

Rapid preparation of highly luminescent CdTe nanocrystals in an ionic liquid via a microwave-assisted process†Yu Hayakawa,^a Yoshiyuki Nonoguchi,^a Hui-Ping Wu,^b Eric W.-G. Diau,^b Takuya Nakashima^{*a} and Tsuyoshi Kawai^{*a}

Received 11th March 2011, Accepted 14th April 2011

DOI: 10.1039/c1jm11059d

Thiol-capped CdTe nanocrystals are synthesized directly in an ionic liquid by means of microwave irradiation in a similar manner to an aqueous synthetic route. The combination of ionothermal synthesis with microwave heating offers a quick route to highly luminescent CdTe nanocrystals with zincblende crystal structure. The growth of nanocrystals is considered based on a universal growth model under the assumption that the growth rate exponentially converges as the reaction proceeds. The analysis indicates that the ionothermal conditions with high temperature promote the steady growth of nanocrystals after the nucleation, while the microwave irradiation plays a pivotal role in the limiting step of the growth of nanocrystals including the activation of nanocrystal precursor and the subsequent formation of nuclei.

Introduction

Semiconductor nanocrystals (NCs) have attracted considerable interest in recent years as light emitters having remarkable photostability as well as spectral tunability via a single synthetic route by means of bandgap engineering.^{1–3} These advantages have stimulated various possible applications of NCs including light emitting and photovoltaic devices^{4,5} and labeling of biomolecules.⁶ Unlike bulk semiconductors, the wet chemically synthesized semiconductor NCs^{7,8} offer chemical and physical flexibility and thus dimensionally controlled superstructures of a single component or multiple components with extraordinary properties.^{9,10} Recent progress in the wet-chemical synthesis of semiconductor NCs includes a microwave-assisted process for quick preparation of NCs.¹¹ Microwave routes are often performed on the synthesis of semiconductor NCs such as CdS,¹² CdTe,¹³ CdSe,¹⁴ and their core/shell NCs¹⁵ in high polar media. Combined with hydrothermal conditions, the microwave route affords high quality NCs with a high photoluminescence (PL) quantum yield as high as 60% in a short reaction time, whereas it involves safety concern because of the high temperatures required and autogenous pressure.

Recently, room-temperature ionic liquids¹⁶ are receiving much interest as media for synthesis of inorganic nanomaterials.^{17,18} The importance of ionic liquids in the field of inorganic nanosynthesis

has been realized in terms of their properties such as thermal stability, low vapor pressure, low interfacial tension, and supra-molecular property, while these properties are dependent on the structures and combinations of ionic components. Highly luminescent semiconductor NCs including CdSe,¹⁹ CdS,²⁰ and ZnO²¹ were synthesized by means of ionothermal synthesis in ionic liquids. Meanwhile we have reported efficient phase transfer of cationic CdTe NCs to hydrophobic ionic liquids from an aqueous solution.^{22,23} In hydrophobic ionic liquids, the CdTe NCs showed great improvements in PL intensity as well as photostability in a wide range of temperature, which enabled us to figure out the specific quantum size effect in the exciton fine structure of zincblende CdTe NC.²⁴ The improved PL property was attributed to the stabilization of the capping layer of cationic thiols on the NC-surface by the salt effect of ionic components and generally observed for hydrophobic ionic liquids, especially those with bis(trifluoromethanesulfonyl)amide (TF₂N) anion. The heat-treatment of CdTe NCs at 120 °C in the ionic liquid further improved the PL quantum yield up to more than 50%.²¹ However, the post-treatment by heating in ionic liquids also led to the increase in the size of NCs and the corresponding spectral shift to longer wavelength. In the present study, we synthesized thiol-capped CdTe NCs directly in an ionic liquid at high temperature (~150 °C) with the aid of microwave irradiation. Since microwaves directly excite polar molecules and ions, ionic liquids are essentially ideal media absorbing microwave.²⁵ Back-and-forth oscillation of ions with friction induced by the electromagnetic field of microwaves raises the temperature rapidly, which substantially shortens the reaction times compared to the convective heating method. Furthermore, in contrast to the hydrothermal synthesis, the ionothermal one has no requirement for pressure conditions due to high thermal stability and low vapor pressure of ionic liquids. The combination

