Stability studies of CdSe nanocrystals in an aqueous environment

Lifei Xi[1]**, Jun Yan Lek**[1]**, Yen Nan Liang**[1]**, Chris Boothroyd**[2]**,
Wenwen Zhou**[1]**, Qingyu Yan**[1]**, Xiao Hu**[1]**, Freddy Boey Yin Chiang**[1]
and Yeng Ming Lam[1,3]

[1] School of Materials Science and Engineering, Nanyang Technological University,
Nanyang Avenue, 639798, Singapore
[2] Center for Electron Nanoscopy, Technical University of Denmark, DK-2800 Kongens
Lyngby, Denmark

E-mail: ymlam@ntu.edu.sg

Abstract

In this paper, CdSe nanocrystal dissolution in an aqueous solution was studied. It was found that light is a key factor affecting the dissolution of nanocrystals. In the presence of light, the electrons generated from CdSe nanocrystals reduce water to hydrogen and hydroxide ions (OH^-) while photo-generated holes oxidize CdSe to Cd^{2+} and elemental Se. The dissolution was accelerated in an acidic medium while moderate alkalinity (pH = 10.3) can slow down the dissolution possibly due to precipitation of nanocrystals. This study has strong implications for the use of these crystals in aqueous environments (bioimaging and dye-sensitized solar cells).

S Online supplementary data available from stacks.iop.org/Nano/22/275706/mmedia

(Some figures in this article are in colour only in the electronic version)

In recent years, the synthesis of colloidal cadmium selenide (CdSe) nanocrystals has attracted considerable interest due to their potential electronics, optical and life sciences applications [1, 2]. A variety of methods has been employed to synthesize colloidal CdSe nanocrystals. These methods include solution–liquid–solid (SLS) growth, the micelle/reverse micelle method, the hydrothermal/solvothermal method and the hot coordinating/noncoordinating solvents method [3–7]. High quality CdSe nanodots, nanorods, tetrapods, and nanowires can be produced with these methods [8–10]. Although extensive work has been carried out to study the growth and application of CdSe nanocrystals, little has been done on the stability or the dissolution of CdSe nanocrystals [11–13]. For effective application of such quantum dots, understanding of their stability under specific environments is critical. It is well known that colloidal nanocrystals are metastable species as compared to the bulk materials and they are kinetically stabilized by ligands and surfactants [11]. The function of these ligands and surfactants is to protect the surface atoms of the nanocrystals and provide the necessary chemical accessibility. However, this protection is temporary and is readily destroyed under certain conditions. Thus understanding of the stability of nanocrystals in the environment is an essential first step before large scale applications [14, 15]. Aldana *et al* studied the photochemical instability of CdSe nanocrystals in aqueous solution [11]. They proposed three stages to the instability of CdSe nanocrystals: photocatalytic oxidation of the thiol ligands on the nanocrystal surface, photooxidation and precipitation of the nanocrystals from aqueous solution. Mulvihill *et al* studied the stability of CdSe nanocrystals modified with thiolate ligands in sodium chloride aqueous solution [12]. However, these results mainly focused on the influence of thiolate ligands on the stability of nanocrystals in aqueous solution and the effect of light was not considered. Recently, we found that the dissolution of CdSe nanocrystals in aqueous solution is due to a photoredox process. In this communication, we will report our preliminary findings.

In this study, colloidal CdSe nanocrystals capped with octadecylphosphonic acid (ODPA) were first dispersed in toluene and added to cetyltrimethylammonium bromide (CTAB) aqueous solution. The solution was then stirred under room light and temperature. We found that even if powder-formed CdSe nanocrystals were added directly to the aqueous

