltd, Dunhon-daero 457 beon-gil, Jungwoun-gu, Seongnam-si, Gyeonggi-do, Korea

*Corresponding authors: Tel/Fax: +82 55 280 3606/3289, E-mail address: voice21@kims.re.kr

ABSTRACT

Scale-up of synthesis process is highly required for commercial application of quantum dots (QDs). Although batch-type hot injection method is most popular synthesis route for QDs, its commercial scale-up version only gives non-uniform and less luminescent QDs with broad size distribution. In this study, we introduce a novel and facile method of large-scale synthesis of QDs using a fluid-dynamically controlled reactor, Taylor-Couette reactor (TCR). We successfully synthesized CdSe QDs with TCR and as-synthesized QDs were capped with epitaxial CdS layers using the molecular precursors for enhanced luminescence. The synthesis process was stabilized after 20 minutes from the start of initial injection of precursors and standard deviation of luminescence wavelength and spectral linewidth was less than 1 nm. After shell capping process based on pyrolysis of Cd-diethyldithiocarbamate, CdSe QDs synthesized from continuous processing route based on TCR showed intense photoluminescence at 640 nm with a spectral linewidth of 33 nm, which is much narrower than PL spectra of QDs synthesized from conventional batch-type synthesis route using reaction vessel with large volume capacity. We demonstrated high throughput synthesis of highly luminescent CdSe QDs using TCR as a platform for continuous synthesis with very large production yield ($22,560 \text{ kg} \cdot \text{day}^{-1} \cdot \text{m}^{-3}$ in space-time yield).

Keywords: Quantum dots, Semiconductor nanocrystals, Continuous synthesis, Taylor-Couette flow

1. INTRODUCTION

Synthesis of semiconductor nanocrystals, or quantum dots (QDs), have received much attention over the last decade due to their outstanding optical properties and availability of narrow size distribution [1-7]. In particular, practical application of QDs requires industrially scalable cost-effective and massive synthesis process. However, large-scale synthesis of QDs based on conventional batch-type processing usually yields polydispersed nanocrystals with broad emission spectra [8]. The optical performance of QDs was highly circumscribed by inhomogeneous size and compositional distribution. Those heterogeneities in QDs are exceptionally sensitive to various processing factors that are difficult to control, such as the injection process, local fluctuation of temperature and concentration, the rate of mixing, and the dimensions of the reactor [9]. Precise control of those parameters has become more challenging when the large-scale preparation is the subject of main concern. Although the continuous synthesis of the high quality QDs using the microfluidic reactor or the capillary reactor is actively being pursued to meet the requirement [10-14], the amount of precursors injected during synthesis and their reaction time are highly limited due to the narrow inner volume of reactors. As a result, mass production of high quality QDs for industrial application takes a lot of time. As an alternative to already-known microfluidic process, we propose a novel continuous synthesis method based on the Taylor-Couette reactor (TCR) for synthesis of high quality QDs. Due to extreme susceptibility of optical properties on processing conditions of QDs, high throughput synthesis of high quality QDs is highly difficult to be achieved with conventional batch-type synthesis method. Owing to the distinctive fluid dynamics inside TCR, preparation of the high-quality nanocrystals is available. Then, there have been several reports on the TCR-based continuous synthesis of various particles such as BaSO_4 [15], $(\text{Ni,Mn,Co})(\text{OH})_2$ [16], Cs_4PbBr_6 [17]. However, successful synthesis of QDs with this high throughput synthesis route has never been reported

previously, partially due to lack of knowledge about processing parameters regarding the synthesis of QD with TCR. Assisted by the search of optimal processing parameters, TCR-based synthesis of QDs will pave a novel and efficient way to industrial scale-up for commercial application of QDs. In this study, we propose a new process that can massively synthesize QDs of uniform particle size without fluctuation in the properties. It is also aimed to synthesize the core-shell structure based on the QDs synthesized with continuous process by finding optimal processing conditions to enhance their luminescence properties.

2. EXPERIMENTAL PROCEDURE

2.1. Materials

Reagent-grade cadmium oxide (CdO; Sigma-Aldrich, 99%), selenium powder (Se; Sigma-Aldrich, 99%), sulfur powder (S; Sigma-Aldrich, 99%), 1-octadecene (ODE; Sigma-Aldrich, 90%), oleic acid (OA; Sigma-Aldrich, 90%), trioctylphosphine (TOP; Sigma-Aldrich, 90%), cadmium chloride (CdCl₂; Sigma-Aldrich, 99%), sodium diethyldithiocarbamate (NaDDTC; Sigma-Aldrich 97%) were used without further purification.

