



Original Research Article

Synthesis of a Fluorescent Mechanochromic Polymer Based on TGA-Capped CdTe Quantum Dots and Liquid Latex

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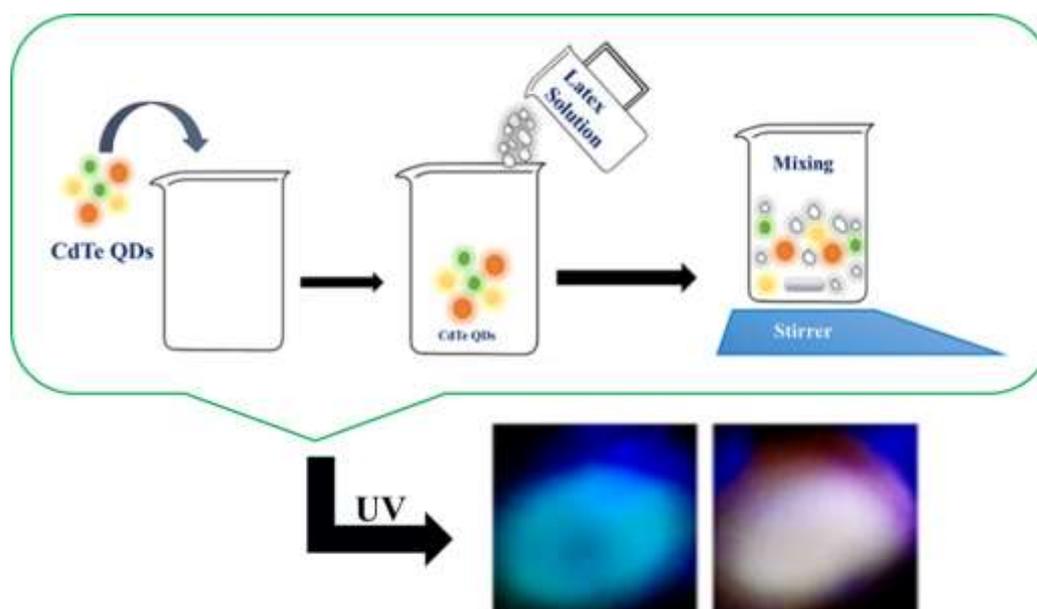
Mechanochromic Polymers

Quantum Dots

ABSTRACT

A flexible polymer based on latex and CdTe Quantum Dots (QDs) is introduced here which shows color changing properties under UV light as the polymer is stretched. After synthesis of TGA-capped CdTe QDs with different sizes and emissions in the optimal conditions, the flexible polymer is synthesized and different colors such as green, pale green, white, and pale red were observed under UV light. The effective parameters of fluorescent QDs such as size, extinction coefficients, and concentrations were calculated by absorption and emission spectra.

GRAPHICAL ABSTRACT



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Introduction

Many chameleons enjoy the notable skill to reveal complex and quick color changes for thermoregulation, predator avoidance, sexual selection, and camouflage. This remarkable capability has long inspired researcher to develop materials and devices to mimic similar functions [1-4]. Teyssier et al [5] demonstrated that chameleons shift colour through active tuning of a lattice of guanine nanocrystals within a superficial thick layer of dermal iridophores. However, some researchers believe that these changes are due to dispersion/aggregation of pigment-containing organelles within dermal chromatophores [6, 7]. In anyway, the synthesis of chromogenic materials has been an attractive topic because of their abundant potential applications in numerous fields, including drug delivery [8, 9], sensors, [10, 11] catalysts [12], optical data storage [13], and optoelectronic devices [14], etc .

Mechanochromic materials are force sensitive materials that provide new comprehension into the effects of stress on the polymeric materials. There is great interest in polymers in which the application of an external force causes the color changing. Many such materials have been made, but comparably few materials have been synthesized that respond in a suitable manner to mechanical pressure under UV light.

The polymers showing luminescence mechanochromism have potential applications in optical recording, pressure sensing, memory, or motion systems [15-17]. In general, the colour changes are produced by several mechanisms: differences in the molecular connections between dye compounds joined into the polymers, or in the molecular structures of combined dyes, and changing distance between particles in the material's lattice structure [5, 18].

