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Automatically Purification of Aqueous CdTe Nanocrystals in Water-ethanol Co-environment

Yuan Jiang · Chunlei Wang · Shuhong Xu · Haibao Shao ·
Xiaoyan Lin · Zhuyuan Wang · Yiping Cui

Abstract Purification is a separated post-treatment step after the synthesis of nanocrystals (NCs) in order to exclude excess ligands and monomers in NC solution. The common purification process involves many manipulations, such as concentrating, addition of anti-solvents and centrifugation, which are troublesome and time consuming. In this work, we originally integrate NC synthesis and NC purification in one-pot via selecting water-ethanol co-environment for NC synthesis and NC purification. Our research shows that NCs can grow in water-ethanol mixture. When growing into critical size, NCs will automatically precipitate from the solution. Element analysis demonstrates that precipitates fraction fits well with stoichiometric of ligand-capped NCs. Excess monomers are left in supernatant, and thus achieving automatically purification of NCs in the water-ethanol co-environment. By adjusting the volume ratios of water and ethanol in bi-solvent system, different-sized purified NCs can be controlled. Besides, this water-ethanol co-environment can be used in both thermal-promoted and hydrazine-promoted growth.

Introduction

Semiconductor nanocrystals (NCs) exhibit unique size-dependent optical properties due to quantum confinement effect [1]. NCs can be synthesized either in high temperature organnic media via organicmetally synthesis method [2] or in boiling water via aqueous synthesis method [3]. As compared with the organic one [4], aqueous synthesis of nanocrystals is more reproducible, cheaper, and less toxic. The hydrophilicity of the products holds a great promise in biological application.

During NC synthesis process, excess ions, ligands, and compounds are introduced into NC solution to maintain compact ligand modification on NC surface. These matters may cause damage in application [5–7], especially in bio-application [8, 9]. Thus it is necessary to remove these excess materials by purification. Moreover, unlike NC purification usually proceeds in water-ethanol solution at room temperature, NC synthesis usually realizes in water solution at elevated temperature such as the boiling point of water. Due to the different solution environment and temperature, NC synthesis and NC purification usually manipulate via two separated steps and lots of time and energy should be devoted in. Besides, the purification process also involves many complicated manipulations, such as concentrating, addition of anti-solvents [10] or salt [11] and then centrifugation, which are also time-consuming and energy-consuming.

If NC synthesis and NC purification can be integrated in one step, lots of time and energy could be saved. We herein develop a new method for one-pot preparing purified NCs by selecting water-ethanol mixture as NC synthesis and NC purification co-environment. Our research shows that NCs can grow in water-ethanol mixture. After NC growth by thermal-promoted or by hydrazine-promoted into critical size, NCs will automatically precipitate from the solution. By separating the precipitates, purified NCs are obtained. Furthermore, simply by controlling the ethanol concentration in water-ethanol co-environment, the critical size of NCs precipitates can be controlled and thus automatically purified NCs with different sizes and emission can be obtained.

Y. Jiang · C. Wang · S. Xu · H. Shao · X. Lin · Z. Wang · Y. Cui (✉)
Advanced Photonics Center, School of Electronic Science and
Engineering, Southeast University, Nanjing 210096, China
e-mail: cyp@seu.edu.cn

Experimental

Materials

Mercaptopropionic acid (MPA) and Te powder were purchased from Aldrich. Hydrazine ($N_2H_4 \cdot H_2O$, 85 %), $CdCl_2$, $NaBH_4$, NaOH and ethanol were commercially available products and used as received. NaHTe solution was prepared by using Te and $NaBH_4$ according to the reference methods [5]. Deionized water was used in all preparation.

Synthesis of CdTe NCs Precursors

MPA capped CdTe NCs were prepared according to the reference methods [12]. Namely, the mixture of $CdCl_2$ and MPA was adjusted to pH 9.1 by using 1.0 mol/L NaOH solution, and then the mixture was aerated with N_2 for 30 min. After injection of freshly prepared NaHTe solution into the mixture, CdTe crude solution was obtained. The initial molar ratio of $CdCl_2$/MPA/NaHTe was 1.0/2.4/0.2.

