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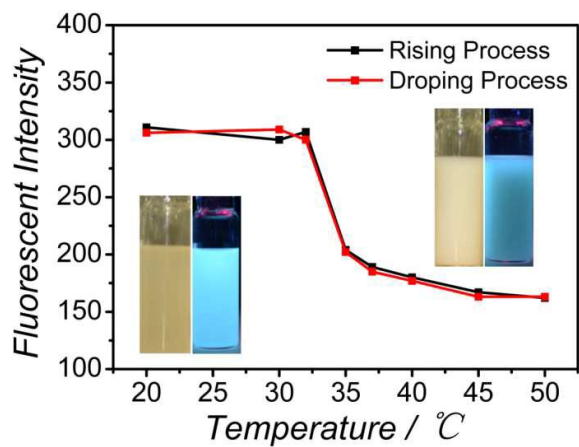
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PNIPAM & CDs composites have been used as a sensor of temperature. At around 32 °C, the fluorescent intensity decrease sharply because of CDs' self-quenching effect.



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Thermal Responsive Fluorescent Nanocomposites Based on Carbon Dots

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Currently, a broad series of methods to obtain photoluminescent (PL) carbon dots (CDs) have been developed. The CDs are one of novel fluorescent materials with the advantages of easy chemical modifications, chemical stability, biocompatibility as well as low toxicity. As a result, the nanocomposites based on CDs are of great potential for functional applications. In this paper, Poly (N-isopropylacrylamide) (PNIPAM)/CDs composites have been used as a temperature sensor. The detection signal is luminescence which possesses high sensitivity, improved facility and provides the possibility in visual detection. With the temperature increasing, the fluorescence intensity of the composites decreased sharply at around 32 °C with the existence of PNIPAM. The composites show perfect reversibility after 12 times of heating and cooling process. Moreover, compared with CDs, the CDs composites also show good UV resistance at high power UV exposure.

1. Introduction

In recent years, carbon dots (CDs) have drawn dramatical attention by scientists around the world.¹⁻⁴ Compared with traditional semiconductor quantum dots, CDs possess many distinct advantages, such as their excellent water solubility, biocompatibility as well as low toxicity.^{1, 5, 6} As a result, the CDs are mostly applied in the fields of bioimaging⁷, medical diagnosis⁸, catalysis^{9, 10} and photovoltaic devices¹¹. Generally, CDs distinguish themselves from other carbon materials due to their easy synthesis routes and high quantum yield.⁵ Lots of methods have been developed to prepare the fluorescent CDs, and they can be classified in two categories: One is “top-down” cutting method from kinds of carbon sources, and the other is “bottom-up” thermal dehydration route from organic molecules.⁶ The CDs synthesized from the “top-down” cutting route always possess low quantum yields and need further modification. While the CDs prepared from “bottom-up” thermal dehydration always possess enhanced quantum yields.¹²⁻²⁹ Up to now, CDs from “bottom-up” thermal dehydration could be synthesized from polymer³⁰, amino acid³¹, protein³², sugar²⁵, and some small molecules like citric acid^{14, 18, 19}.

The nanocomposites based on processable polymers and functional nanoparticles have lots of advantages in multifunction integration, chemical sensor, optical materials as well as reinforcing material.³³⁻³⁷ The composites based on polymers and nanoparticles always possess varied integrated routes for chemical sensor. The luminescence analysis possesses high sensitivity, improved facility and provides the possibility in visual detection. As a result, it is significant to apply the

composites of responsive polymer/fluorescent nanoparticles in luminescent sensor fields.³⁸

Poly (N-isopropylacrylamide) (PNIPAM)³⁹, a classic thermal responsive polymer, could dramatically change its size at around 32 °C.⁴⁰ The combination of PNIPAM and heavy-metal-based quantum dots (QDs)⁴¹⁻⁴⁵ endowed the thermal responsive polymer with fluorescent property. This kind of composites can detect the change of temperature and make it visible by the fluorescent intensity drop. However, this kind of composites is unsuitable for biomedical and environmental applications due to the high toxicity of the QDs.