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† Electronic supplementary information (ESI) available. See DOI: 10.1039/c1jm11059d

of a microwave-assisted process with ionothermal synthesis therefore provides a great advantage for the inorganic synthesis in ionic liquids. Tellurium nanorods and nanowires,²⁶ aluminophosphate molecular sieves,²⁷ and other inorganic nanoparticles^{28–30} were successfully produced by the microwave-assisted ionic liquid methods. The effect of the small amount of ionic liquid as a microwave sensitizer on the growth of CdSe NCs was also investigated and found to improve the growth rate of NCs in alkanes.³¹

We herein report the microwave-assisted synthesis of highly luminescent CdTe NCs capped with cationic thiol in a similar manner to an aqueous synthetic route.⁸ While syntheses of luminescent NCs in ionic liquids have been already reported,^{19–21} they are based on the decomposition of organometallic precursors or metal salts in the presence of elemental chalcogenides, which follows the organometallic route as demonstrated in highly boiling organic solvents.⁷ The colloidal approach where the thiolate–metal interaction controls the growth of nanoparticles based on ionic association between metal and chalcogenide ions has been first demonstrated in an ionic liquid. The microwave irradiation of an ionic liquid solution of the NC-precursor gave highly luminescent CdTe NCs passivated with a thiol ligand. The CdTe NCs prepared in the ionic liquid at 150 °C possessed a zincblende crystal structure as well as NCs produced *via* the aqueous route, whereas the PL quantum yield was much higher than NCs obtained in an aqueous solution.

Experimental

Materials

CdCl₂·2.5H₂O (99.9%), 2-(dimethylamino)ethanethiol hydrochloride (DMAET, 95%), and Al₂Te₃ were purchased from Wako, Aldrich, and Hayashi Chemical, respectively. A hydrophobic ionic liquid, 1-methoxymethyl-1-methylpyrrolidinium bis(trifluoromethanesulfonyl)amide (MOMPyrTf₂N), was used as a solvent. All chemicals were used without further purification.

Synthesis of CdTe NCs

CdTe NCs were synthesized following the reported procedure³² with some modifications. Briefly, 29 mg (1.3×10^{-4} mol) of CdCl₂·2.5H₂O and 43 mg (3.0×10^{-4} mol) of DMAET were dissolved in 10 mL of deionized water, and the pH of the aqueous solution was adjusted to 5.5 by 1 N NaOH. The aqueous solution of cadmium salt and DMAET was mixed with the same amount (10 mL) of MOMPyrTf₂N and stirred vigorously to extract cadmium–DMAET complex from the aqueous solution to the hydrophobic ionic liquid. After being stirred for more than 10 h, the upper aqueous solution was removed and the lower ionic liquid solution was dried *in vacuo*. The ionic liquid solution of cadmium–DMAET complex was then subjected to the injection of H₂Te gas, which was generated by the reaction of 20 mg of Al₂Te₃ with 5 mL of 0.5 M H₂SO₄, under N₂ atmosphere to give a CdTe NC-precursor solution as a brownish suspension. The CdTe NCs were prepared by heating the precursor suspension at 150 °C by microwave irradiation and also by convective heating (mantle heater) for various periods. The microwave irradiation was conducted by IMCR-25003 Green-Motif I (iDX corp.), which operates at 2450 MHz frequency and 0–300 W power range.

Characterization

The growth of CdTe NCs was characterized by UV-vis and PL spectroscopy using a JASCO V-550 spectrometer and a Hitachi F-4500 spectrofluorophotometer, respectively. PL quantum yields of CdTe NCs were determined by using a Hamamatsu Absolute PL Quantum Yield Measurement System (C9920-02). Transmission electron microscopy (TEM) measurements were carried out by a JEOL, JEM-2100 operated at 200 kV and a JEM-3100FEF operated at 300 kV for high-resolution measurement. For TEM observation, a drop of the ionic liquid solution of CdTe NCs was cast on a carbon-coated copper grid and the excess ionic liquid was washed with methanol. X-Ray powder diffraction (XRD) patterns were recorded using a Rigaku RINT-TTR III/NM X-ray diffractometer. CdTe NCs in the ionic liquid were precipitated by methanol and centrifuged for the XRD measurement. ¹H NMR spectra were recorded on a JEOL AL-300 spectrometer (300 MHz).