Synthesis of Automatically-precipitated CdTe NCs by Refluxing

50 mL CdTe precursors (2.6 mmol/L referring to Cd^{2+}) was mixed with ethanol varied from 20 mL to 140 mL, and then the mixture was refluxed for specific time until CdTe NCs naturally precipitated. The precipitates would not sink to the bottom until storage about 48 h in the dark and N_2 atmospheres. For the sake of fast precipitation, we centrifuged resultant precipitated NCs at 8000 r/min for 20 min and then redispersed precipitates in water.

Synthesis of Automatically-precipitated CdTe NCs at Room Temperature

Ethanol (3, 5, 6, 7, 8, 10, 12 mL) was mixed with water keeping total volume in 16 mL. The series of ethanol-water mixture was mixed with 40 mL of CdTe precursors (5 mmol/L referring to Cd^{2+}) and 7 mL hydrazine. The concentration of the diluted solution was 3.18 mmol/L referring to Cd^{2+}. The concentration of ethanol varied from 0.8 to 3.3 mmol/L. The mixture was stored at room temperature to maintain the growth of CdTe NCs. The resultant precipitated NCs were centrifuged at 8000 r/min for 20 min and were redispersed in water before spectra measurements.

Characterization

UV–vis absorption spectra (UV) were recorded with a Shimadzu 3600 UV–vis near-infrared spectrophotometer. Fluorescence experiments and PL decay experiments were performed with an Edinburgh FLS 920 spectrofluorimeter.

The excitation wavelength was 400 nm. Transmission electron microscopy (TEM) was recorded by a Tecnai F20 electron microscope with an acceleration voltage of 200 kV. X-ray photoelectron spectroscopy (XPS) was investigated by using a PHI550 spectrometer with an Mg Kα excitation (1253.6 eV). Binding energy calibration was based on SiO_2 at 103.0 eV. X-ray powder diffraction (XRD) investigation was carried out by using the D/max-2500/PC diffractometer with Cu Kα radiation (λ=1.5418A°). For XPS and XRD measurements, CdTe NCs powder was used. To obtain the powder, freshly prepared NCs were precipitated from the solution and then dried in vacuum.

Results and discussion

Automatically-precipitated NCs by Reflux

The mixture of water and ethanol is selected as NC synthesis and NC purification co-environment for one-step synthesis of purified NCs. In a typical synthesis process, NCs nucleate in water environment. Then, ethanol is added into aqueous NC nuclei solution to provide a water-ethanol co-environment for the subsequent NC growth and NC automatic precipitation. NC nuclei can well disperse in water-ethanol co-environment without precipitation. Once growth to a critical size, NCs will automatically precipitate from the water-ethanol co-environment, leaving excess materials in the solution. These precipitates well redisperse in water and purified NCs are obtained. (Scheme 1)

Taking green emitted NCs for example, water and ethanol were mixed in a volume ratio of 5:14 as NC growth environment. After reflux for about 3 min, NCs precipitated from the solution. The precipitated NCs could perfectly dissolve in water. The exciton peak of NCs is 445 nm (Fig. 1a).