Herein, we apply a kind of CDs synthesized by one-step hydrothermal approach from citric acid and ethylenediamine, which performed as a highly photoluminescent carbon dots¹⁹, as the alternate of QDs in the composites. This kind of CDs has obvious self-quenching effect, with a little change in concentration. After composition, the volume of the composites could change with the surrounding temperature. Thus, the luminescent intensity of the inner CDs would change with the varied volume of the PNIPAM carrier. Figure 1a shows schematic illustration of the preparation strategy for thermal responsive fluorescent nanocomposites and the size at different temperature. The temperature sensor also performed excellent reversibility. It is of great significance to apply this kind of nanocomposite in related temperature sensor.

2. Experimental

2.1 Materials and instrumentation

N-isopropylacrylamide (NIPAM, 99%, J&K SCIENTIFIC), citric acid (CA, 99.5%, Alfa Aesar), ethylenediamine (99%, Alfa

Aesar), Ammonium Persulfate (98%, Tianjin Shuangfu institute of chemical reagents), and N, N'-methylene bis (2-propanamide) (98%, Beijing reagent) were used as received. AFM images were performed in the tapping mode with a Nanoscope IIIa scanning probe microscope from Digital Instruments under ambient conditions. Fluorescence spectroscopy was conducted with a Shimadzu RF-5301 PC spectrophotometer. SEM images were taken with a JEOL JSM 6700F field-emission scanning electron microscope.

2.2 Synthesis of CDs

The CDs were synthesized according to the previously reported procedure in literature.¹⁹ Specifically, citric acid (5 mmol, 0.96 g) and ethylenediamine (5 mmol, 335 μ L) were dissolved in 10 mL deionized water. Then the acquired solution was transferred to a poly (tetrafluoroethylene) (Teflon)-lined autoclave (25 mL) and heated at 200 $^{\circ}$ C for 8 h. Then the reactors were cooled to room temperature naturally. The obtained brown-black and transparent solution was transferred to dialysis bag (3500 D) in order to remove the large particles for two days. After evaporation of water, the CDs are obtained.

2.3 Synthesis of PNIPAM & CDs composites

1.5687 g N-isopropylacrylamide, 0.0277 g N, N'-methylene bis (2-propanamide), 0.0346 g ammonium persulfate and 0.002, 0.005, 0.01, 0.02, 0.03, 0.05 g CDs were dissolved in 100 mL deionized water, respectively. After that, the solution was stirred at 350 rpm with the protection of N₂ for 30 min. After that the solution was heat to 70 $^{\circ}$ C with water bath under reflux. Five hours later, the system was cooled naturally. The obtained solution was transferred to dialysis bag (3500 D) in order to remove the CDs that weren't packed in PNIPAM for two days. Here, we applied the PNIPAM composites with 0.01 g CDs as model.

3. Results and discussion

3.1 Structure of the composites

The SEM image in Fig. 1b showed that the average diameter of this kind of composites was around 1.12 μ m. The AFM image in Fig. 1c showed the height of this kind of composites was around 30 nm, which indicated their low degree of cross linking. And the composites possessed large hydrate diameter in aqueous solutions. These images were taken after 50 times dilution of the original sample. At high concentration, the sample appeared like a film instead of particles at SEM image, as shown in Fig. S1. These phenomena indicated the high concentration of the composites in the original solution.

The UV absorption spectrum of pure PNIPAM composites showed no obvious peaks as shown in Fig. S2a. In the CDs solution, the peaks were found on 340 nm and 240 nm. While in the PNIPAM & CDs composites there was no obvious peak observed, which may be due to the high absorption of PNIPAM and the low percentage of the CDs (ca. <2%). On the contrary, the composites with higher amount of CDs, 0.05 g, show an absorption peak at 340 nm, which is identical with one of CDs' peaks. This indicates the existence of CDs in the composites. In the FTIR spectrum, the results were similar to the UV results. The absorption of PNIPAM was so strong that the absorption of

CDs can hardly be detected as shown in Fig. S2b. Also, the peak of CDs and the peak of PNIPAM have some similarities, which made it more difficult to distinguish the signal of CDs from that of PNIPAM. When the amount of CDs was increased, some differences were showed in the spectra. But the peaks of CDs still cannot be observed.