2.2. Batch-type synthesis of CdSe QDs

CdSe QDs were prepared with conventional batch-type synthesis route based on hot injection method. In detail, initial precursor solution was prepared by mixing CdO (6.4mmol), ODE (10ml) and OA (6ml). Subsequently, the mixture was heated at 120 °C for 20 minutes. Under reflux condenser. The reaction mixture was further heated up to 275 °C for complete dissolution of precursors under nitrogen (N₂) atmosphere. Separately, elemental Se powders (0.8mmol) were dissolved in TOP (1.2ml) and the TOP-Se solution was rapidly injected into Cd-ODE-OA mixture at 275 °C and further reacted for 10 minutes. Sometimes, large-scale

synthesis of the QDs was performed by scaling the amount of precursor solutions by the factor of 20 while maintaining concentration of precursors.

2.3. Continuous synthesis of CdSe QDs

Continuous synthesis of CdSe QDs were carried out by Taylor-Couette fluid flow reaction method as shown in Fig. 1. Taylor-Couette reactor (TCR, inner volume: 10ml, cylinder diameter : 25mm, gap : 2.5mm) consists of two coaxial cylinders consisting of the fixed outer cylinder and the rotating inner cylinder. This shows a unique flow characteristic as the outer cylinder is fixed and the inner cylinder rotates. For continuous synthesis of QDs, we used the same precursor solution as was used for batch-type synthesis process except that Cd-ODE-OA precursor solution was mixed with TOP-Se solution at 30°C to suppress nucleation of QDs prior to main processing. Typically, the CdSe precursor solution were injected at a constant rate using a liquid dosing pump (SIMDOS 10, isocratic pump, KNF, Switzerland) into the reactor and continuous synthesis of QDs was carried out in TCR at a constant rotation speed ranging from 200 to 400 rpm at 275°C. During the continuous synthesis, QDs were sampled with a fixed temporal interval.

2.4. Growth of CdS shell layer for improved optical properties

Sometimes, CdS shell layers were grown on surface of as-prepared CdSe QDs by incorporating cadmium diethyldithiocarbamate (CdDDTC) at 225°C for 1 hour. Here, CdDDTC was prepared by reacting NaDDTC with CdCl₂ in the aqueous solution. CdS shell layers were formed by injecting a CdDDTC sol of into as prepared QD solution at 225°C. CdDDTC sol was prepared by dissolving 0.38mmol of CdDDTC in 1.2ml of TOP. Finally, the reaction mixture was cooled to room temperature and nanocrystals were precipitated by

centrifugation after addition of hydrophilic solvent such as acetone and ethanol. In this process, the supernatant was discarded and precipitates were re-dispersed in toluene.

2.5. Characterization

Absorption spectra were acquired using a UV/Vis spectrophotometer (V-670, JASCO, Japan) and photoluminescence (PL) of the samples were measured with a fluorescence spectrometer (DARSA PRO-5200, PSI, Korea) equipped with a xenon flash lamp with scan speed of 100 nm/min, excitation wavelength of 400 nm. The wavelength and linewidth of PL spectra were extracted by fitting with Gaussian using Origin 2015 software (Microcal, USA). In particular, linewidth of the spectrum was denoted with FWHM (Full width at half maximum) of PL intensity. The size and shape of QDs were investigated with a field emission transmission electron microscope (FE-TEM, JEM 2100F, JEOL, Japan). The chemical composition and oxidation state of samples were studied by X-ray photoelectron spectroscopy (XPS; ESCALAB 250, USA) using Al-K α lines. The C1s at 285 eV was used to calibrate peak position of insulating samples.

3. RESULTS AND DISCUSSIONS

In this study, continuous synthesis of CdSe QDs was carried out by Taylor-Couette fluid flow reaction method as depicted in Fig. 1. A TCR consists of two coaxial cylinders consisting of the fixed outer cylinder and the rotating inner cylinder. Fluids within the gap between the cylinders formed axisymmetric toroidal vortices or Taylor vortex flow (TVF) when the rotating speed of inner cylinder increases beyond a certain threshold [18]. The threshold can be described with Taylor number (T_a) which is defined by a function of gap size (d), the dynamic viscosity of fluid (η), angular speed (ω) and radius (R) of the inner

cylinder as $T_a = R d^3 \omega^2 \eta^{-2}$. The unique feature of TVF is the formation of uniform toroids which are stacked vertically along the rotation axis of TCRs [19]. Intense mixing within each vortex and homogeneous distribution of the mixing intensity throughout reaction volume of the reactor lead to an efficient synthesis route to nanoparticles having high uniformity in size and composition [20].