Baseline of NCs absorption spectra is used here to judge whether NCs precipitate or not. Before precipitation, absorption spectra of NC solution has a horizontal baseline between 650 and 800 nm since NCs are too small to absorb light in this wavelength range. After precipitation, baseline of NCs absorption spectra will slope or rise up due to light scattering brought by NC precipitates. As shown as in Fig. 1a, an obvious slope and rise up in 650–800 nm band of NCs absorption spectra is observed after precipitation. Herein, we take an elevation of 0.02 at 800 nm as an indicator for NC precipitation. When NC growth is terminated at this time, we calculated the ratio between NC exciton peak intensity in the redispersed solution and the sum of NC exciton peak intensity in the redispersed solution (blue dot line in Fig. 1b) and in supernatant solution (red dash line in Fig. 1b). Since absorbance is proportional to the concentration of NCs, The ratio 85 % was considered to be the yield rate of NCs. That is 85 % NCs can be precipitated from the solution. As shown in TEM images (Fig. 1c), CdTe NCs appear as monodispersed
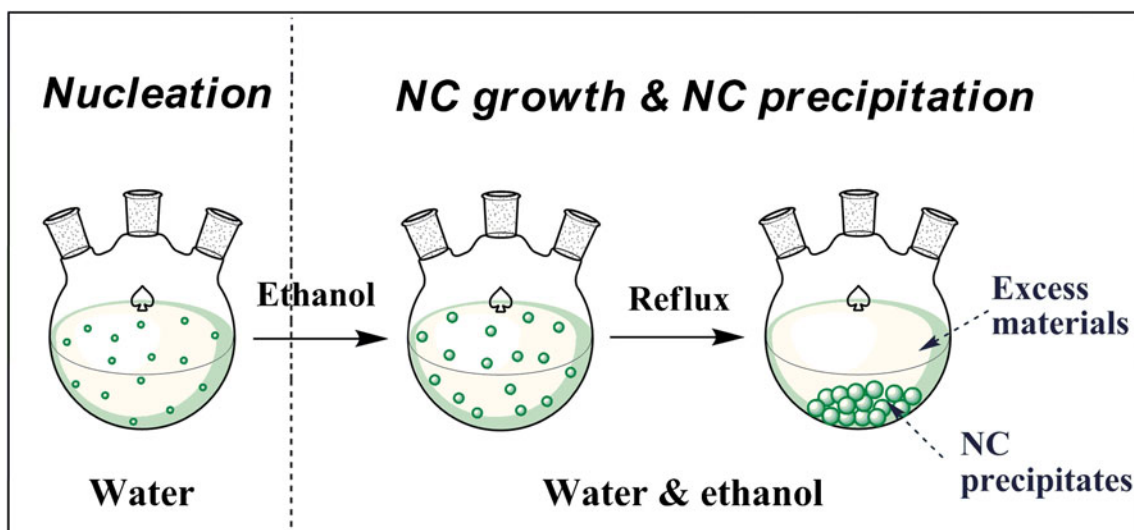
**Scheme 1** Sketch of NCs automatically purification via a water-ethanol co-environment system

spherical particles with single-crystalline structures. The size of CdTe NCs is about 2.7±0.5 nm according to histogram associated with TEM images.

XRD is applied to detect the structure of NCs. Figure 2a showes XRD patterns obtained from CdTe NCs powders. Diffraction peak at 24.03, 39.7 and 47.0° assign to (111), (220) and (311) facet of cubic bulk CdTe, respectively. This result indicates that the lattice parameters fitted well to the zinc blende structure of bulk CdTe crystal.

XPS characterizes NC precipitates surface structure. The Te_{3d}, Cd_{3d} and S_{2p} energy level of CdTe nanoparticles are represented in Fig. 2b. The binding energy peak at 161.2 eV assigns to 2p energy level of S^{2-}. Since S^{2-} can only come from thiol group on NC surface, the present form of S in XPS result indicates no oxidation of thiol ligands outside NCs. Besides, no oxidation peaks of Te atoms are observed, indicating no oxidation of Te inside NCs. This result also implies the thiol ligands outside NCs well protect NCs from oxidization. Furthermore, the Cd/Te/S atoms ratios obtained from XPS data is 1.8:1.0:1.6. It should be mentioned that one Cd^{2+} ion link two thiol group in MPA molecule(HS-CH2-CH2-COOH). The Cd/Te/S ratios fits well with Cd=Te+1/2S, indicating that precipitates fraction fits

