

Controlled optical properties of water-soluble CdTe nanocrystals via anion exchange

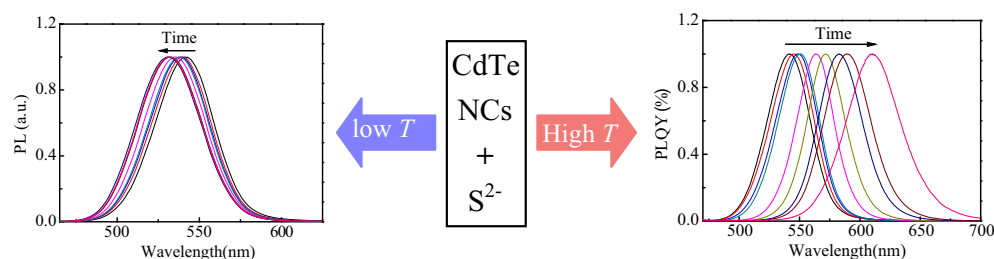


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GRAPHICAL ABSTRACT



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ABSTRACT

We report a study on anion exchange reaction of CdTe nanocrystals with S^{2-} in aqueous solution under ambient condition. We found that the optical properties of CdTe nanocrystals can be well tuned by controlling the reaction conditions, in which the reaction temperature is crucially important. At low reaction temperature, the product nanocrystals showed blue-shifts in both absorption and PL spectra, while the photoluminescence quantum yield (PLQY) was significantly enhanced. When anion exchanges were carried out at higher reaction temperature, on the other hand, obvious red shifts in absorption and PL spectra accompanied by a fast increase followed by gradual decrease in PLQY were observed. On variation of S^{2-} concentration, it was found that the overall kinetics of Te^{2-} for S^{2-} exchanges depends also on $[S^{2-}]$ when anion exchanges were performed at higher temperature. A possible mechanism for anion exchanges in CdTe NCs was proposed.

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1. Introduction

Semiconductor nanocrystals have attracted considerable interest because of their potential attractive applications in optoelectronics, photovoltaic devices, bio-labeling, and so forth [1–7]. To fulfill the requirement of the devices, many synthetic approaches have been developed to control their structures and thereby their properties of the resultant nanocrystals. Among those, the recent

developed ion exchange reaction has been demonstrated to be a fascinating way because of its simplicity as well as enables to fabricate a variety of inorganic semiconductor NCs with high compositional and structural complexity [8–13]. For example, by using CdE (E = S, Se, Te) as the starting materials, Alivisatos et al. reported that Cd^{2+} can be replaced by Ag^+ to form Ag_2E (E = S, Se, Te), while their original morphologies were preserved [13]. Nevertheless, ion exchange reactions are largely limited to cations, little work has been reported on anions [9,14,15]. Dloczik et al. reported that the oxygen in ZnO can be exchanged by sulfur to produce ZnS [14]. Saruyama et al. reported that ionic CdS can be transformed to CdS/CdTe heterodimers via a partial anion

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exchange reaction of CdS with octylphosphine telluride at high temperature (260 °C) [15].

To precisely control the structure and thus the property of nanocrystal prepared through ion exchange reaction, it is very important to control the kinetics and thermodynamics of the ion exchanges [11,16]. Miszta et al. studied the cation exchange of octapod-shaped CdSe/CdS with Cu^+ , and found that the structure of the product nanocrystals can be controlled by alternating the amount of Cu^+ [17]. By changing the solvent environment to modify the cation solvation conditions, Wark et al. found that the cation-exchange efficiency of metal chalcogenide nanocrystals can be well controlled [18]. In principle, ion exchange involves diffusions and reactions of ionic reactants. Due to the important role of temperature in controlling the kinetics of diffusion and chemical reaction, it is expected that the structure of the product nanocrystals and thus their properties can be controlled by varying the temperature of the exchange reactions. Nevertheless, little work has been reported regarding this issue [19]. This is partly due to the fast ion exchange rate of nanocrystals especially for cation exchanges [6,13].

In the present work, we demonstrate an anion-exchange reaction of water-soluble CdTe NCs with S^{2-} under ambient condition, which is thermodynamically favorable because of the larger formation Gibbs energy of CdTe ($\Delta_f G = -92.0 \text{ kJ mol}^{-1}$) than CdS ($\Delta_f G = -156.5 \text{ kJ mol}^{-1}$) [20]. We focused mainly on the control of kinetics and thermodynamics of the exchange reactions to tune the optical properties of nanocrystals. On variation of the reaction temperature, we noticed that the optical properties (absorption and emission) of the product NCs were largely varied, showing a strong temperature-dependent behavior. On the other hand, it was observed that S^{2-} concentration has also impact on the overall kinetics of reactions when the exchanges were performed at higher temperature. The results revealed that reaction temperature is key important in controlling the dynamics of Te^{2-} for S^{2-} exchanges and thus the properties of the resultant NCs.