In this work, we demonstrate a continuous synthesis of high-quality CdSe QDs via chemical processing based on the TCR and we optimize the stability of continuous processing by adjusting rotation speed of the inner cylinder (V_i) and injection rate of solution, while concentration of metal ions was fixed to be $[Cd^{2+}] = 0.064$ M. As shown in Fig. S1 and Fig. S2,[†] fluctuation of optical spectra of QDs and temperature of the TCR was mitigated when processed under optimal condition. To enhance the production rate of high quality QDs, we applied thick and concentrated precursor solution having 4 times large concentration of Cd ions ($[Cd^{2+}] = 0.256$ M). Here, the precursor solution was prepared by mixing Cd solution and Se solution at room temperature to suppress unwanted nucleation of nanoparticles. The mixed precursor solution was injected to the TCR at a constant rate using a liquid dosing pump and continuous synthesis of QDs was carried out in TCR at a constant rotation speed of 300rpm at 275°C. For stable synthesis of QDs without significant fluctuation of PL spectra, injection rate of precursor solution was also fixed to be 5 ml/min. Fig. 2(a) shows temporal variation of PL spectra from QDs sampled with some time intervals during continuous synthesis with TCR. Parameters defining PL spectra of QDs were stabilized after initial jolting of the wavelength and FWHM (full width at half maximum) of PL spectra continued by 40 minutes. The change in PL wavelength can be explained by quantum size effect by insufficient growth of particles at the initial stage of synthesis before stabilization. In contrast, stable processing was hardly achieved with furtherly higher concentrated precursor solution ($[Cd^{2+}] = 0.320$ M) as seen in Fig. 2(c). Instability of the quality of QDs synthesized from

concentrated solution can partly be attributable to large viscosity in the concentrated solution. Viscosity of fluid can be enlarged by concentration [21] and may diminish the level of T_a which is inversely proportional to the square of dynamic viscosity. Conventional laminar flow stable at low T_a lacks intensive and uniform mixing advantageous to synthesis of high quality QDs.

Aliquots of QDs sampled from continuous synthesis at steady processing state using precursor solution with $[Cd^{2+}] = 0.256$ M showed only broad PL spectra (FWHM ~ 48 nm) even after arriving at steady state in processing. However, after dilution with solvent, PL spectra from QDs were narrowed and their FWHMs were minimized to 38 nm as shown in Fig. S3.[‡] Since Stokes shifts or gaps between the absorption and photoluminescence spectra of QDs are quite small compared with conventional organic dye, re-absorption of emitted light is popularly found with concentrated QDs dispersed in solution. Dilution of QDs with suitable solvent is required to remove ambiguity in PL spectra of QDs and to reduce effect of re-absorption or particle-to-particle energy transfer. That is, FWHM of the PL spectrum from synthesized QDs was estimated to be 38 nm in the absence of extrinsic disturbance in PL spectra. With optimal processing condition, the production rate of QDs with reactor volume of 10 ml was measured to be 9.4 g/hour corresponding to $22560 \text{ kg} \cdot \text{day}^{-1} \cdot \text{m}^{-3}$ in space-time yield (STY). Since reactor volume of TCR can be scaled up by small modification [22], one can see that TCR-based processing can be a promising solution for commercial scale production of high quality QDs. Even after continuous synthesis of QDs persisted for 100 minutes, there was no significant fouling of reactor which can cause poor product control and failure of reactor [23] as shown in Fig. S4.[‡]

Fig. 3(a,b) shows microscopic images of QDs prepared with a batch process based on conventional hot injection synthesis. For large-scale batch synthesis of QDs, 20 times larger volume of reactants were used than the volume of reactants for the small scale batch

synthesis. Broad PL spectra were obtained from QDs processed with large scale batch process. Broad PL spectra indicates non-uniformity in QDs and the origin of the non-uniformity can be ascribed to inhomogeneous processing parameters (temperature, concentration of precursors, etc.) caused by convection and turbulence in the batch-type reactor. As a result, QDs prepared with small-scale batch process showed much narrower PL spectrum (FWHM ~ 34nm) in contrast to large-scale processed counterpart which showed broader and asymmetric PL spectrum (FWHM ~ 42nm) as shown in Fig. 3d. Contrary to the batch-processed QDs, QDs synthesized from continuous process based on TCR (denoted as TCRP) showed a relatively narrow emission at 610 nm (FWHM ~ 38nm) and the quantum yield was estimated to be 36%. In addition, the wavelength of PL spectrum from TCRP was red-shifted from batch-processed QDs. The shift in PL spectra can popularly explained with quantum size effect [24]. In addition, PL wavelength can be varied with surface composition of QDs [25]. Interestingly, significant variation of composition was found from X-ray photoelectron spectroscopy of QDs processed with different method. Peak areas of the Cd and Se were measured and used to calculate Cd to Se ratios as shown in Fig. 4. Cd to Se atomic ratios estimated from XPS were 5.98 for BP and 1.93 for TCR, respectively. Since the mean free path of the photoelectron in CdSe when excited with Al K α line was estimated to be 1.6 nm [26], calculated Cd/Se ratio from XPS can be regarded as composition of the entire CdSe nanocrystal of which diameter is near 3nm. Different Cd/Se ratio can affect the peak position of PL spectra [25], which explains difference in emission wavelength of PL spectra from QDs processed with different methods. The significant shear mixing in TCR may affect the composition by affecting mass transport of precursors during synthesis of QDs [27]

