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Photostable epoxy polymerized carbon quantum dots luminescent thin films and the performance study

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ABSTRACT

High photostable epoxy polymerized carbon quantum dots (C-dots) luminescent thin films were prepared and their performances were compared with the CdTe quantum dots (QDs). First, water soluble C-dots (λem = 543.60 nm) were synthesized. Poly (ethylene glycol) diglycidyl ether (PEG) and diaminooctane were used as the polymer matrix to make the epoxy resin films. FT-IR spectra showed that there were vibration at 3448 cm^{-1} and 1644 cm^{-1} which contributed to -OH and -NH respectively. SEM observations showed that the polymerizations of the films were uniform and there were no structure defects. Mechanical tests showed the tensile modulus of C-dots composite films were 4.6, 4.9, 6.4 and 7.8 MPa respectively with corresponding 0%, 1%, 2% and 5% mass fraction of C-dots, while the tensile modulus of CdTe QDs films were 4.6 MPa under the same mass fraction of CdTe QDs. Compared with semiconductor QDs, the decay of quantum yield were 5% and 10% for the C-dots and CdTe QDs, respectively. The pictures in the continuous irradiation of 48 h showed that the C-dots film was more photostable. This study provides much helpful and profound towards the fluorescent enhancement films in the field of flexible displays.

Introduction

Quantum dots (QDs), a kind of three-dimensional particles with the size in the range of 1–10 nm, have attracted the attention of numerous researches nowadays due to their unique optical properties, such as spectral purity, wide absorption range and photo/-chemical stability [1–3]. However, with people's consciousness of environment protection rising gradually, semiconductor QDs are losing its dominance because of the heavy metal element they contain. On the contrary, due to the advantages of water solubility, chemical inertness, low toxicity, easy functionalization, preferable biocompatibility [4–6], carbon quantum dots (C-dots) as a new class of QDs can be a very promising candidate taking place of conventional semiconductor QDs which show great potential into some advanced devices, such as light-emitting diodes, flexible displays [7–9] and so on. C-dots are generally defined as small carbon nanoparticles with various forms of surface passivation [10–12]. The chemical modification or functionalization with organic molecules or polymeric species of C-dots has been proved to be more effective for bright fluorescent emissions [13]. Till now, several methods have been established to make the good preparation of C-dots, such as etching with lager carbon materials, laser ablation, microwave irradiation, thermal oxidation and pyrolysis [14–17].

In recent years, flexible display materials are gradually applied into displayers like television, screens, diodes, etc. by the world-class display manufacturers, such as LG, Samsung, Sharp and Epson Corporations [18–20]. Fluorescent QDs films are one of the promising display materials in the years to come. Generally speaking, QDs displays are made of LED light source, QDs films and some other components. The high fidelity of red and green light will be irradiated from the membrane excited by the blue light of the LED light source, which presents a much more vivid picture on the display with bright red and green color [21]. And the size of QDs can be controlled to some extent, which means the light irradiated from the QDs can be manipulated as well. The matrix of the film recently links to the polymer materials, which are gradually applied into display materials. For example, Wei et al. reported the QDs luminescent materials based on polyurethane acrylate [22]; Deng et al. studied systematically the epoxy encapsulated silicon nanocrystals in the photoluminescent materials [23]. There are some main challenges in preparing the fluorescent QDs film. For example, the QDs nanocrystals often undergo the aggregations during the process [1,18,22]. These unfavorite conditions can

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decrease the fluorescent performance in the display quality. Therefore, the dispersion of the QDs in the polymer matrix is very important for the fluorescent enhanced films in the displays [1].

In this work, we prepared the C-dots luminescent thin film based on the water-soluble Poly (ethylene glycol) diglycidyl ether (PEG), a kind of epoxy resin. Owing to the good dispersion of C-dots in the PEG, the method carried out in the experiment has various advantages in the preparation of C-dots involved nanocomposites. The results prove that the C-dots composite film has better mechanical strength and stability comparing to the CdTe QDs composite materials and the resultant luminescent thin membrane is promising in the applications in the photoluminescent devices.

Experimental

Chemicals and materials

Sodium citrate (AR, 99.0%), Carbamide (99.999%), Poly(ethylene glycol) diglycidyl ether (PEG, Mn = 500) were obtained from Aladdin. Diaminooctane was purchased from Macklin. CdTe QDs solution was home-made. All the chemicals purchased were used as received.

The synthesis of carbon dots

Sodium citrate [1 g (3.88 mmol)] and carbamide [0.5 g (8.33 mmol)] were added into 30 ml distilled water in a 100 ml beaker and homogenized by stirring. Then the mixture solution was heated in a domestic microwave oven under 500 W. The water in the beaker was evaporated as time went by and the white solid appeared eventually. The beaker was cooled down subsequently from the oven before the distilled water was added to make the carbon dots solution (C-Dots). Then the resultant C-dots solution was processed with the dialysis bag for two days to remove the residual unreacted species and sodiums.