2. Experimental

CdTe NCs were prepared as reported before [21]. Typically, $\text{CdCl}_2 \cdot 5\text{H}_2\text{O}$ was dissolved in distilled water and thioglycolic acid (TGA) was added under stirring. After TGA was complete dissolved, the pH of the solution was adjusted to ca. 11 by dropwise addition of 1 M NaOH solution. H_2Te gas (generated by the reaction of 1 M HCl with 1 M KHTe) carried by N_2 gas, was passed through the solution under violent stirring. After stirring for ca. 30 min in an ice-water bath, the reaction mixture was refluxed at 90 °C to get TGA stabilized CdTe NCs. The as prepared CdTe NCs was precipitated and washed with ethanol to remove the unreacted reactants and TGA. After redissolved in distilled water, the pH of the solution mixture was adjusted to ca. 10 using 1 M NaOH solution. The resultant CdTe NCs were then mixed with Na_2S solution under ambient condition at different temperature to initiate anion exchange. The concentration of CdTe stock solution was determined from the maximum of the lowest energy absorption peak.

UV–Vis absorption and photoluminescence (PL) spectra were measured using Lab Tech-UV2000 UV–Vis spectrophotometer and a HITACHI F-4500 FL Spectrophotometer (excitation wavelength: 400 nm) respectively. PL quantum yields (QY) of the NC solutions were determined using rhodamine 6G (laser grade, Lambda Physik) in ethanol as a standard (QY = 95%). The crystallographic structures of the CdTe NCs were analyzed by X-ray diffraction (XRD) (Shimadzu 2500VB2) at 40 kV, 200 mA with Ni filter and Cu α -radiation. Transmission electron microscope (TEM) was recorded on a JEOL JEM-2100F, operating at an acceleration voltage of 200 kV. TEM samples were prepared by dropping diluted CdTe

NC solution onto carbon-coated copper grids. Energy dispersive X-ray (EDX) spectrometers fitted to electron microscopes were used for elemental analysis.

3. Results and discussion

Anion exchange reactions were carried out by refluxing CdTe NCs and S^{2-} mixture under ambient condition at a preset temperature as stated in the experimental section. On increasing the reaction time, we found that the color of the solution is gradually changed. Interestingly, we noticed that the change of solution color was closely related to the reaction temperature. At lower temperature, continuous lightening of the solution color from orange-red to yellowish-green¹ was observed, but it underwent a fast lightening followed by gradually change to the final dark-red when the reaction was carried out at higher temperature (Fig. 1). Fig. 2 shows the representative PL spectra (normalized to the first emission maximum) of the product NCs as a function of time at reaction temperature of 40 °C, 50 °C and 90 °C respectively. The reaction conditions were identical, apart from the reaction temperature. As clearly displayed in the figure, the prolonging of time resulted in gradual shifts of PL spectra to short wavelength when anion exchanges were performed at 40 °C (Fig. 2A), while their full widths at half maximum (FWHM) were maintained between 36 nm and 38 nm. When temperature was increased to 50 °C, however, PL spectra together with their FWHMs were found to keep almost unchanged during the period of refluxing (Fig. 2B). When reaction temperature was further increased to 90 °C, on the other hand, obvious shifts of PL spectra to longer wavelength were observed (Fig. 2C). Their FWHMs of the PL spectra were found to be kept unchanged during the first stage of the reaction (<9 h), which was slightly broadened with further prolonging the reaction time. The corresponding absorption spectra showed the similar tendencies to the PL spectra, which demonstrated blue- and red-shifts at lower and higher temperature respectively (insets of Fig. 2). These results indicate that absorption and emission properties of the resultant NCs prepared through Te^{2-} for S^{2-} anion exchanges is closely related to the reaction temperature, which was further confirmed by varying the reaction temperature in more detail (Fig. 2D). As shown in Fig. 2D, we also noticed that the extent of PL shifts is depended on the reaction temperature, where the increase of temperature leads to the larger shifts of PL spectra. Note that, sole peak in either PL or absorption spectra of all the cases were observed, implying the high purity of NCs without the formation of any other separate semiconductors.

Moreover, photoluminescence quantum yields (PLQY) of the product NCs collected at different time point during anion exchanges were calculated. Fig. 3 presents the temporal evolution of PLQY at different reaction temperatures. It is clear that PLQY of the product NCs is continuously changed during the Te^{2-} for S^{2-} anion exchanges. In particular, we noted that the variation of PLQY is strongly depending on the reaction temperature. At lower temperature, gradually increases in PLQY were observed as the anion exchange progressed. While reached its maximum value, PLQY kept almost unchanged even the reaction time was further prolonged. In contrast, when reactions were carried out at higher temperature, a first increase followed by decrease in PLQY was observed. The time to reach its maximum PLQY is in inverse proportion to the reaction temperature. For example, it took 9 h to reach its maximum PLQY at 40 °C, but only 5 min was needed to reach its maximum at 90 °C. Meanwhile, we noted that the maximum PLQY of the product NCs depends also on the reaction

¹ For interpretation of color in Fig. 1, the reader is referred to the web version of this article.

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