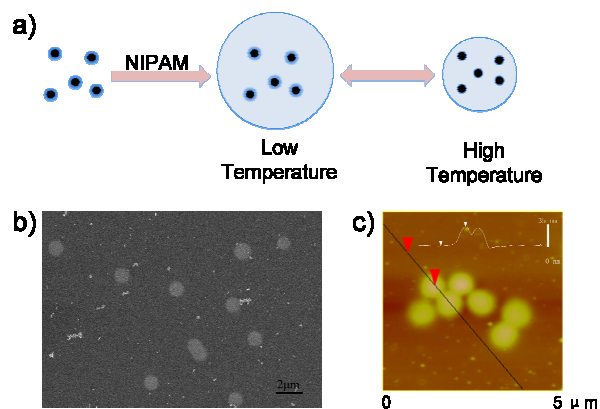


Fig. 1 a) Schematic illustration of the preparative strategy for thermal responsive fluorescent nanocomposites and their morphology under different temperature. b) The SEM image of PNIPAM & CDs composites. c) The AFM image of PNIPAM & CDs composites.

The loading capacity of CDs was also calculated. In this part, we collected the solution out of the dialysis bag, and tested the fluorescent intensity. Based on the standard fluorescent intensity curve of CDs (shown in Fig. S3), the unloaded CDs were calculated to be ca. 0.6917 mg when the initial amount of CDs was 10 mg. Finally, the calculated loading capacity was 93.1%.

3.2 Fluorescent properties of CDs and PNIPAM & CDs composites

The fluorescent emission of CDs had some excitation-dependence, as shown in Fig. S4a. The best excitation wavelength of CDs was 360 nm. After loaded in PNIPAM composites, the fluorescent emission was also excitation-dependent, but the ratio of the highest fluorescent intensity to the lowest fluorescent intensity was much lower compared with the pure CDs solution, as shown in Fig. S4b. In the composites, the best excitation wavelength was 400 nm, pretty different from that of CDs. These phenomena could be attributed to the influence of the PNIPAM, and the influence of free radical to CDs should also be considered. Free radicals that triggered the polymerization of PNIPAM could also react with the C=C bonds that existed in CDs,^{17, 19, 46} and further change the fluorescent properties. In order to make sure that the fluorescence comes from the CDs, the fluorescence of pure PNIPAM was also tested at the same condition of PNIPAM & CDs composites, as shown in Fig. S4c. And the fluorescent signal of pure PNIPAM was low enough to be ignored compared with that of the composites.

We also tested the tendency of CDs' fluorescent intensity with the increasing of their concentration, which was shown in Fig. 2a. The fluorescent intensity increased with the concentration of CDs before 0.05 mg/mL. And it decreased with the increasing of CDs' concentration when the concentration is over 0.05 mg/mL. These phenomena could be attributed to the self-quenching effect and the excitation dependence of CDs. The original fluorescence was absorbed by the other CDs as the

excitation wavelength. The emission wavelength further red shifted, and the intensity decreased.

In order to further prove this phenomenon can also be observed in polymer, composites with different CDs loading amount have been synthesized. In Fig. 2b, the horizontal axis represents the weight ratio between CDs and polymer. When the loading amount of CDs is 0.03 g, the composites reached the highest fluorescent intensity at 20 °C. When the amount of CDs was further increased, the fluorescent intensity decreased. This phenomenon is similar to the self-quenching effect of CDs in water. The fluorescent intensity increased with the increasing CDs' concentration. But when the concentration of CDs is too high in polymer, the fluorescent intensity will decrease. This indicated that self-quenching effect can be observed even in polymer. Based on this property, PNIPAM is apply to change the size of the composites and further change the concentration of CDs in the composites to make fluorescent intensity different beyond and below the LCST.