Further shell capping process was carried out with TCR-processed QDs (TCRP) using cadmium diethyldithiocarbamate (CdDDTC) dissolved in trioctylphosphine as precursors for

shell layers. As a result, the average diameter (d_{avg}) of QDs were enlarged to $d_{\text{avg}} \sim 9$ nm and more uniform size distribution were found in the microscopic image depicted in Fig. 5. From the difference in d_{avg} , thickness of the grown shell layers was estimated to be *ca.* 2.5 nm. After shell capping process, the PL spectrum of QDs became narrower (FWHM ~ 33 nm) and red-shifted to 640 nm in wavelength. The redshift in wavelength of PL spectra after shell capping can be explained with quantum size effect caused by electron delocalization with hole confinement in the CdSe/CdS core-shell nanoparticles [28]. The quantum yield of photoluminescence was measured to be 90% which approaches maximum value obtained with CdSe-based QDs. The same capping process was applied to batch-processed QDs (BP), but resulted only broad PL spectrum (FWHM ~ 42 nm), although as-synthesized BP showed narrower PL spectra than TCRP before capping process.

4. CONCLUSIONS

A continuous synthesis was developed with TCR as an efficient processing tool for synthesis of highly luminescent QDs. We demonstrate high throughput synthesis of highly luminescent CdSe QDs using TCR as a platform for continuous synthesis with very large production yield. The estimated throughput in space-time yield was $22,560 \text{ kg} \cdot \text{day}^{-1} \cdot \text{m}^{-3}$. Finally obtained QDs after shell capping process with molecular precursors showed narrow and intense PL spectra which can be parameterized by small FWHM and near unity quantum yield after thick shell capping. The composition of CdSe nanocrystals was analyzed with XPS and different Cd/Se ratios were obtained from QDs processed with different methods.

ACKNOWLEDGEMENT

This work was Basic Science Research Program (PNK5590) through the Korea Institute of Materials Science (KIMS) and partially supported by the Technological Innovation R&D Program(S2528762) funded by the Ministry of Small and Medium Business Administration of Republic of Korea.

REFERENCES

- [1] A. S. Fuhr, H. J. Yun, N. S. Makarov, H. Li, H. McDaniel, and V. I. Klimov, Light Emission Mechanisms in CuInS₂ Quantum Dots Evaluated by Spectral Electrochemistry, *ACS Photonics*, 4, 2425-2435 (2017).
- [2] Y. K. Kim, S. H. Ahn, K. Chung, Y. S. Cho, C. J. Choi, The photoluminescence of CuInS₂ nanocrystals: effect of non-stoichiometry and surface modification, *Journal of Materials Chemistry*, 22, 1516-1520 (2012).
- [3] W. K. Bae, K. Char, H. Hur, S. Lee, Single-step synthesis of quantum dots with chemical composition gradients, *Chemistry of Materials*, 20, 531-539 (2008).
- [4] K. Han, S. Yoon and W. J. Chung, CdS and CdSe Quantum Dot-Embedded Silicate Glasses for LED Color Converter, *International Journal of Applied Glass Science*, 6, 103-108 (2015).
- [5] N. Shukla, M. M. Nigra, A. D. Ondeck, One-Step Synthesis and Photoluminescence Evaluation of Cadmium-containing Quantum Dots, *Nano-Micro Letters* 4(1), 52-56 (2012).
- [6] T. Trindade, P. O'Brien, and N. L. Pickett, Nanocrystalline semiconductors: synthesis, properties, and perspectives, *Chemistry of Materials*, 13, 3843-3858 (2001).
- [7] M. M. Moghaddam, M. Baghbanzadeh, A. Sadeghpour, O. Glatter, and C. O. Kappe, Continuous-Flow Synthesis of CdSe Quantum Dots: A Size-Tunable and Scalable Approach, *Chemistry—A European Journal*, 19, 11629-11636 (2013).
- [8] C. D. Dushkin, S. Saita, K. Yoshie, Y. Yamaguchi, The kinetics of growth of semiconductor nanocrystals in a hot amphiphile matrix, *Advances in colloid and Interface science*, 88, 37-78 (2000).
- [9] C. Ippen, B. Schneider, C. Pries, S. Kröpke, T. Greco, A. Holländer, Large-scale synthesis of high quality InP quantum dots in a continuous flow-reactor under supercritical conditions, *Nanotechnology*, 26, 085604 (2015).
- [10] M. Pumera, Nanomaterials meet microfluidics, *Chemical Communications*, 47, 5671-5904 (2011).
- [11] C.-X. Zhao, L. He, S. Z. Qiao, A. P. Middelberg, Nanoparticle synthesis in microreactors, *Chemical Engineering Science*, 66, 1463-1479 (2011).
- [12] I. Bilecka, M. Niederberger, Microwave chemistry for inorganic nanomaterials

synthesis, *Nanoscale*, 2, 1358-1374 (2010).