Results and discussion

Since inorganic salts are not well soluble in hydrophobic Tf₂N-based ionic liquids due to the relatively low dielectric constants of ionic liquids, the cadmium–DMAET complex was dissolved in MOMPyrTf₂N *via* a simple extraction process from the aqueous solution. The phase transfer from water to the ionic liquid was confirmed by ¹H NMR (see the ESI[†]). The ¹H NMR signals of the cadmium–DMAET complex before the extraction disappeared and the new signals assigned to the pyrrolidinium cation of MOMPyrTf₂N appeared in D₂O after the extraction, indicating the cation-exchange mechanism.^{23b} Upon injection of gaseous H₂Te with N₂ flow to the ionic liquid solution, the CdTe NC-precursor formed to give a brownish suspension. The precursor suspension was then subjected to microwave irradiation at 150 °C under ambient conditions (open air and atmospheric pressure). The brownish suspension turned to a clear yellowish solution within two minutes by microwave irradiation, indicating the dissolution of precursor aggregates and the formation of very small CdTe NCs. This change was also observed for the aqueous synthesis of CdTe NCs capped with cationic DMAET, while it took about 10 min *via* the convective heating method.³² Further microwave irradiation promoted the growth of CdTe NCs.

Fig. 1 shows the representative TEM images of CdTe NCs prepared *via* microwave irradiation. The average diameter of CdTe NCs obtained by microwave irradiation for 80 min at 150 °C was measured to be 4.1 nm with a standard deviation of 14%, which was determined by measuring more than 150 individual NCs. The lattice fringes observed in the high-resolution TEM image (Fig. 1b) indicate that the CdTe NCs are composed of a high crystalline single crystal. XRD peaks of CdTe NCs prepared by the microwave-assisted method can be indexed as (111), (220) and (311) crystallographic planes and match well with the zincblende crystal structure of CdTe as indicated by lines (Fig. 2). The crystal size of CdTe calculated using the Scherrer's equation from the diffraction peak (111) was found to be 2.5 nm for NCs grown for 20 min. The zincblende crystal structure is consistent with the dominant crystal phase of bulk CdTe and also with that of CdTe NCs prepared in the aqueous conditions (see

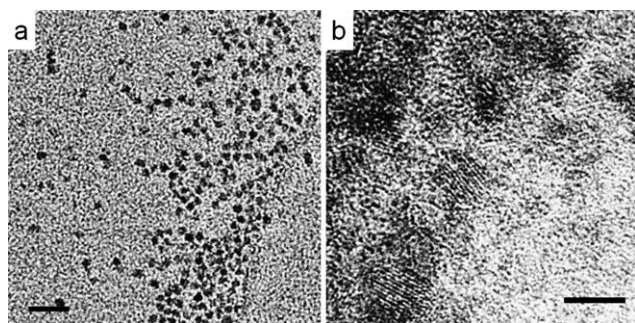


Fig. 1 Representative TEM (a) and high-resolution TEM (b) images of CdTe NCs prepared in the ionic liquid *via* microwave irradiation at 150 °C. Scale bars: 20 nm for (a); 5 nm for (b).

the ESI†).⁸ There was no marked difference between the XRD profiles of CdTe NCs prepared by microwave irradiation and convective heating (also see the ESI†). Unlike CdTe NCs prepared in the aqueous conditions employing thioglycolic acid (TGA) as a capping ligand,^{8,13b} formation of CdS shell due to the partial hydrolysis of TGA was not suggested from XRD patterns. Thus, TEM and XRD results showed no substantial difference in the size, morphology and crystal structure between CdTe NCs prepared in the ionic liquid and in water. Some recent studies have reported that ionic liquids have an effect on the regulation of size and shape of NCs due to their low interfacial tension and the adsorption of ionic components to the polar facets of the NC-surface.^{18–20} In the present case, the thiol ligand, DMAET, which sticks to the surface of CdTe NCs more strongly than the ionic liquid components, would predominantly control the growth of NCs in a similar manner to the aqueous synthetic route employing thiol ligands.⁸