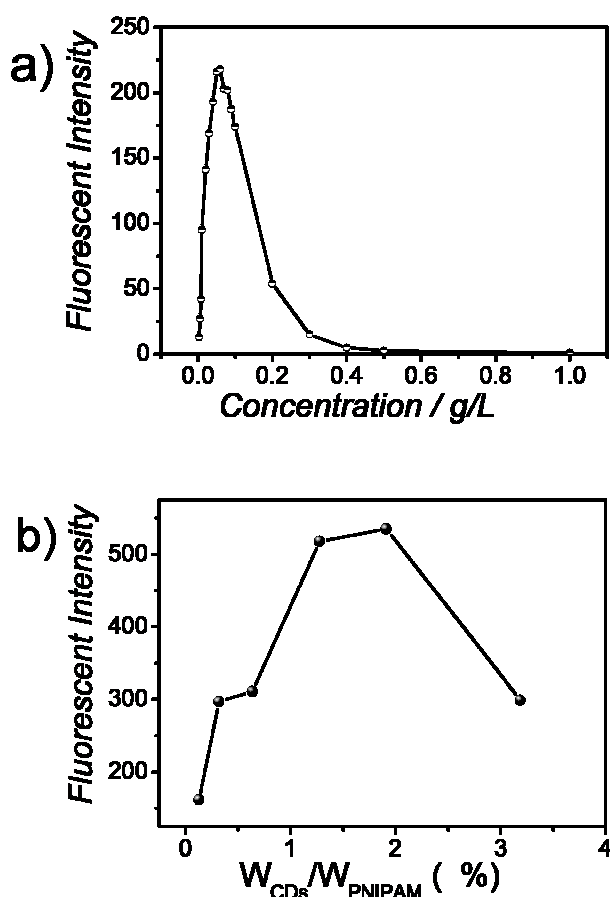


Fig. 2 a) The tendency of fluorescent intensity with concentration of CDs in water. b) The tendency of fluorescent intensity with the weight ratio of CDs to polymer in the composites.

3.3 Thermal responsive ability of the composites

The fluorescent intensities of the composites at different temperature are showed in the Fig. 3. Insert, the images of the composites under sunlight and under 365 nm UV at low temperature are on the left; the images at high temperature are showed on the right. The dark line represented the fluorescent

intensities of temperature rising process, and the red line showed the intensities of dropping process. It is obviously seen that the fluorescent intensity decrease sharply at around 32 °C, and the process is reversible.⁴⁰

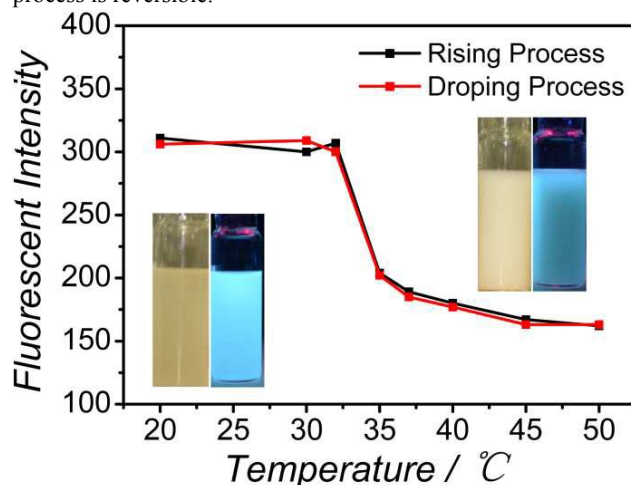


Fig. 3 The original PNIPAM & CDs composites' fluorescent intensity at different temperature. Insert: Digital photos taken under nature light (left panel) and UV light (right panel) of the nanocomposites dissolved in water under low (left) and high (right) temperature, respectively.

In order to make sure this decrease comes from size change of PNIPAM composites, other control experiments were also conducted. The fluorescent intensity of pure CDs solution slightly decreased with the increasing temperature as shown in the Fig. 4a. On the contrary, the fluorescent intensity of the mixture of PNIPAM and CDs showed sharply increase at around 32 °C, as shown in Fig. 4b. All these phenomena suggested the sharp decrease of fluorescent intensity comes from the shrinking size of PNIPAM composites.⁴⁷⁻⁴⁹ The difference in size was directly proved by DLS measurements. As shown in Figure S5, the size of the composites was much larger at 25 °C compared to that at 45 °C.

The reversibility of the composites was also tested. As shown in Fig. 4c, the fluorescent intensity changed little after 12 cycles of heating and cooling process, which indicated the stability of the composites.