[3] Author to whom any correspondence should be addressed.
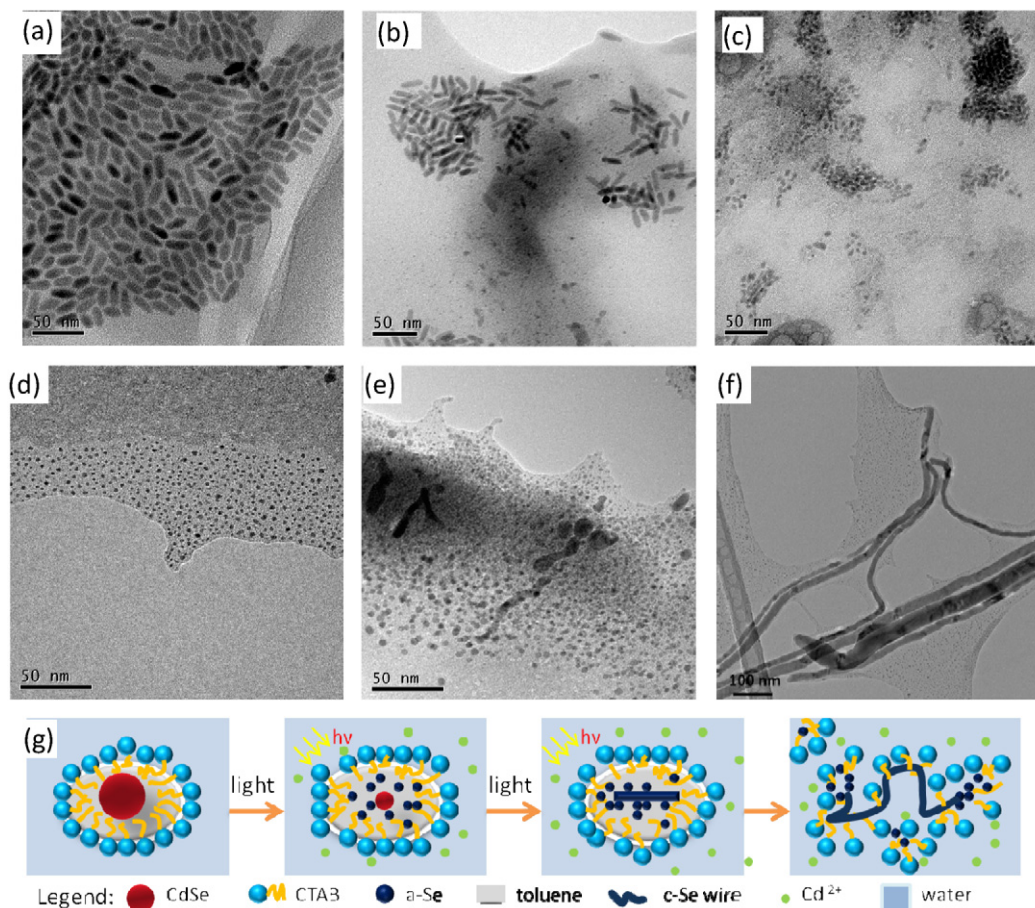
Figure 1. TEM images as a function of time showing the dissolution of CdSe nanocrystals in aqueous solution under room light: ((a)–(f)) samples after 0, 1, 3, 5, 7 and 24 h, respectively. (g) Schematic illustration of the dissolution of CdSe nanocrystals.