The absorption and PL spectra showed red-shift as a function of reaction period for both CdTe NCs prepared *via* microwave irradiation and convective heating methods (Fig. 3), suggesting the continuous growth of NC size. Broadening of PL spectra as the increase of reaction time was observed for both CdTe NCs (Fig. 3a and b), which was generally found for the aqueous synthesis of CdTe NCs⁸ and attributed to the growth *via* Ostwald ripening at the later stage of NC formation. Fig. 4 summarizes the temporal evolution of PL peak position, size and PL quantum yield of CdTe NCs. For comparison, evolution plots for CdTe NCs prepared in water by microwave and convective

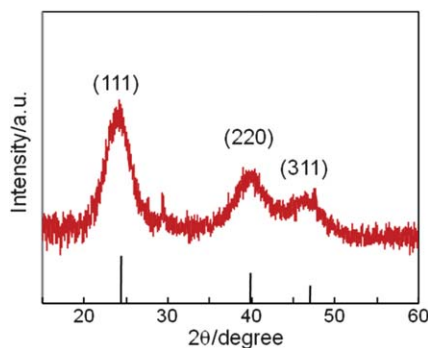


Fig. 2 XRD profile of CdTe NCs prepared by microwave irradiation for 20 min in the ionic liquid. The calculated peaks of the CdTe zincblende structure are indicated by lines (ICSD 31844).

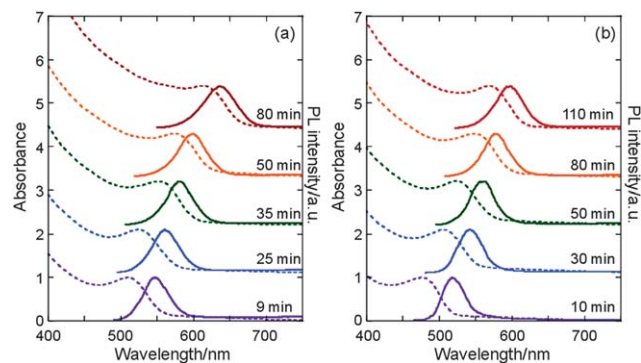


Fig. 3 Absorption (broken lines) and the corresponding PL ($\lambda_{\text{ex}} = 400 \text{ nm}$, solid lines) spectral changes of CdTe NCs prepared by (a) microwave irradiation and (b) convective heating in the ionic liquid at 150 °C.

heating methods at 100 °C are also shown. Continuous shift of PL peak positions (Fig. 4A) represents the growth of NC size since the PL peak position clearly correlates the degree of quantum confinement effect. The microwave-assisted method in the ionic liquid gave CdTe NCs with strong red emission by 80 min irradiation, while only green emissive CdTe NCs with PL peak at 540 nm were obtained by the conventional aqueous synthesis for the reaction period as long as 6 h. The conventional aqueous synthesis gave DMAET-capped CdTe NCs whose PL peak position appeared at 600 nm with broad size-distribution even for a 24 h reaction period.²² Given the linear progression of PL peaks, whereas the formation of NCs indeed involves multiple and complex growth kinetics, the rate of PL peak shift

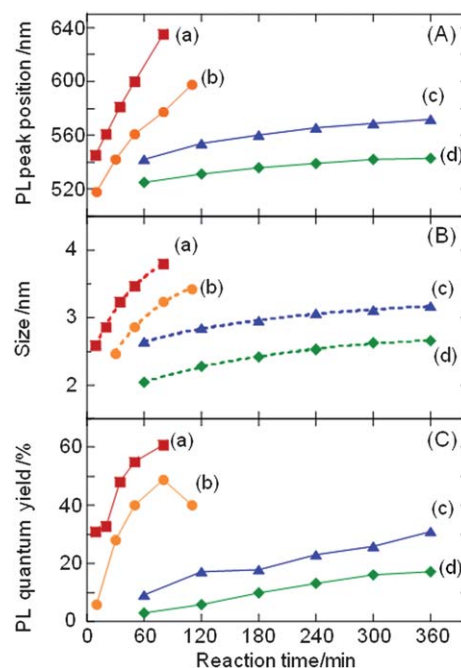


Fig. 4 Evolutions of the PL peak position (A), size (B) and PL quantum yield (C) of CdTe NCs prepared by four-different methods: (a) microwave irradiation in the ionic liquid at 150 °C, (b) convective heating in the ionic liquid at 150 °C, (c) microwave irradiation in water at 100 °C, and (d) convective heating in water at 100 °C. The broken lines in (B) represent the fitting curves following eqn (1).

for a microwave-assisted ionic liquid method was roughly 20 times faster than that for conventional aqueous synthesis. Compared in terms of the heating method, the microwave irradiation showed a small effect on the growth rate of NCs. That is, the reaction temperature and media seem to play a dominant role in the steady growth stage of NC formation.