[13] S. Krishnadasan, J. Tovilla, R. Vilar, A. J. deMello, J. C. deMello, On-line analysis of CdSe nanoparticle formation in a continuous flow chip-based microreactor, *Journal of Materials Chemistry*, 14, 2655-2660 (2004).

[14] A. Toyota, H. Nakamura, H. Ozono, K. Yamashita, M. Uehara, H. Maeda, Combinatorial synthesis of CdSe nanoparticles using microreactors, *J. Phys. Chem. C* 114, 7527-7534 (2010)

[15] M. F. Aljishi, A. Ruo, J. H. Park, B. Nasser, W. S. Kim, Y. L. Joo, Effect of flow structure at the onset of instability on barium sulfate precipitation in Taylor–Couette crystallizers, *Journal of Crystal Growth*, 373, 20-31 (2013).

[16] J. E. Kim, W. S. Kim, Synthesis of Core–Shell Particles of Nickel–Manganese–Cobalt Hydroxides in a Continuous Couette-Taylor Crystallizer, *Crystal Growth & Design*, 17, 3677-3686 (2017).

[17] Y. H. Song, S. H. Choi, W. K. park, J. S. Yoo, S. B. Kwon, B. K. Kang, S. R. Park, Y. S. Seo, W. S. Yang, D. H. Yoon, Innovatively Continuous Mass Production Couette-Taylor Flow: Pure Inorganic Green-Emitting Cs₄PbBr₆ Perovskite Microcrystal for Display Technology, *Scientific reports*, 8, 2009 (2018).

[18] M.N. Noui-Mehidi, N. Ohmura, K. Kataoka, Numerical computation of apex angle effects on Taylor vortices in rotating conical cylinders systems, *Journal of Chemical Engineering of Japan*, 35(1), 25-31 (2002).

[19] G. I. Taylor, Distribution of velocity and temperature between concentric rotating cylinders, *Proceedings of the Royal Society of London A*, 151, 494-512 (1935).

[20] B. Judat, A. Racina, and M. Kind, Macro-and Micromixing in a Taylor-Couette Reactor with Axial Flow and their Influence on the Precipitation of Barium Sulfate, *Chemical Engineering & Technology: Industrial Chemistry-Plant Equipment-Process Engineering-Biotechnology*, 27, 287-292 (2004).

[21] R. J. Silbey, R. A. Alberty, and M. G. Bawendi, *Physical Chemistry*, 4th ed., John Wiley & Sons (2005).

[22] <http://www.laminarm.co.kr/>

[23] A. M. Nightingale, T. W. Philips, J. H. Bannock, and J. C. de Mello, Controlled multistep synthesis in a three-phase droplet reactor, *Nature communications*, 5, 3777 (2014).

[24] M. Zalewska, B. B. Lipowska-Lastowka, A.M. Klonkowski, Quantum size effect and emission enhancement by energy transfer in system: Nanosized SrTiO₃ and Tb(III) ions entrapped on silica support, *J. Non-Cryst. Solids*, 356, 2070-2076 (2010)

[25] J. Jasieniak and P. Mulvaney, From Cd-rich to Se-rich the manipulation of CdSe nanocrystal surface stoichiometry, *Journal of the American Chemical Society*, 129, 2841-2848 (2007).

- [26] D. D. Sarma, P. K. Santra, S. Mukherjee, A. Nag, X-ray photoelectron spectroscopy: a unique tool to determine the internal heterostructure of nanoparticles, *Chemistry of Materials*, 25, 1222-1232 (2013).
- [27] T. S. Tran, S. J. Park, S. S. Yoo, T. R. Lee, T. Y. Kim, High shear-induced exfoliation of graphite into high quality graphene by Taylor–Couette flow, *RSC Advances*, 6, 12003 (2016)
- [28] X. Peng, M. C. Schlamp, A. V. Kadavanich, A. P. Alivisatos, Epitaxial growth of highly luminescent CdSe/CdS core/shell nanocrystals with photostability and electronic accessibility, *J. Am. Chem. Soc.*, 119, 7019-7029 (1997)

LIST OF CAPTIONS

Figure 1. A schematic of a continuous synthesis of quantum dots with a Taylor-Couette reactor (TCR).

Figure 2. (a) Temporal variation PL spectra during continuous synthesis carried out with precursor solutions ($[\text{Cd}^{2+}] = 0.256 \text{ M}$). Emission wavelength (λ_{em}) and FWHM of the PL spectra of QDs prepared with different concentration: (b) $[\text{Cd}^{2+}] = 0.256 \text{ M}$, (c) $[\text{Cd}^{2+}] = 0.320 \text{ M}$.

Figure 3. (a-c) Microscopic images of QDs synthesized with a conventional batch process (BP), QDs synthesized with a large-scale batch process (BPL) and QDs synthesized with a TCR (TCRP); (d) Photoluminescence (PL) spectra of QDs synthesized with various method. Inset shows FWHM of their PL spectra.