solution of surfactant, they still slowly dissolved under light. The transformation of CdSe nanorods to Se nanocrystals is clearly shown in figures 1(a)–(f). It can be seen that after 1 h of reaction, some of the CdSe nanorods have dissolved (see figure 1(b)). After a longer reaction time (3 h), the diameter and length of the nanocrystals have decreased substantially compared to the nanocrystals after 1 h (figure 1(c)). After 4 h of reaction, tiny black dots have appeared (figure 1(d)) which we expect to be Se clusters. They have nucleated from amorphous Se. Se nanowires are then formed within micelles and grow longer in the presence of surfactant (figures 1(e) and (f)). XRD patterns and an EDX spectrum from the Se nanocrystals are shown in figure S1 (available at stacks.iop.org/Nano/22/275706/mmedia).
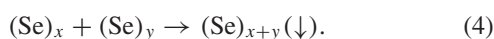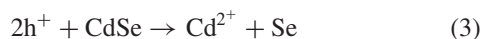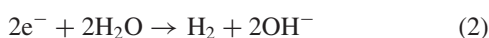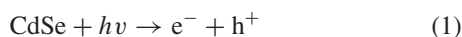
When the above solution was stirred under light, electron–hole pairs were generated upon absorption of light because absorption by CdSe extends into the visible range [16]. The photo-generated electrons reduce water to hydrogen and hydroxide ions (OH$^-$) while the photo-generated holes oxidize CdSe to Cd^{2+} and elemental Se. Based on the standard oxidation potential of Se^{2-}/Se (0.924 V) [17] and the standard oxidation potential of H$_2$/H$^+$ (−0.83 V), the dissolution reaction is thermodynamically favorable since the Gibbs free energy for the dissolution reaction is negative. The overpotential required for this reaction is provided by the

photon absorbed by the nanocrystals. Due to the concentration gradient of Cd^{2+} and elemental Se between the surface of the nanocrystals and the solution, there is a driving force for the outward diffusion of the ions from the surface of the nanocrystals (Kirkendall effect) [18]. This results in a hollow structure in the solid through an inter-diffusion process between different elements driven by their concentration gradient. The Kirkendall effect will also cause a reduction in the size of the nanocrystals. The concentration of Cd^{2+} in the aqueous solution was measured and was found to increase during the reaction (figure S3 available at stacks.iop.org/Nano/22/275706/mmedia). Due to the smaller ionic radius of Cd^{2+} (0.95 Å) compared to the atomic radius of elemental Se (1.90 Å), Cd^{2+} diffuses away from the nanocrystal faster than elemental Se. We propose that the dissolution reaction occurs at the interface of the micelles (oil-in-water). This is because CdSe nanocrystals are stable for several months in toluene under room light based on UV–vis absorption measurements. So the presence of water in this study is crucial for the dissolution. These fast moving Cd^{2+} may diffuse into the water phase as they carry charge while the slow moving elemental Se stays in the oil phase. This rapid loss of cadmium ions in CdSe nanocrystals leaves behind elemental Se, possibly in amorphous form [18]. This amorphous Se will nucleate and grow within the micelles when the Se concentration reaches
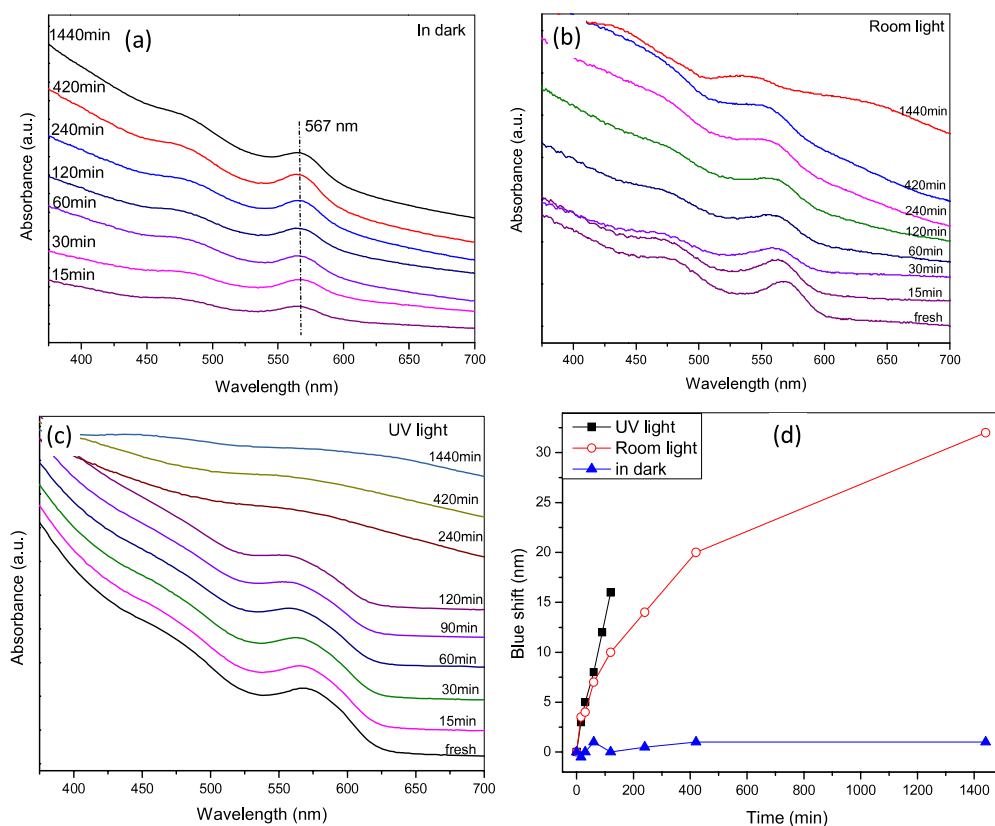
Figure 2. Temporal UV–vis absorption of CdSe nanocrystals in aqueous solution: (a) in darkness, (b) under room light and (c) exposed to UV light ($\lambda = 450$ nm). (d) Blue-shifts of the first excitonic absorption peaks derived from plots (a)–(c).