More quantitatively, we introduce a universal growth model under the assumption that the growth rate of NCs exponentially converges to zero as the reaction proceeds.³³ Briefly, the growth rate dD/dt is proportional to $\exp(-t/\tau)$, where τ is a fitting parameter. Integrating the linear relation, the growth eqn (1) was provided as follows:

$$D(t) = D_0 + \alpha\tau(1 - \exp(-t/\tau)), \quad (1)$$

where $D(t)$ is the size of NC at time t , D_0 is the critical size of NC at the early growth stage including nucleation, and α is the initial growth rate after the nucleation. We also assume that the fitting parameter τ is the time constant of growth which depends on precursor concentrations. The equation was applied to the growth plots in Fig. 4B, that were derived from the first excitonic peak positions of NCs according to the empirical equation reported by Peng and co-workers,³⁴ to estimate parameters for the growth of NCs. The fitting curves are depicted as broken lines in Fig. 4B, well tracing the evolution plots of NC-size with the correlation coefficients of 0.999. As summarized in Table 1, the microwave irradiation has little effect on the growth rate α . The same conditions of temperature and solvent gave the similar values of α (ca. 0.03 nm min⁻¹ in the ionic liquid at 150 °C and ca. 0.005 nm min⁻¹ in water at 100 °C). High temperature (150 °C) and ionic liquid solvent conditions provided the faster growth by more than 5 times than the aqueous conditions (100 °C). Since both the ionic liquid and water are good microwave absorbers, the selective activation³⁵ of NCs was not prominent in the steady growth of NCs after nucleation. On the other hand, a noticeable effect of microwave irradiation was found in the values of D_0 . The microwave irradiation conditions gave larger D_0 (a and c; ca. 2.3 nm) than those obtained by convective heating (b and d; ca. 1.7 nm), which implies that the faster consumption of NC-precursor in the microwave conditions at the early growth stage including the nuclei formation shifts the critical size (D_0) of NCs to a larger value.^{13c,36} There are two plausible effects of microwave irradiation on the fast consumption of NC-precursor. One is that the rapid temperature elevation of the system including media due to the high utilization factor of microwave energy accelerates the nucleation. The higher convection heating rate induced by microwave irradiation might result in the faster consumption of all precursors nearby before the diffusion-limited growth of NC starts, affording large D_0 values. The other

possibility is the selective activation of NC-precursor.³⁵ The CdTe precursor composed of ionically associated cadmium and telluride ions and cationic DMAET might have a larger microwave absorptivity than solvents, leading to the direct activation of precursor and subsequent acceleration of nucleation.³⁵ Meanwhile, the CdTe precursor was not well soluble both in water and in the ionic liquid to give suspensions with agglomerates of the precursor. The both suspension solutions of the ionic liquid and water turned to clear yellowish solutions within two minutes by microwave irradiation, indicating the rapid dissolution of agglomerates and the subsequent consumption of NC-precursor. Thus both the rapid elevation of temperature and the selective heating by microwave might be effective for the limiting step of NC growth which includes the first two events (activation of the precursor and nucleation).³⁵

The CdTe NCs prepared in the ionic liquid showed a much higher PL quantum yield than those obtained *via* aqueous routes (Fig. 4C, a, b *vs.* c, d). The higher reaction temperature and the stabilization effect of the ionic liquid would be responsible for the high PL efficiency. As for the heating method, given the same solvent and temperature conditions, the microwave irradiation afforded a higher PL quantum yield than convective heating for the same reaction periods (a *vs.* b, c *vs.* d). The higher PL quantum yields indicate the selective microwave effect on the surface quality of CdTe NCs, which has been generally observed for the microwave synthesis of semiconductor NCs.^{12–15} The PL quantum yield of CdTe NCs prepared by the microwave irradiation in the ionic liquid reached up to 61% with PL peak at 640 nm. The systematic study for the reaction conditions such as the structure of ionic liquids, precursor concentration, temperature, programmed heating, and the ratio of thiol ligand to cadmium ion would offer the optimum conditions for CdTe NCs with a desirable PL peak and high PL quantum yield.¹³