Figure 4. X-ray photoelectron spectra of CdSe QDs synthesized with different methods: (a) Survey scan and close-up scan spectra for (c) Cd 3d and (d) Se 3d

Figure 5. (a) PL spectra of QDs after shell capping with pyrolysis of CdDDTC. Inset is FWHM of PL spectra for two different types of QDs; (b) a microscopic image of TCR-processed QDs after shell capping process.

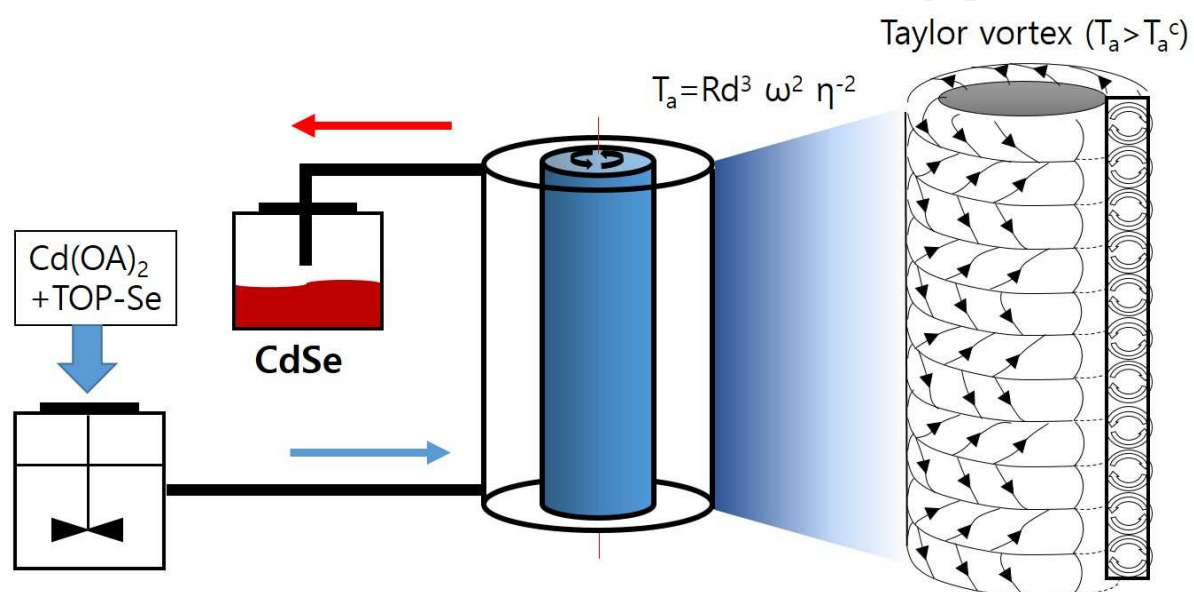


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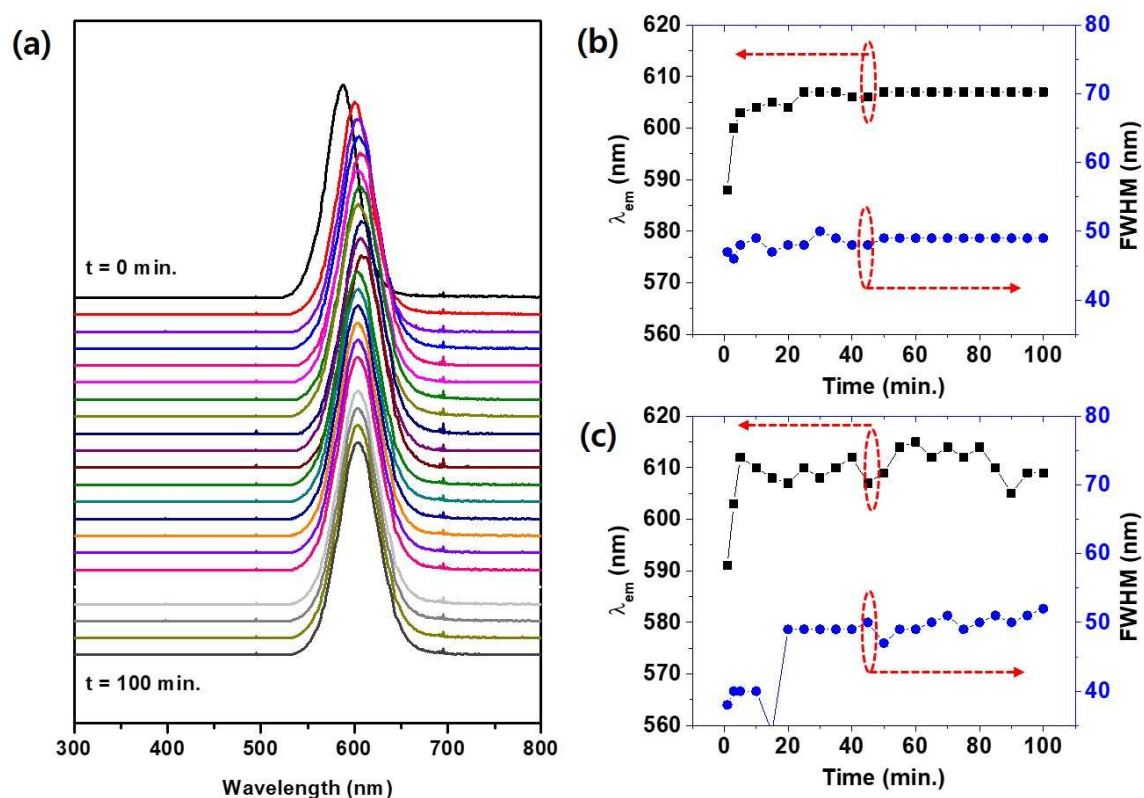