Fig. 1 **a** Absorption of CdTe NCs (*solid*) before and (*dash*) after precipitation (2 and 3 min, respectively); **b** Absorption of CdTe NCs. CdTe NC (*solid*) precipitation solution was centrifuged at 8000 r/min for 20 min. After removing (*dash*) supernatant solution, the precipitates was (*dot*) redispersed in equal volume deionized water; **c** TEM images associated with histogram of NCs after precipitation. The volume ratio of water and ethanol was 5:14
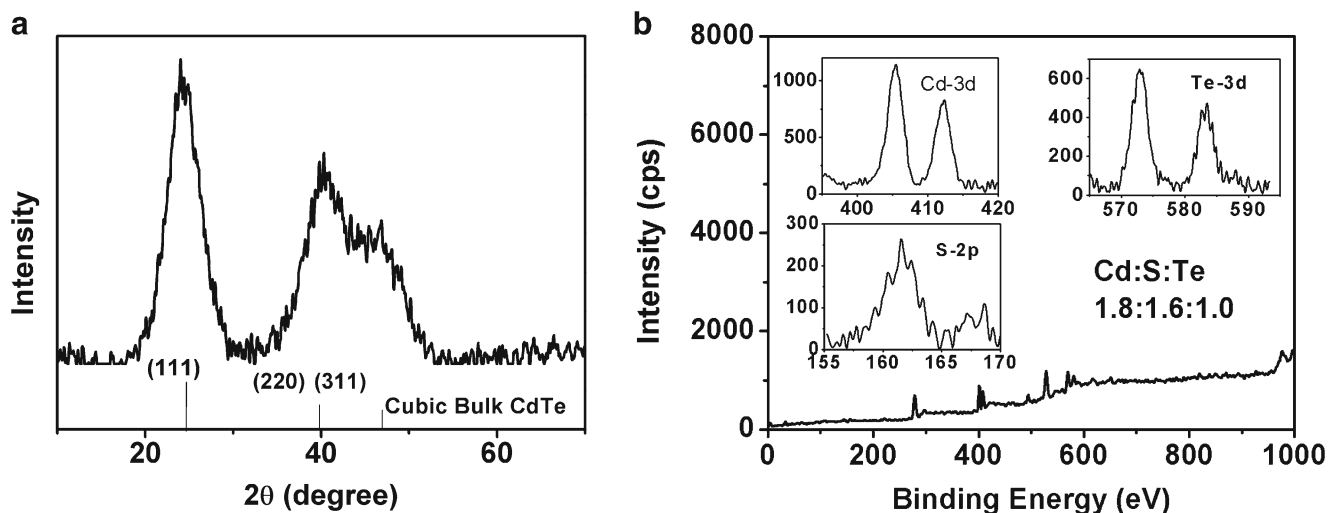
a