The drawback of the ionic liquids as media for NCs is the less accessibility to NCs due to the very stable solvation and poor volatility of ionic liquids. The use of ionic liquids therefore limits the application of ionic liquid–NC composites to photoelectrochemical devices utilizing the electrochemical property of ionic liquids and luminescent polymer composites²³ *via in situ* polymerization of ionic liquid monomers. We therefore investigated the extraction of NCs from the ionic liquid solution to organic media and water by ligand-exchange. The capping ligand DMAET in the ionic liquid was substituted with 1-dodecanethiol so that the NCs are soluble in chloroform.³⁷ The both absorption and PL peak positions shifted to a shorter wavelength from 600 nm to 580 nm and from 570 nm and 550 nm, respectively, by the ligand-exchange from DMAET to 1-dodecanethiol (Fig. 5). The blue-shift in both spectra might indicate the etching of Te during the ligand exchange with 1-dodecanethiol as reported previously.³⁸ The PL quantum yield after the extraction was measured to be 52% in chloroform solution, which is almost identical to that in MOMPyrTf₂N before the extraction. Although DMAET is readily soluble in water, the DMAET-capped CdTe NCs transferred to ionic liquids were hardly back extracted to water due to the stable solvation with ionic components.^{22,23} We therefore extracted the DMAET-capped CdTe NCs by ligand-exchange with anionic TGA. In contrast to cationic DMAET-capped CdTe NCs, the NCs with anionic TGA ligand were not transferred from water to ionic liquids.²³ The CdTe NCs in the ionic liquid were

Table 1 Fitting parameters for eqn (1)

Conditions ^a	D_0/nm	$\alpha/\text{nm min}^{-1}$	τ/min	R^2
a	2.28 ± 0.043	0.036 ± 0.0033	54 ± 7.1	0.999
b	1.67 ± 0.189	0.035 ± 0.0091	61 ± 16	0.999
c	2.39 ± 0.038	0.0050 ± 0.00065	177 ± 23	0.999
d	1.72 ± 0.037	0.0066 ± 0.00067	161 ± 16	0.999

^a Conditions a–d correspond to those in Fig. 4.

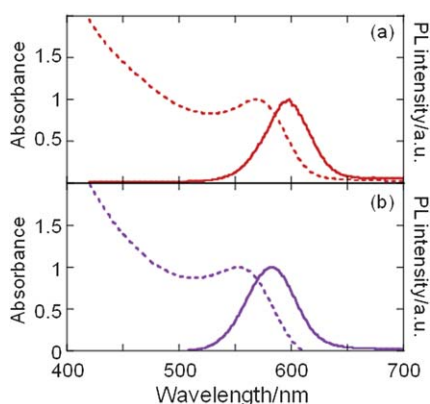


Fig. 5 Absorption (broken lines) and PL spectra (solid lines) of CdTe NCs capped with (a) DMAET in MOMPyrTF₂N and (b) 1-dodecanethiol in chloroform.

precipitated by the addition of a 0.5 M TGA methanol solution. The orange precipitate was re-dissolved in weakly alkaline water (pH = 12) to give a stable dispersion of TGA-capped CdTe NCs in water. The PL quantum yield decreased but was still 14% even after the extraction to water. The optimization of the ligand-exchange conditions might afford the aqueous dispersion of NCs with PL property as high as those in ionic liquids.

Conclusion

We have demonstrated the preparation of thiol-capped CdTe NCs directly in the ionic liquid in a similar manner to the aqueous synthetic route. The combination of microwave irradiation with ionothermal conditions at high temperature offered the quick route to CdTe NCs with a high PL intensity. The specific microwave effect has been found in the activation of NC-precursor both in the ionic liquid and water, which plays a pivotal role in the nucleation of CdTe NCs at the early stage of NC formation. The CdTe NCs prepared in the ionic liquid were transferred in water or organic solvents *via* ligand-exchange. The optimization of conditions would provide the strongly luminescent CdTe NCs in a wide range of media.