The synthesis of the membrane

The diaminooctane was added into C-dots solution in a 50 mL beaker which was thenceforth sealed by preservative film. Then the diaminooctane was accelerated to dissolve into the solution by heating the temperature. Subsequently the Poly (ethylene glycol) diglycidyl ether was added into the mixture solution under magnetic stirring. Later on the mixture solution was kept static for several minutes in order to remove the miniature bubbles. A

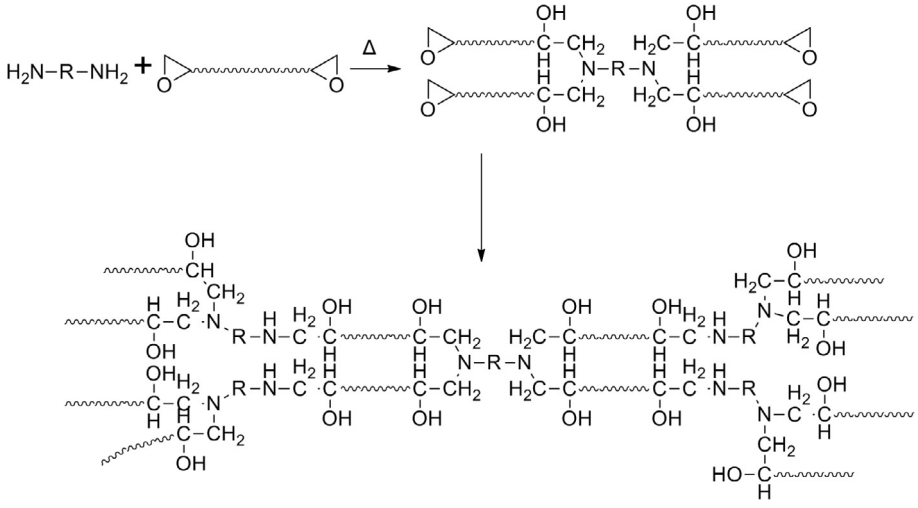

Fig. 1. The mechanism of epoxy resin curing.

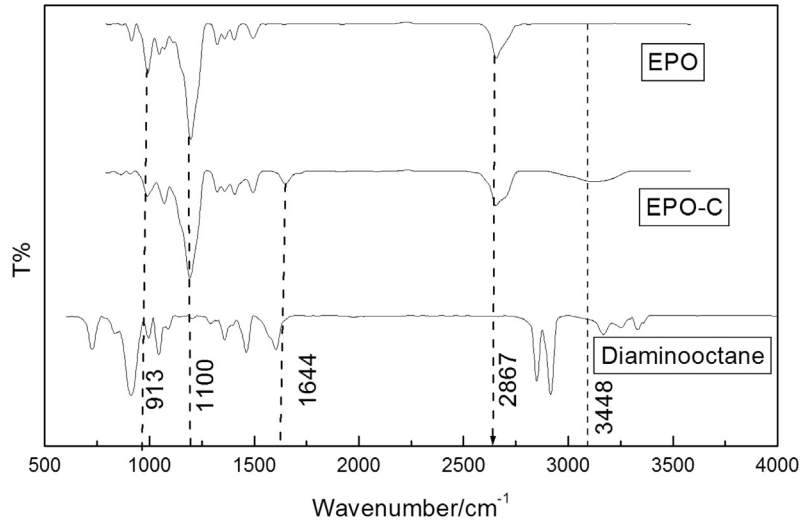

Fig. 2. FT-IR spectra of the EPO, crosslinking EPO and diaminooctane.

film laying machine was used to make the thin film, and the membrane would be cured at 70 °C for 1 h. CdTe QDs solution was also used to make the membrane under the same conditions. Then the different mass fraction as 1%, 2%, 5% (C-dots/CdTe QDs: Poly(ethylene glycol) diglycidyl ether = 1%, 2%, 5%) of C-dots and CdTe QDs solution were carried out to study the effects of mass fraction on the membrane property. The mechanical and fluorescent properties of the membranes were tested eventually.

Characterization

All samples were tested by Fourier Transform Infrared spectrometer (Bruker TENSOR27) and the samples were directly loaded onto the plate after drying; the combined fluorescence lifetime and steady state spectrometer (FLSP920),which were purchased from Edinburgh Instruments Ltd., were used to test the quantum yields (QYs) of the samples; the photoluminescence spectra test was determined by luminescent spectrometer with a low temperature constant temperature bath (DC-2006) at room temperature; and mechanical property tester (SANS CMT6503, China) all are commonly used instruments to analyze the properties of the composite materials. The nanoparticle samples were characterized using a Scanning Electron Microscope (SEM) (FEI Quanta 400 FEG). The fluorescent graphics of C-EPO and CdTe-EPO membrane was carried out by using the continuous irradiation of samples under the UV source of 360 nm, and the photos were taken in different intervals under the same conditions.