Figure 2. (a) Temporal variation PL spectra (excitation: 400 nm) during continuous synthesis carried out with precursor solutions ($[Cd^{2+}] = 0.256$ M). Emission wavelength (λ_{em}) and FWHM of the PL spectra of QDs prepared with different concentration: (b) $[Cd^{2+}] = 0.256$ M, (c) $[Cd^{2+}] = 0.320$ M.

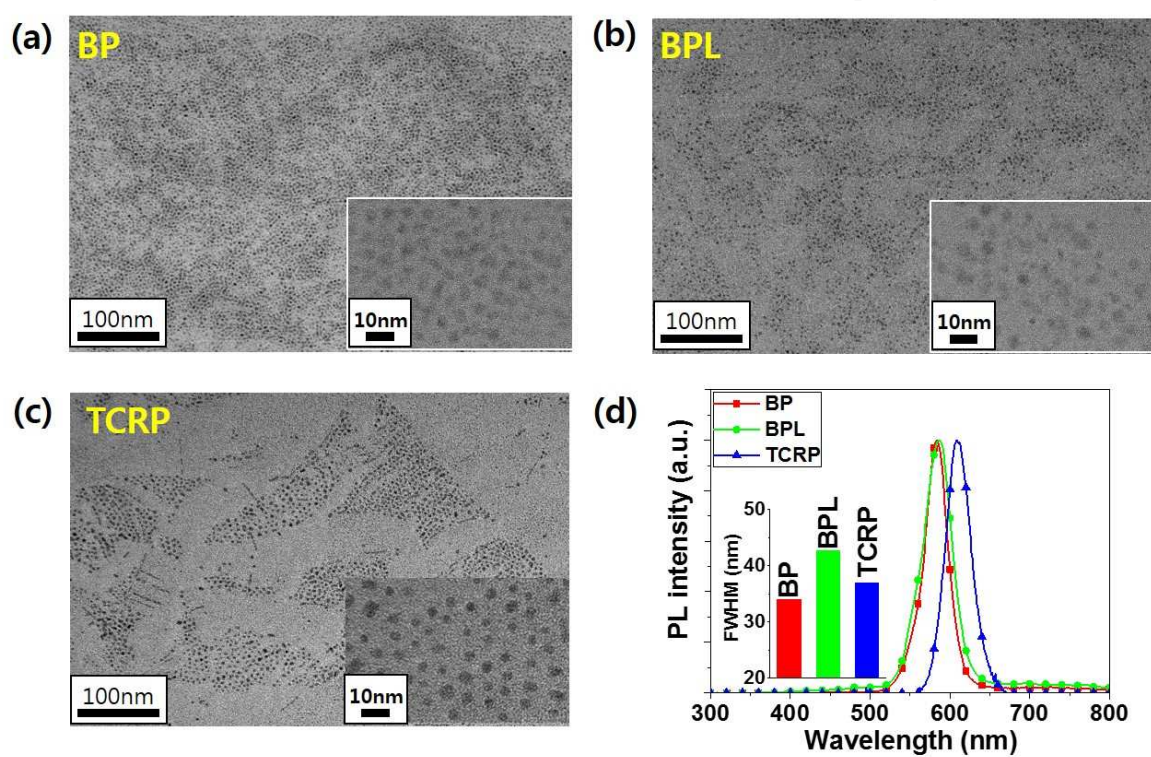


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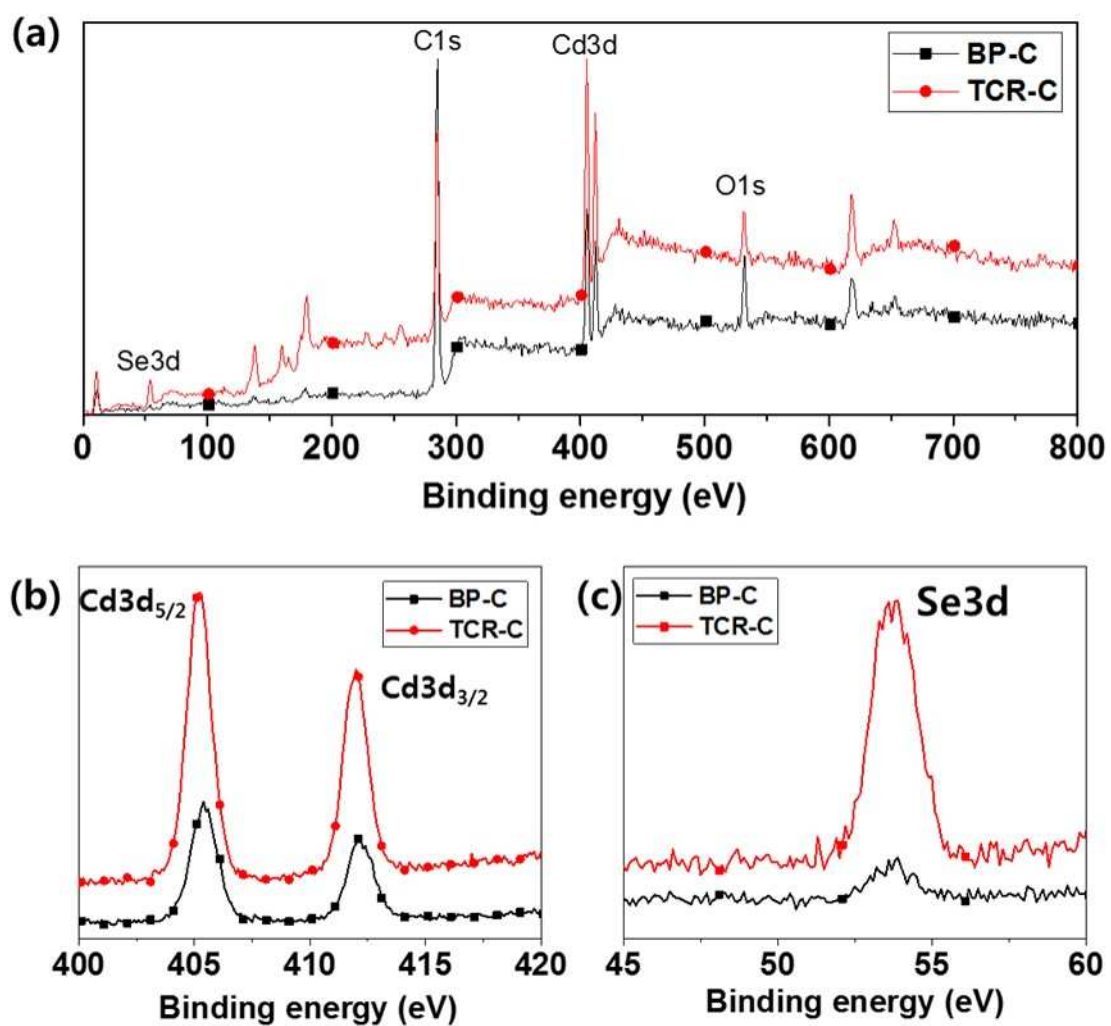