In this study, a fluorescent mechanochromic polymer based on TGA-capped CdTe Quantum Dots and latex polymer is reported. Colloidal semiconductor nanocrystals with inherent

advantages of size-tunable emission, high quantum yield, low photobleaching, and high photochemical stability provide them with potentials to be applied in various applications, such as colloidal quantum dots light-emitting diodes, solar cells, photodetectors, field effect transistors, and bio-medical labeling, etc [19-22]. The intrinsic electronic states of semiconductor nanoparticles are mostly organized by quantum confinement, which makes them to be called as quantum dots (QDs). In a QD solid film, photogenerated excitons can be generally relaxed via radiative recombination and non-radiative recombination paths. The radiative relaxation usually happened in the individual QDs. The non-radiative relaxation procedures in QD groups generally contain: (i) exciton dissociation between adjacent QDs, (ii) photoexcited carrier trapping through inner and/or interfacial defects, and (iii) energy transfer in disordered QDs [23, 24]. When the energy landscape of the QD solid film is disordered, the energy transfer process between semiconductor QDs happens. In addition, the energy transfer can take place from the excited CdTe QDs to a quencher molecule. The recent event is created a great number of applications for fluorescent materials and QDs, especially in analytical chemistry [25-28]. The physical and mechanical properties of latex polymer films provide a great situation for creating a flexible polymer substrate. The formation of a latex film is very simple and does not require any additive or excessive chemical. Hence, it can be a considerable choice as a flexible substrate for TGA-capped CdTe Quantum Dots [29].

2. Materials and Methods

2.1 Chemicals and Materials.

Thioglycolic acid (TGA), sodium borohydride (NaBH₄), tellurium powder (Te), cadmium

chloride ($\text{CdCl}_2 \cdot 2\text{H}_2\text{O}$), and hydrochloric acid were obtained from Sigma-Aldrich. Sodium hydroxide (NaOH) was purchased from Merck. Fresh Latex solution was obtained from Tehran Market for Chemicals (Nasser Khosro St.). Deionized water having a resistivity of $18.2 \text{ M}\Omega$ was used in all the experiments.

2.2 Synthesis of TGA-capped CdTe QDs

The synthesis of QDs was performed by the following method: $160 \mu\text{L}$ of TGA and 0.212 g CdCl_2 (20% hydrated) were added to 30 ml deionized water and pH was adjusted to 9.1 by addition of 1.0 mol L^{-1} NaOH solution (total volume was 100 mL). The solution was deoxygenized by argon bubbling for 15 min (solution No. 1). To prepare the solution No. 2, 0.0524 g Te powder and 0.146 g NaBH_4 were dissolved in 160 mL deionized water under argon bubbling in a three-neck round bottom flask at 55°C to get a purple solution. Then, the solution No. 1 was added to solution No. 2 and the temperature was increased to 95°C . The reflux time can determine the size and emission of QDs.

2.3 Calculation of QDs' sizes

The diameter of the CdTe nanocrystal can be calculated by the following equation [30]:

$$D = (9.8127 \times 10^{-7}) \times \lambda^3 - (1.7147 \times 10^{-3}) \times \lambda^2 + (1.0064) \times \lambda - 194.84 \quad (1)$$

In the equation, λ is the first excitonic absorbance peak.

2.4 Calculation of the QDs' concentration

The extinction coefficient (ϵ) can be calculated by the following equation [30]:

$$\epsilon = 10043 \times (D)^{2.12} \quad (2)$$

D is the diameter of the CdTe nanocrystals, and ϵ is the molar absorptivity (extinction

coefficients) of the sample at a particular wavelength.

Using Beer-Lambert law:

$$A = \epsilon c l \quad (3)$$

Determination of CdTe QD concentration is possible, where A is the absorbance value in the first excitonic absorbance peak, c is the concentration of QDs, and l is the path length, the distance the light travels through the solution.

2.5 Preparation of latex polymer

Latex do not require any addiction to create a flexible rubber. Hence, the latex solution was added to a Petri dish, and it was then placed in an oven for 8 hours (temperature 60°C).

2.6 Preparation the color changing polymers

1.5 ml QDs green (674.52 mM), 3 ml QDs yellow (280.57 mM), and 4 ml QDs red (220.00 mM) dissolved in 20 ml latex liquid. Then, the solution was added to a Petri dish, and it was then placed in an oven for 8 hours (temperature 60°C).

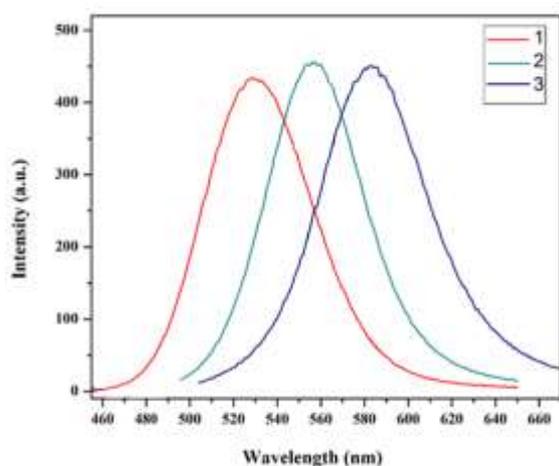
3. Results and Discussion

3.1. Synthesis of TGA capped CdTe QDs

The water-soluble thioglycolic acid (TGA)-capped CdTe quantum dots were synthesized according to a method that was explained in part 2.2. For optimization of the effective parameters, different reflux temperatures of 70°C , 80°C , and 95°C were considered for the QDs. The temperature of 95°C was used as the optimal for the next evaluations, which provide times of 30, 50, and 100 minutes for the synthesis of green (QD 1, 530 nm), yellow (QD 2, 561 nm), and red (QD 3, 588 nm) QDs, respectively (Table 1). Figure 1 shows the fluorescence spectra of the three QDs.