Acknowledgements

The authors thank Mr S. Katao for his assistance in XRD measurements. This work was partly supported by Grant-in-Aids for Scientific Research on Priority Area "Ionic liquids" from the Ministry of Education, Culture, Sports, Scientific and Technology (MEXT) of Japan.

References

- N. Gaponik, S. G. Hickey, D. Dorfs, A. L. Rogach and A. Eychmuller, *Small*, 2010, **6**, 1364–1378.
- (a) A. M. Smith and S. M. Nie, *Acc. Chem. Res.*, 2010, **43**, 190–200; (b) X. G. Peng, *Acc. Chem. Res.*, 2010, **43**, 1387–1395.
- G. D. Scholes, *Adv. Funct. Mater.*, 2008, **18**, 1157–1172.
- P. V. Kamat, *J. Phys. Chem. C*, 2008, **112**, 18737–18753.
- A. L. Rogach, N. Gaponik, J. M. Lupton, C. Bertoni, D. E. Gallardo, S. Dunn, N. L. Pira, M. Paderi, P. Repetto, S. G. Romanov, C. O'Dwyer, C. M. S. Torres and A. Eychmuller, *Angew. Chem., Int. Ed.*, 2008, **47**, 6538–6549.
- (a) A. M. Smith, H. W. Duan, A. M. Mohs and S. M. Nie, *Adv. Drug Delivery Rev.*, 2008, **60**, 1226–1240; (b) A. P. Alivisatos, W. W. Gu and C. Larabell, *Annu. Rev. Biomed. Eng.*, 2005, **7**, 55–76.