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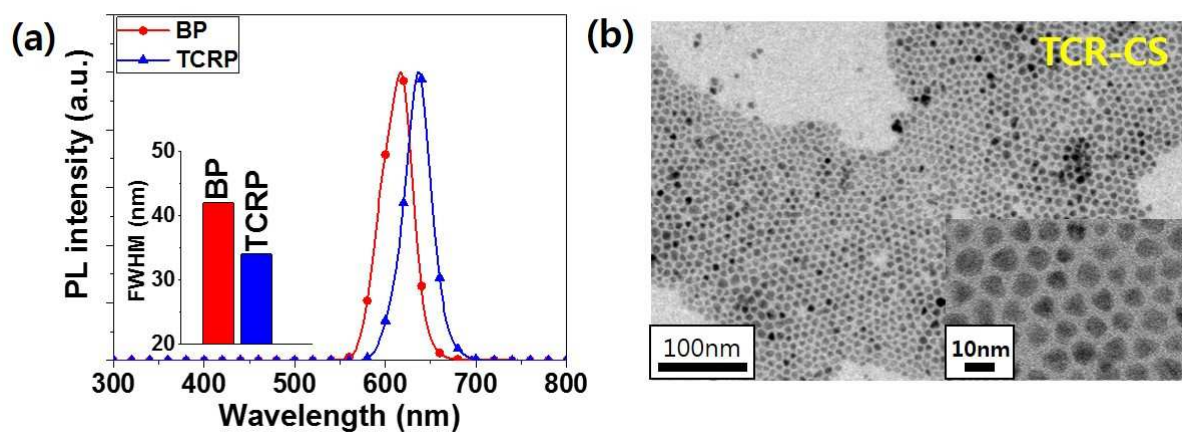


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Highlights

- Quantum dots were synthesized with a novel method based on Taylor-Couette reactor
- High throughput synthesis was achieved with small reactors (~ 10g/hour)
- Near unity (~90%) quantum yield was achieved without multiple surface coating