b

Cd:S:Te
1.8:1.6:1.0
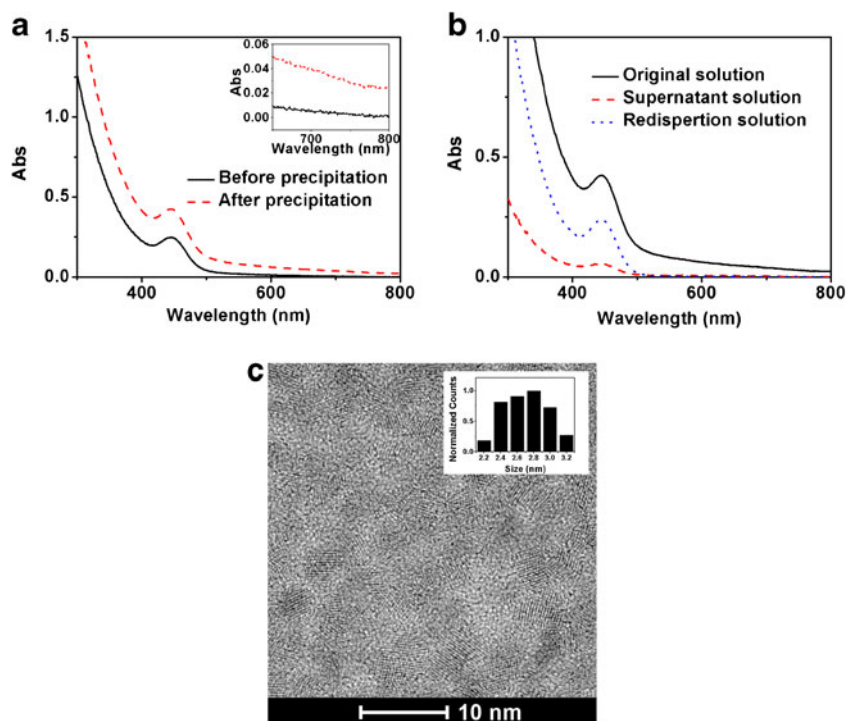
Fig. 2 a XRD patterns of CdTe NCs after precipitation. The standard XRD patterns of bulk cubic zinc blende CdTe (*bottom*) were also indicated; **b** XPS patterns of CdTe NCs after precipitation. Inset picture: zoomed results of Cd, Te and S. The atomic ratio of Cd/Te/S was

calculated according to the integrated intensity and the sensitivity factor of each element. The PL peak position of original CdTe NCs used for XRD measurement was 514 nm

well with stoichiometric of ligand-capped NCs. Compared with the initial feeding ratios of reactants (Cd:Te:S of 5.0:1.0:12.0), the measured Cd/S/Te atoms ratios from XPS only reflect chemical composition of NCs but not chemical composition of feeding ratios. In other words, only NCs can automatically precipitate from the water-ethanol co-environment, leaving excess ions, ligands and compounds in supernatant. Thus, the purificaiton of NCs can be realized during the automatic precipitation process of NCs.

Adjustment of NCs Size

By adjusting volume ratios of water and ethanol during the synthesis process of NCs, as-prepared automatically purified NCs have different diameters and emission. A series of

volume ratios of water and ethanol was tried varying from 5:14 to 5:2. Figure 3 shows the evolution of the UV–vis absorption and PL spectrum of MPA stabilized CdTe NCs with luminescence from green to red. Reducing water-ethanol volume ratios, NCs will not precipitate until grow into larger size. For instance, in the case of the water-ethanol volume ratio 5:14, NCs emit green fluorescence, while in the case of 5:2, NCs will not precipitate until emitting red fluorescence. The sizes of CdTe NCs are calculated from absorption spectra according to the reference method [13] (Table 1).

The relative dielectric constants of NCs solution (ε_{mix}) at different water-ethanol volume ratios are shown in Table 1. Compared with relative dielectric constant of original aqueous NC solution without ethanol ε_{water} (ε_{water}=80.1), ε_{mix} greatly decreases. According to our recent research about the impact
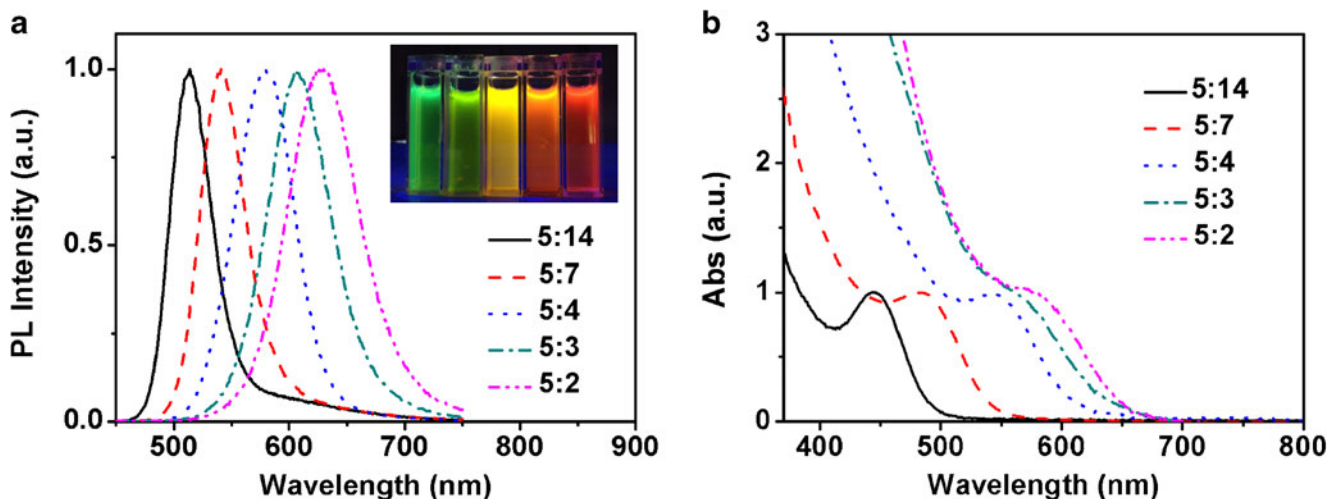
a