supersaturation, as it is a prerequisite for crystal nucleation and growth in solution. The diffusion of Cd^{2+} and consumption of elemental Se causes the gradual dissolution of the nanocrystals. This process also results in an increase in the pH of the solution due to the formation of hydroxide ions. The change in pH over time in the solution will be discussed later. Detailed photoredox reactions are proposed in equations (1)–(4) and shown schematically in figure 1(g).

$$CdSe + h\nu \rightarrow e^- + h^+ \tag{1}$$

$$2e^- + 2H_2O \rightarrow H_2 + 2OH^- \tag{2}$$

$$2h^+ + CdSe \rightarrow Cd^{2+} + Se \tag{3}$$

$$(Se)_x + (Se)_y \rightarrow (Se)_{x+y}(\downarrow). \tag{4}$$

In order to confirm that this is a photo-related process, we performed a series of controlled experiments. In the absence of light, there is no obvious change in the morphology, UV–vis absorption spectra, pH value or color of the solution after one day of constant stirring. Figures 2(a)–(c) show the UV–vis spectra of the solutions kept in the dark, exposed to room light and to UV light ($\lambda = 450$ nm). The blue shift of the first excitonic absorption peak in figures 2(b) and (c) implies a decrease in the diameter of the CdSe nanocrystals. It is observed that the dissolution speed of the nanocrystals is faster under UV light (figure 2(d)) than under room light. After 2 h, the blue shift is about 16 nm under UV light. The CdSe absorption peak is completely missing after 4 h. This implies

the dissolution of CdSe nanocrystals or the precipitation of them from the solution. The size of the nanocrystals is reduced slowly under room light illumination. The CdSe absorption peak is still observable even after one day of stirring. This implies that the wavelength of the radiation is a factor that governs the dissolution speed (figure 2(d)). In addition, there are two new absorption peaks observed in the absorption spectra after one day under UV light and room light exposure. These can be attributed to the formation of Se nanowires [19]. In the absence of light, the position of the first excitonic absorption peak does not change after one day of stirring, as shown in figure 2(c). This clearly indicates that light is essential to the dissolution process. It also implies that the dissolution is not simply caused by the hydrolysis of the cadmium–ligand bonds at the surface of the nanocrystals. This finding is similar to that of Aldana *et al* [11].