3.4 Further exploration to thermal responsive behaviors of the system

Besides the results listed above, other interesting phenomena were also investigated. When the original solution was diluted two times and ten times, their response signals changed as Fig 5a. After diluted two times, the decrease tendency became much less obvious compared with the original one. Besides, the fluorescent intensity increased with the increasing of temperature when the sample was diluted ten times.

What is the reason of the antipodal change tendency? In Fig. S1, the film formed with the original solution suggested the high concentration of PNIPAM composites particles in the solution. This high particle concentration also provided a reasonable explanation of the suppressing high loading capacity. The cross linking degree was so low, and the composites could absorb a lot of water. So the particles squeezed with each other in the aqueous solution, and only a little free water was left. If the composites particles were so dense, the quenching effect between particles

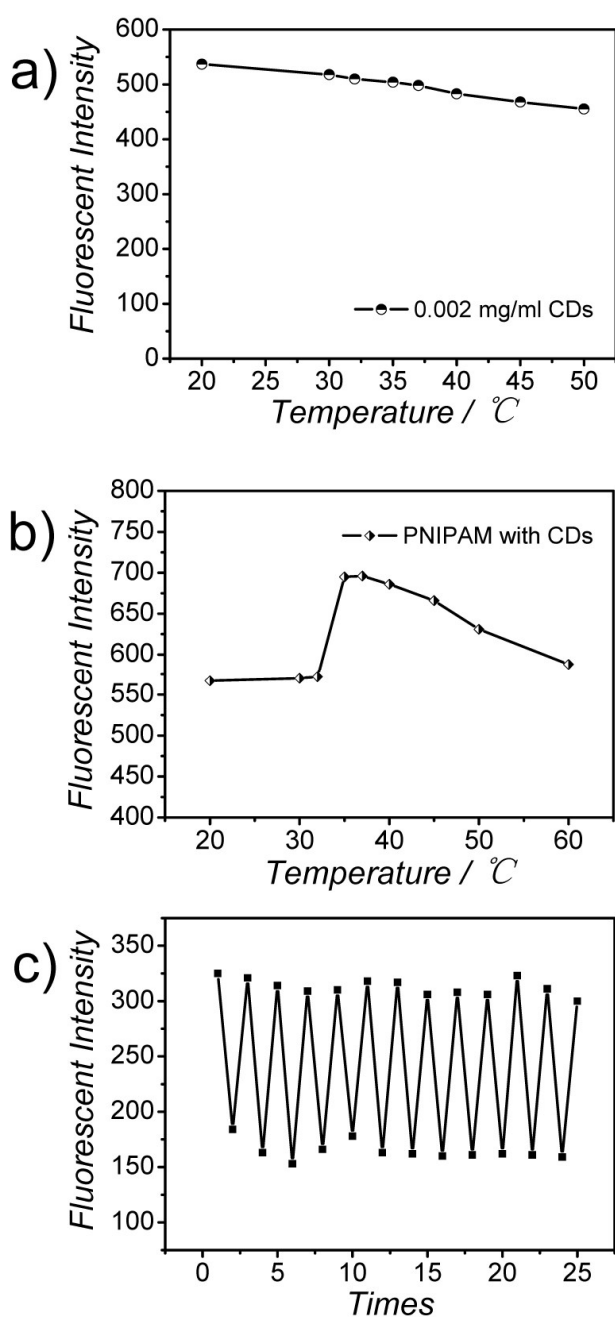


Fig. 4 a) Fluorescent intensity of CDs at different temperature. b) Fluorescent intensity of the mixture of PNIPAM and CDs. c) The fluorescent intensity of PNIPAM & CDs composites at low temperature and at high temperature for 12 cycles.

cannot be ignored. At low temperature, the particles were squeezed with each other. The CDs in different composite particles behave quenching effect with each other, and the CDs in the same particle also have quenching effect.⁵⁰ At high temperature, the distance between adjacent composites became larger so that the particles were not that squeezed. The quenching effect between adjacent composites particles became weaker, while the quenching effect in the same particle became pretty obvious.