b

Fig. 3 a PL Spectra and (**b**) absorption Spectra of CdTe NCs. Inset: images of redispersed NC solution under the irradiation of a UV lamp (365 nm). The volume ratio of water and ethanol was varied from 5:14 to 5:2 (from *left* to *right*). The excitation wavelength of PL spectra was 400 nm

Table 1 Evolution of reaction time, excition peak., PL peak, size, critical relative dielectric constants (ε) and Quantum yield (Q.Y.) of CdTe NC solution

Volume ratios of water & ethanol	Reaction Time (h)	Exciton Peak (nm)	PL peak (nm)	Size[a] (nm)	Critical ε_{mix}	Q.Y.[b]
5:14	0.08	445	514	2.7	35.2	10.0 %
5:7	6	485	541	3.1	42.6	6.4 %
5:4	14	540	581	3.5	50.1	7.3 %
5:3	14	563	607	3.7	54.2	9.1 %
5:2	25	587	628	4.0	60.0	5.7 %

[a] The sizes of CdTe NCs are calculated from absorption spectra according to the reference method [13]

[b] The relative dielectric constants of NCs solution (ε_{mix}) are calculated according to the reference method [14]

of ethanol during NC precipitaion [7, 14, 15], the decrease of ε_{mix} will lead to the reduced inter-particle electrostatic repulsion of NCs, which then promotes the precipitation of NCs from the solution. Obviously the current work realizes NCs automatically precipitation with water-ethanol mixture system by decreasing inter-particle electrostatic repulsion via ε_{mix}. An interesting phenomenon is that the critical value ε_{mix} leading to precipitation is exactly size dependent (Table 1). Large sized NCs have large critical value ε_{mix} for NC precipitation, whenas small sized NCs can only precipitate in the solution with small critical value ε_{mix}.

Automatically-precipitated NCs at Room Temperature

For the sake of energy-saving, we also obtained automatically purified aqueous CdTe NCs at room temperature. In 2010, researchers have achieved NCs growth at room temperature by adding hydrazine to the growing system [16]. This method

provided an alternative drive force for NC growth beside thermal-promoted NC growth at elevated temperature. Hydrazine-promoted NC growth can proceed at room temperature without extra thermal energy. In this work, we also verify that whether this water-ethanol co-environment can be used in such hydrazine-promoted growth. As shown in Fig. 4, we successfully obtain NC synthesis and NC purification at room temperature after adding hydrazine into water-ethanol mixture. Similarly to thermally-promoted growth, by adjusting concentration of ethanol during the hydrazine -- promoted growth, as-prepared automatically purified NCs also emit PL from green to red (Fig. 4a). For instance, in the case of the volume ratio of water-ethanol-hydrazine 46:10:7, NCs emitted green fluorescence (527 nm), while in the case of 53:3:7, NCs emitted red fluorescence (628 nm). Likewise, with the decrease of ε_{mix}, size of automatically precipitated NCs also decreases.