It was found that the presence of surfactants (such as CTAB) in the solution can accelerate the dissolution speed. This is because surfactants help to form micelles, thus increasing the surface area of the nanocrystals exposed to water and light during the photoredox reaction. It was also found that the type of surfactant is not important. Regardless of whether the surfactant was a cationic (CTAB), anionic (AOT or SDS) or nonionic surfactant (Pluronic P123), the CdSe nanocrystals dissolved after a day of stirring. In addition, it was also found that the presence of oxygen in the solution is not a key factor for the dissolution. Although the Se surface sites on the CdSe nanocrystals may be oxidized to SeO_2 due to the presence of
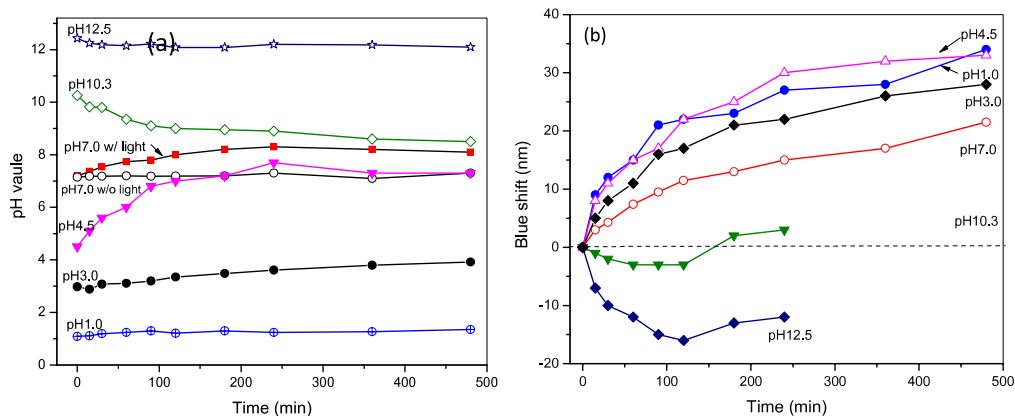
Figure 3. (a) Change of pH with time for CdSe nanocrystals starting from pH values of 1.0, 3.0, 4.5, 7.0, 10.3 and 12.5, and (b) blue-shifts of the first excitonic absorption peaks of samples starting with different pH values.

small amounts of oxygen in the aqueous solution [20], our results showed that the presence of oxygen did not significantly affect the dissolution speed of the CdSe nanocrystals.

The evidence that supports the mechanism proposed for this dissolution can be seen from the change in the pH of the solution. The pH increases as hydroxide ions are generated based on equation (2). The pH of the original solution (around 7) gradually increased as the reaction continued (figure 3). It reached a maximum after 4 h of reaction. Comparing the pH value of nanocrystal systems with or without light, the change in pH in the absence of light is negligible. This confirms that the dissolution is a photo-related process. We then investigated the effect of the initial pH of the solution on the dissolution of CdSe nanocrystals. The pH of the solutions was adjusted by adding small amounts of NaOH or HCl. It was found that if the medium were strongly acidic (pH between 1.0 and 3.0), the pH value of the solution would not change too much during the reaction. When the medium is moderately acidic (pH = 4.5), the pH increases very quickly as the reaction takes place. It is observed that a rapid increase in the blue shift occurs for pH = 1.0, 3.0 and 4.5 (figure 3(b)). This is consistent with fast dissolution. An acidic medium is more favorable toward hydrogen and OH$^-$ generation since the forward reaction is more favorable (refer to equation (2)). This study implies that the dissolution was accelerated in an acidic medium, whereas when the initial solution pH was alkaline (e.g. between 10.3 and 12.5), pH values decreased gradually for pH = 10.3 and slightly for pH = 12.5 within the first 2 h. This may be due to the formation of Cd(OH)$_2$ precipitates which consume Cd^{2+} and OH$^-$. An alkaline condition may cause the micelles to agglomerate and precipitate. This is consistent with the red shift of the absorption peak from these samples. This conclusion is contrary to that of Mulvihill *et al* [12]. They found that higher pH values (pH > 8.7) drove the equilibrium toward lower degrees of aggregation. It is because of the precipitate that slower dissolution of CdSe nanocrystals in alkaline conditions occurs.