In the original solution, the quenching effect in the same particles take the leading role, and the quenching effect among

different particles still obvious at high temperature. So the final signal was the decreasing of the fluorescent intensity. After ten times of dilution, the quenching effect among different composite particles became negligible at high temperature, but it was not at low temperature, as shown in Fig. 5b. At this circumstance, the quenching effect in the same particles decrease the fluorescent intensity, but the quenching effect among different particles are relieved, which will increase the fluorescent intensity. The final result was the increase in fluorescent intensity.

This assumption also explained the increased fluorescent intensity in the mixture of PNIPAM and CDs. The CDs were dispersed in little solvent (free water) at low temperature, because most of the solution was occupied by PNIPAM composite particles. In this circumstance, the CDs were actually at self-quenching concentration. At high temperature, the particles became smaller, and there were more free water for CDs to disperse. The self-quenching effect was relieved a little, so the fluorescent intensity increased a little, as shown in Fig. 4b.

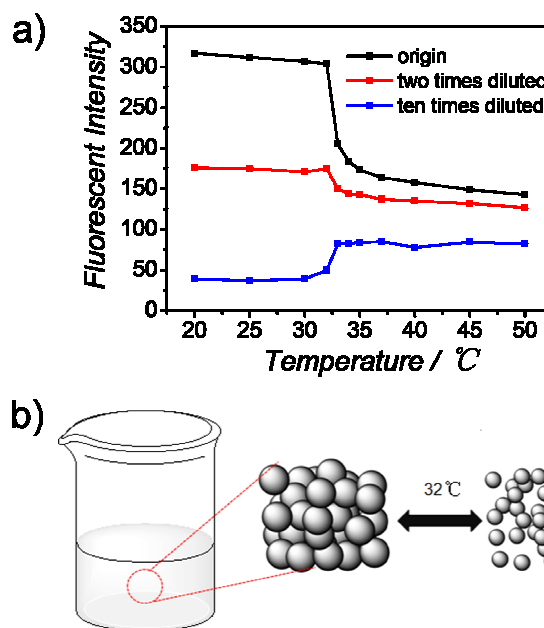


Fig. 5 a) Fluorescent intensity of the original composites solution, two times diluted solution, and ten times diluted solution at different temperature. (b) The model of composites after ten times dilution.

3.5 UV resistance ability and control experiment.

Compared with pure CDs solution, the composites showed excellent UV resistance. As shown in the Fig. 6a, only 4.85% fluorescent intensity of CDs was kept after 10 min 2000 W UV exposure, and only 2.43% after 20 min.

On the contrary, the PNIPAM & CDs composites kept 54.5% of their original fluorescence after 10 min 2000 W UV exposure, and 43.1% after another 10 min UV exposure, as shown in Fig. 6b. It proved the composites were equipped with excellent UV resistance.¹⁹

Besides of composites with 0.01 g CDs, the thermal responsive abilities of other composites with different amount of CDs were also tested. In Fig 6c, the decreasing tendency of fluorescence increases with the content of CDs from 0.002 to 0.02 g. In Figure 6d, with the further increased CDs content, from

0.02 to 0.05 g, the tendency became much less obvious, which may be due to the high concentration of CDs in the composites. At high concentration, the fluorescent intensity changed little with

the increasing of temperature. After the test of the composites with different CDs loading amount, the composites with 0.02 g CDs showed the best sensitivity.