Table 1. Optimization of reflux temperatures and time for appearing fluorescence emissions of QDs.

Reflux Temperature (°C)	Green Emission (530 nm)	Yellow Emission (561 nm)	Red Emission (588 nm)
70	11 hours	13 hours	14 hours
80	5 hours	6 hours	8 hours
95	30 min	50 min	100 min

**Fig 1.** The fluorescence spectra of QD 1 (green), QD 2 (yellow), and QD 3 (red).

pH is another factor that can effect on the synthesis of QDs. To optimize it, different pH amounts of 7.5, 9.1, and 10.5 were considered that the intensities of 38, 137, and 89 were obtained. It is clear that 9.1 is the suitable pH for the synthesis of CdTe QDs.

To optimize molar ratio of Cd:Te:TGA, different amounts of molar ratios were considered in 95°C and pH=9.1. After 30 min, the fluorescence

intensities of TGA-capped CdTe QDs with green emission were measured (Table 2). By doing so, the molar ratio of 3:1:6 (for Cd:Te:TGA) was considered as the optimal ratio.

3.2 Optical characterization of TGA capped CdTe QDs

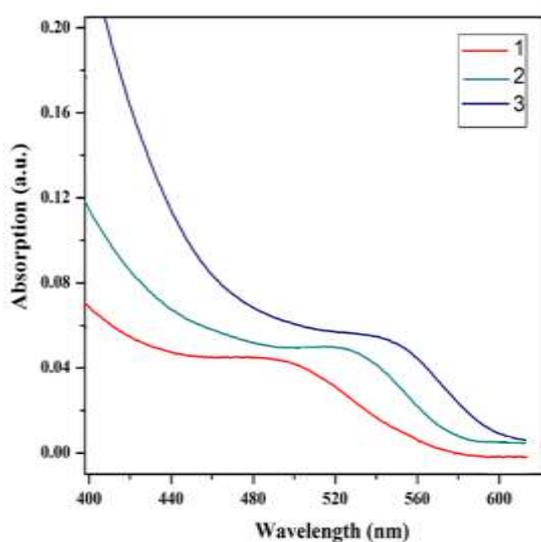
Size of QDs is a significant factor that is measurable by absorption properties of these nanoparticles. To do so, maximum wavelengths in absorption spectra (Figure 2) were used as λ in equation 1 (see section 2.3). As a result, the sizes of 1.9 nm, 2.79 nm, and 3.15 nm were obtained for green, yellow, and red QDs, respectively (Table 3). After using these calculated diameters in equation 2, the extinction coefficient (ϵ) can be calculated (Table 3). Extinction coefficient paves the way for the calculation of QDs concentration using the Beer-Lambert law (equation 3). The obtained concentrations are shown in Table 3.

Table 2. Optimization of molar ratio for CdTe QDs with green emission.

Cd:Te:TGA	1:1:1	1:2:1	1:2:2	2:1:1	3:1:1	3:1:3	3:1:6	3:1:9
Intensity (a. u.)	125	2	63	167	237	533	821	594

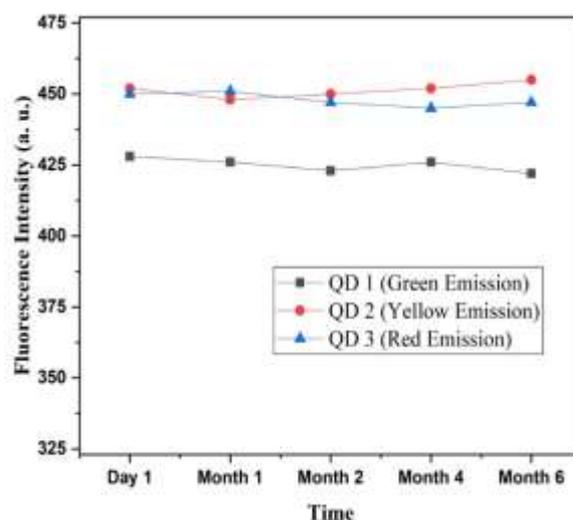
Table 3. Optical characterization of TGA-capped CdTe Quantum Dots with different sizes.