In summary, we propose a dissolution pathway for CdSe nanocrystals in aqueous solution. It was found that light is a key factor affecting the dissolution of nanocrystals. In

the presence of light, the electrons generated from CdSe nanocrystals reduce water to hydrogen and hydroxide ions (OH$^-$) while photo-generated holes oxidize CdSe to Cd^{2+} and elemental Se. Cd^{2+} and elemental Se diffuse from the surface of the nanocrystals to solution driven by the concentration gradient. This results in an increase in both the Cd^{2+} concentration and the pH of the solution. In the absence of light, there is no obvious change in the nanocrystal morphology, UV–vis absorption spectra, pH value or color for the solution after a day of stirring. We also studied the effect of the initial pH of the solution on the dissolution of CdSe nanocrystals. It was found that the dissolution was accelerated in an acidic medium while moderate alkalinity (pH = 10.3) can slow down the dissolution, possibly due to precipitation of nanocrystals. This study has strong implications for the use of these crystals in aqueous environments (bioimaging and dye-sensitized solar cells). For such applications, these nanocrystals need a shell to improve their stability.

Acknowledgments

References

[1] Huynh W U, Dittmer J J and Alivisatos A P 2002 *Science* **295** 2425–7
[2] Fahmi A, Pietsch T, Bryszewska M, Rodríguez-Cabello J C, Koceva-Chyla A, Arias F J, Rodrigo M A and Gindy N 2010 *Adv. Funct. Mater.* **20** 1011–8
[3] Kumar S and Nann T 2006 *Small* **2** 316–29
[4] Wang N, Cai Y and Zhang R Q 2008 *Mater. Sci. Eng.* R **60** 1–51
[5] Lu W and Lieber C M 2006 *J. Phys. D: Appl. Phys.* **39** 387–406
[6] Xi L F, Tan W X W, Boothroyd C and Lam Y M 2008 *Chem. Mater.* **20** 5444–52
[7] Zou G, Li H, Zhang Y, Xiong K and Qian Y 2006 *Nanotechnology* **17** S313–20

[8] Xi L F, Boothroyd C and Lam Y M 2009 *Chem. Mater.*
     21 1465–70
 [9] Peng X 2003 *Adv. Mater.* **15** 459–63
[10] Manna L, Scher E C and Alivisatos A P 2000 *J. Am. Chem.
     Soc.* **122** 12700–6
[11] Aldana J, Wang Y A and Peng X 2001 *J. Am. Chem. Soc.*
     123 8844–50
[12] Mulvihill M J, Habas S E, Plante I J, Wan J and Mokari T 2010
     Chem. Mater. **22** 525–52
[13] Shibasaki Y, Kim B S, Young A J, McLoon A L, Ekker S C and
     Taton T A 2009 *J. Mater. Chem.* **19** 6324–7
[14] Nowack B and Bucheli T D 2007 *Environ. Pollut.* **150** 5–22
[15] Lin D and Xing X 2008 *Environ. Sci. Technol.* **42** 5580–5

[16] Schiavello M (ed) 1985 *Proc. NATO Advanced Study Institute
     on Photoelectrochemistry, Photocatalysis, and
     Photoreactors: Fundamentals and Developments* (Berlin:
     Springer) part II
[17] Tang Z, Wang Y, Sun K and Kotov N A 2005 *Adv. Mater.*
     17 358–63
[18] Zeng J, Liu C, Huang J, Wang X, Zhang S, Li G and
     Hou J 2008 *Nano Lett.* **8** 1318–22
[19] Gates B, Mayers B, Cattle B and Xia Y 2002 *Adv. Funct.
     Mater.* **12** 219–27
[20] Li R, Lee J, Yang B, Horspool D V, Aindow M and
     Papadimitrakopoulos F 2005 *J. Am. Chem. Soc.*
     127 2524–32