- (a) C. B. Murray, D. J. Norris and M. G. Bawendi, *J. Am. Chem. Soc.*, 1993, **115**, 8706–8715; (b) C. D. Donega, P. Liljeroth and D. Vanmaekelbergh, *Small*, 2005, **1**, 1152–1162.
- A. L. Rogach, T. Franzl, T. A. Klar, J. Feldmann, N. Gaponik, V. Lesnyak, A. Shavel, A. Eychmuller, Y. P. Rakovich and J. F. Donegan, *J. Phys. Chem. C*, 2007, **111**, 14628–14637.
- D. V. Talapin, J. S. Lee, M. V. Kovalenko and E. V. Shevchenko, *Chem. Rev.*, 2010, **110**, 389–458.
- S. Srivastava and N. A. Kotov, *Soft Matter*, 2009, **5**, 1146–1156.
- I. Bilecka and M. Niederberger, *Nanoscale*, 2011, **2**, 1358–1374.
- (a) Y. Wada, H. Kuramoto, J. Anand, T. Kitamura, T. Sakata, H. Mori and S. Yanagida, *J. Mater. Chem.*, 2001, **11**, 1936–1940; (b) T. Ni, D. K. Nagesha, J. Robles, N. F. Materer, S. Mussig and N. A. Kotov, *J. Am. Chem. Soc.*, 2002, **124**, 3980–3992.
- (a) L. Li, H. F. Qian and J. C. Ren, *Chem. Commun.*, 2005, 528–530; (b) Y. He, L. M. Sai, H. T. Lu, M. Hu, W. Y. Lai, Q. L. Fan, L. H. Wang and W. Huang, *Chem. Mater.*, 2007, **19**, 359–365; (c) Y. He, H. T. Lu, L. M. Sai, W. Y. Lai, Q. L. Fan, L. H. Wang and W. Huang, *J. Phys. Chem. B*, 2006, **110**, 13352–13356.
- (a) J. J. Zhu, O. Palchik, S. G. Chen and A. Gedanken, *J. Phys. Chem. B*, 2000, **104**, 7344–7347; (b) H. Han, G. Di Francesco and M. M. Maye, *J. Phys. Chem. C*, 2010, **114**, 19270–19277.
- (a) W. Schumacher, A. Nagy, W. J. Waldman and P. K. Dutta, *J. Phys. Chem. C*, 2009, **113**, 12132–12139; (b) M. D. Roy, A. A. Herzing, S. Lacerda and M. L. Becker, *Chem. Commun.*, 2008, 2106–2108.
- N. V. Plechkova and K. R. Seddon, *Chem. Soc. Rev.*, 2008, **37**, 123–150.
- (a) Z. Ma, J. H. Yu and S. Dai, *Adv. Mater.*, 2010, **22**, 261–285; (b) T. Torimoto, T. Tsuda, K. Okazaki and S. Kuwabata, *Adv. Mater.*, 2010, **22**, 1196–1221.
- (a) Z. G. Li, Z. Jia, Y. X. Luan and T. C. Mu, *Curr. Opin. Solid State Mater. Sci.*, 2008, **12**, 1–8; (b) M. Antonietti, D. B. Kuang, B. Smarsly and Z. Yong, *Angew. Chem., Int. Ed.*, 2004, **43**, 4988–4992.
- M. Green, P. Rahman and D. Smyth-Boyle, *Chem. Commun.*, 2007, 574–576.
- K. Biswas and C. N. R. Rao, *Chem.–Eur. J.*, 2007, **13**, 6123–6129.
- D. P. Liu, G. D. Li, Y. Su and J. S. Chen, *Angew. Chem., Int. Ed.*, 2006, **45**, 7370–7373.
- T. Nakashima and T. Kawai, *Chem. Commun.*, 2005, 1643–1645.
- (a) T. Nakashima, T. Sakakibara and T. Kawai, *Chem. Lett.*, 2005, 1410–1411; (b) T. Nakashima, Y. Nonoguchi and T. Kawai, *Polym. Adv. Technol.*, 2008, **19**, 1401–1405.
- (a) Y. Nonoguchi, T. Nakashima and T. Kawai, *J. Phys. Chem. C*, 2007, **111**, 11811–11815; (b) Y. Nonoguchi, T. Nakashima and T. Kawai, *J. Phys. Chem. C*, 2008, **112**, 19263–19267.
- J. Hoffmann, M. Nuchter, B. Ondruschka and P. Wasserscheid, *Green Chem.*, 2003, **5**, 296–299.
- Y. J. Zhu, W. W. Wang, R. J. Qi and X. L. Hu, *Angew. Chem., Int. Ed.*, 2004, **43**, 1410–1414.
- Y. P. Xu, Z. J. Tian, S. J. Wang, Y. Hu, L. Wang, B. C. Wang, Y. C. Ma, L. Hou, J. Y. Yu and L. W. Lin, *Angew. Chem., Int. Ed.*, 2006, **45**, 3965–3970.
- D. S. Jacob, L. Bitton, J. Grinblat, I. Felner, Y. Kolytyn and A. Gedanken, *Chem. Mater.*, 2006, **18**, 3162–3168.
- K. L. Ding, Z. J. Miao, Z. M. Liu, Z. F. Zhang, B. X. Han, G. M. An, S. D. Miao and Y. Xie, *J. Am. Chem. Soc.*, 2007, **129**, 6362–6363.
- G. Buehler and C. Feldmann, *Angew. Chem., Int. Ed.*, 2006, **45**, 4864–4867.
- J. A. Gerbec, D. Magana, A. Washington and G. F. Strouse, *J. Am. Chem. Soc.*, 2005, **127**, 15791–15800.
- Z. Y. Tang, Z. L. Zhang, Y. Wang, S. C. Glotzer and N. A. Kotov, *Science*, 2006, **314**, 274–278.
- D. N. Futaba, K. Hata, T. Yamada, K. Mizuno, M. Yumura and S. Iijima, *Phys. Rev. Lett.*, 2005, **95**, 056104-1–056104-4.
- W. W. Yu, L. H. Qu, W. Z. Guo and X. G. Peng, *Chem. Mater.*, 2003, **15**, 2854–2860.
- A. L. Washington and G. F. Strouse, *J. Am. Chem. Soc.*, 2008, **130**, 8916–8922.
- D. V. Talapin, A. L. Rogach, E. V. Shevchenko, A. Kornowski, M. Haase and H. Weller, *J. Am. Chem. Soc.*, 2002, **124**, 5782–5790.
- T. Nakashima, Y. Kobayashi and T. Kawai, *J. Am. Chem. Soc.*, 2009, **131**, 10342–10343.
- K. Akamatsu, T. Tsuruoka and H. Nawafune, *J. Am. Chem. Soc.*, 2005, **127**, 1634–1635.