No.	Maximum wavelength in absorption spectrum	Maximum wavelength in emission spectrum	Size (nm)	(ϵ)	Concentration (mM)
1	486	530	1.90	39435.34	674.52
2	519	561	2.79	88299.81	280.57
3	542	588	3.15	114328.54	220.00

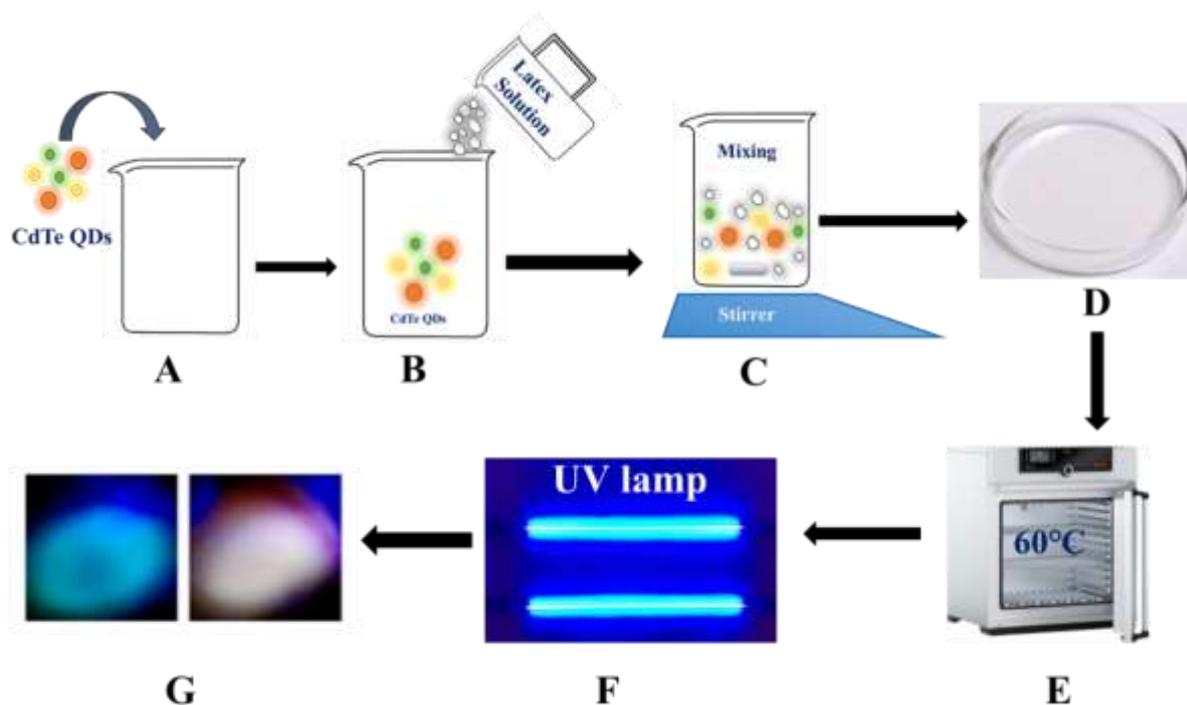
**Fig 2.** Absorption spectra of QD 1 (green), QD 2 (yellow), and QD 3 (red).

3.3 The stability of CdTe QDs

After synthesis, the stability of QDs was evaluated based on the emission spectra. Accordingly, the fluorescence spectra for several months after synthesis was compared with emissions of QDs at the first day. As shown in the figure 3, there is not a considerable change in the emission properties of CdTe QDs after six months. This is a significant factor for the applications of quantum dots in solar cells, bio-medical labeling, and color changing polymers.

**Fig 3.** Optical stability of TGA-capped CdTe quantum dots with green, yellow, and red emissions, over six months.

(B) 20 ml latex solution was added to the solution step A, (C) the obtained solution was mixed by a stirrer for 3 min, (D) then, the solution was poured into a Petri dish to create a layer of 3 mm thick, (E) the Petri dish was inserted into an oven (60°C) for 8 hours. The produced polymers showed fluorescence properties and by stretching them under UV light, various colors including green, white, and pale red were appeared.



Scheme 1. Synthesis of color changing polymers.

4. Conclusion

In summary, a new flexible polymer based on latex liquid and TGA-capped CdTe Quantum Dots with different sizes is presented in this study. It displays color changing capability under UV light as the polymer is stretched. After synthesis of TGA-capped CdTe QDs with different emissions of green, yellow, and red in the optimal conditions, sizes of QDs, extinction coefficient (ϵ), and QDs concentrations were calculated. In addition, the emission stability of CdTe QDs was evaluated that show a constant situation after six months. Finally, the synthesized flexible polymer showed different colors of green, pale green, white, and pale red under UV light.

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