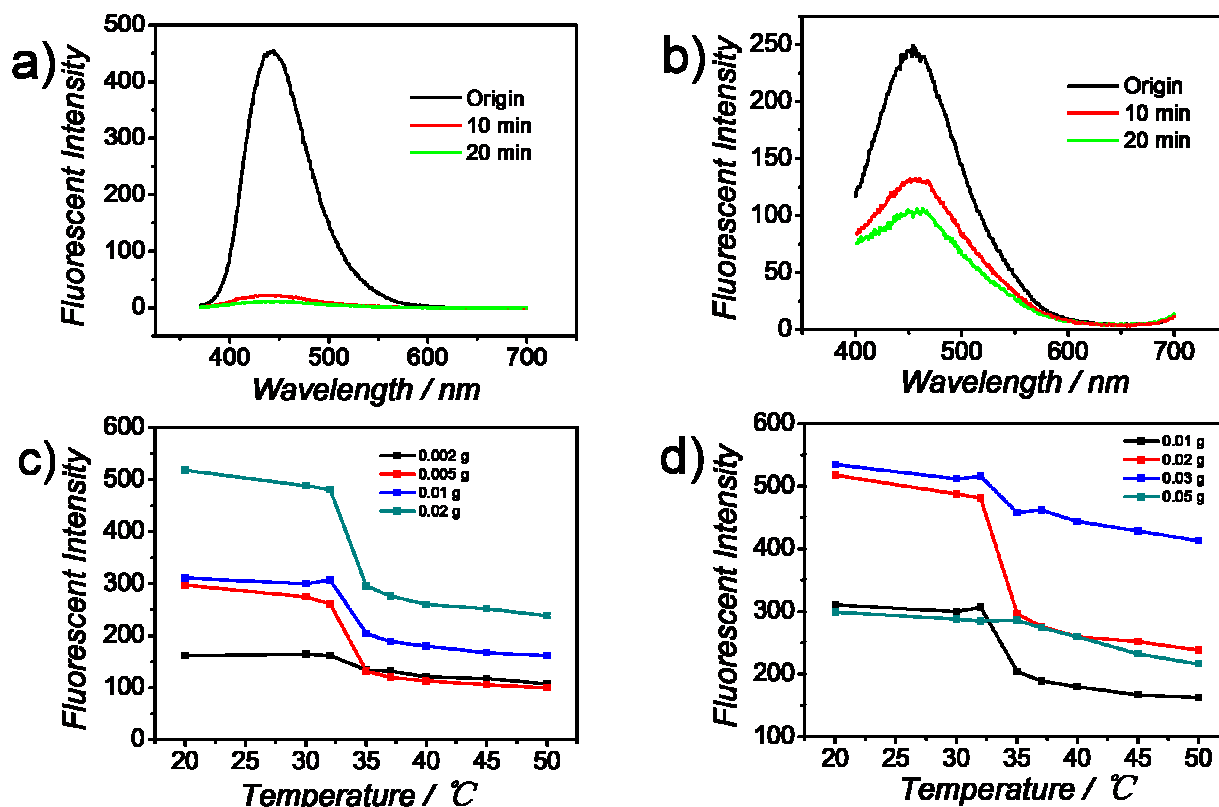


Fig. 6 a) Fluorescent intensity of CDs solution without UV exposure, after 10 min UV exposure, and after 20 min UV exposure. b) Fluorescent intensity of PNIPAM & CDs composites solution without UV exposure, after 10 min UV exposure, and after 20 min UV exposure. c) The fluorescent intensity of PNIPAM & CDs composites with 0.002 g, 0.005 g, 0.01 g, 0.02 g CDs at different temperature. d) Fluorescent intensity of PNIPAM & CDs composites with 0.01 g, 0.02 g, 0.03 g, 0.05 g CDs at different temperature.

We also found out that the polymerization can be prevented when too much CDs were added to the system. Although the composites with 0.05 g CDs were successfully synthesized, the composites solution showed obvious different appearance (in Fig. S6). When the amount of CDs was 0.1 g, the composites cannot be synthesized. Free radicals can quench the fluorescence of CDs. On the other hand, CDs can also reduce the amount of free radicals, and further affect the polymerization. When 0.1 g CDs was put into the system, the free radicals that are used to start the polymerization were quenched by CDs and the polymerization was stopped before it happened.

4. Conclusions

This work utilized the self-quenching effect of CDs to form the thermal responsive composites, which also showed excellent reversibility, and good stability. The AFM and SEM images showed its low cross linking degree. The fluorescence characterization showed the sharp decrease of their fluorescent intensity and their good reversibility. At UV resistance test, the composites behaved distinct UV resistance ability, compared with pure CDs solution. The present work is significant in developing CDs based nanocomposites as sensor. Moreover, the present nanocomposite is an ideal system to investigate the PL quenching behaviour of the CDs, which is very important for the clarifying

the PL mechanism of CDs based materials.

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Notes and references

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