Conclusions

To realize the automatic purification of NCs, the mixture of water and ethanol is selected as the co-environment for NC synthesis and NC purification. NCs nucleate in water at first, and then NC nuclei disperse in water-ethanol mixture system without precipitation. When NCs grow into critical size, they will automatically precipitate from the mixture, leaving excess materials in supernatant. After decantation of supernatant solution, the precipitates well disperse in water again and the redispersed solution shows strong PL. In addition, the adding ethanol concentration plays a key factor in the automatic purification process of NCs. With the increased ethanol concentration, as-prepared auto-purified NCs have much larger diameters. In other words, through controlling the ethanol concentration, we can obtain auto-purified NCs with different
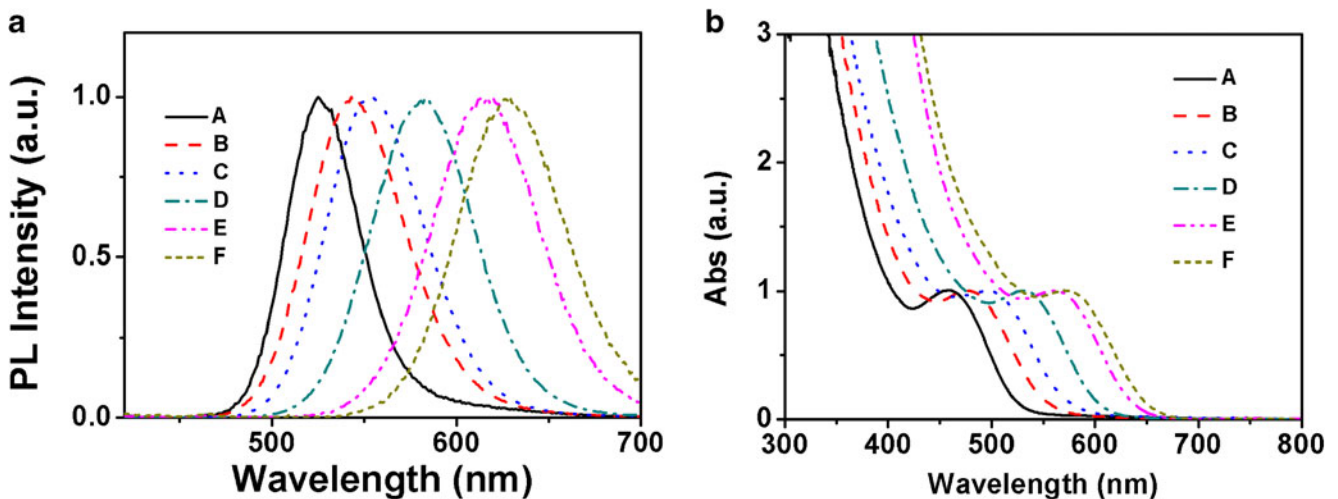

Fig. 4 **a** PL Spectra and (**b**) absorption Spectra of CdTe NCs. The excitation wavelength was 400 nm. The volume ratio of water-ethanol-hydrazine was (**A**) 46:10:7, (**B**) 48:8:7, (**C**) 49:7:7, (**D**) 50:6:7, (**E**) 51:5:7, and (**F**) 53:3:7. The concentration of hydrazine was unchanged

sizes. What's more, our research indicated that automatically purification can be realized in water-ethanol co-environment, no matter in thermally-promoted growth or hydrazine-promoted growth. Compared to the traditional NCs synthesis and post-treatment, this method simply realizes the integration of purification and synthesis of NCs in one-pot. Moreover, the current work also benefits for comprehending NC behaviors in a complex solvent system. We expect that the current work aids deep insight into NC behaviors at various chemical, physical, or biological environments in practical applications from academic to technical interests.

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