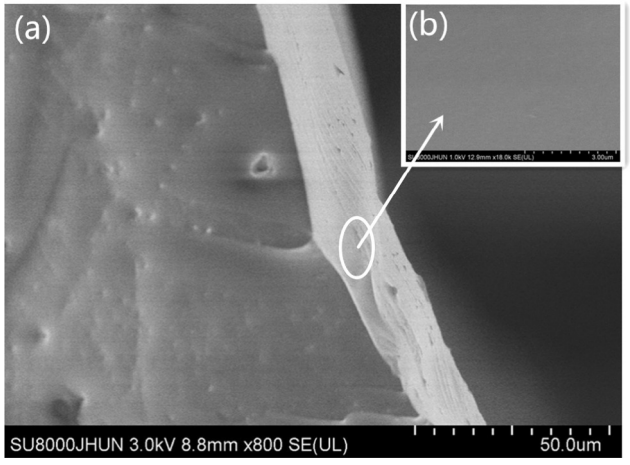

Fig. 3. The SEM observations of the cross-section of EPO films with carbon dots (a) and the amplified part of the cross-section (b).

Results and discussions

The molecular structure of the as-used epoxy was showed in Fig. 1. One of the advantages of the water-soluble epoxy resin used in the paper is that compared to the traditional epoxy resin, water-soluble epoxy resin is much more environment-friendly because of no organic solvent. The curing process of epoxy resin is convenient and the membrane after crosslinking has good properties of transparency and mechanical strength. And most importantly, it is compatible with the C-dots which lead to the well dispersion of the nanoparticles in the polymer matrix.

FT-IR spectra results showed in Fig. 2. From the spectrum of pure epoxy resin (EPO), we can see that there were strong vibration at 1100 cm^{-1} which contributed from the C-O and 910 cm^{-1} contributed from the end epoxy groups, and the vibration at 2867 cm^{-1} can also be observed that contributes to the C–H of the Poly(ethylene glycol) diglycidyl ether (PEG) skeleton. And we can see the vibration at 1644 cm^{-1} which indicates the end -NH in the diaminooctane spectrum. Compared with the spectrum of PEG and diaminooctane, we can see there were vibration at 3448 cm^{-1} and 1644 cm^{-1} which contributed to –OH and –NH respectively after polymerization, while the epoxy group near 910 was much weakened. The results elucidate that the curing of epoxy resin was successful using the diaminooctane as the curing agent.

The scanning electron microscope (SEM) was used to observe the cross-section of the specimen (Fig. 3), so as to observe the compatibility of the carbon dots added into the membrane. According to the Fig. 3(a), we can see the cross-section of the membrane clearly. The C-dots-EPO film shows the uniform structure in Fig. 3(b), which indicates the well dispersion of the C-dots in the EPO matrix and the addition of C-dots does not affect the crosslinking process. The results elucidate that the C-dots are much compatible the water-soluble epoxy resin.

Various aspects may have impacts on the mechanical property of the resultant material, such as crosslink degree, molecular, structures and curing agent conditions. Here we studied the mass fraction of C-dots and CdTe QDs respectively, as this is one of the

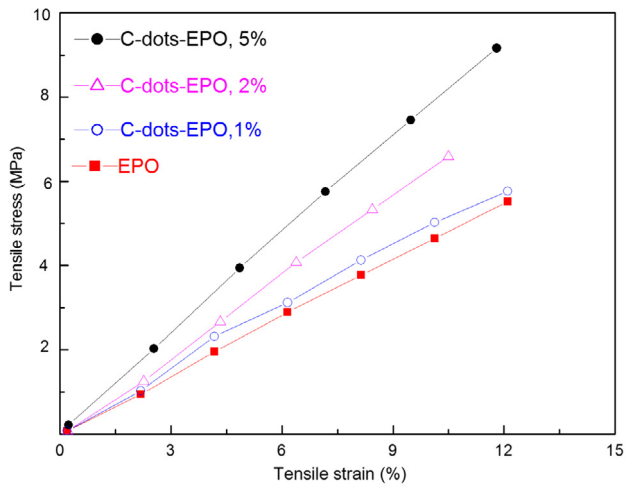

Fig. 4. Tensile strength test of the epoxy resin luminescent film with different mass fraction of C-dots.

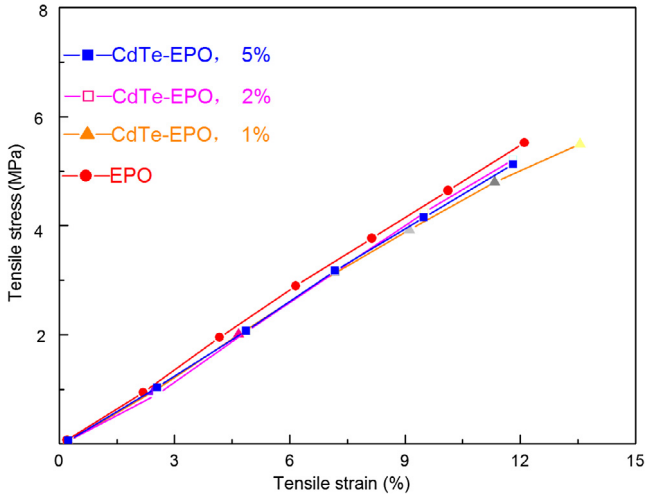

Fig. 5. Tensile strength test of the epoxy resin luminescent film with different mass fraction of CdTe QDs.

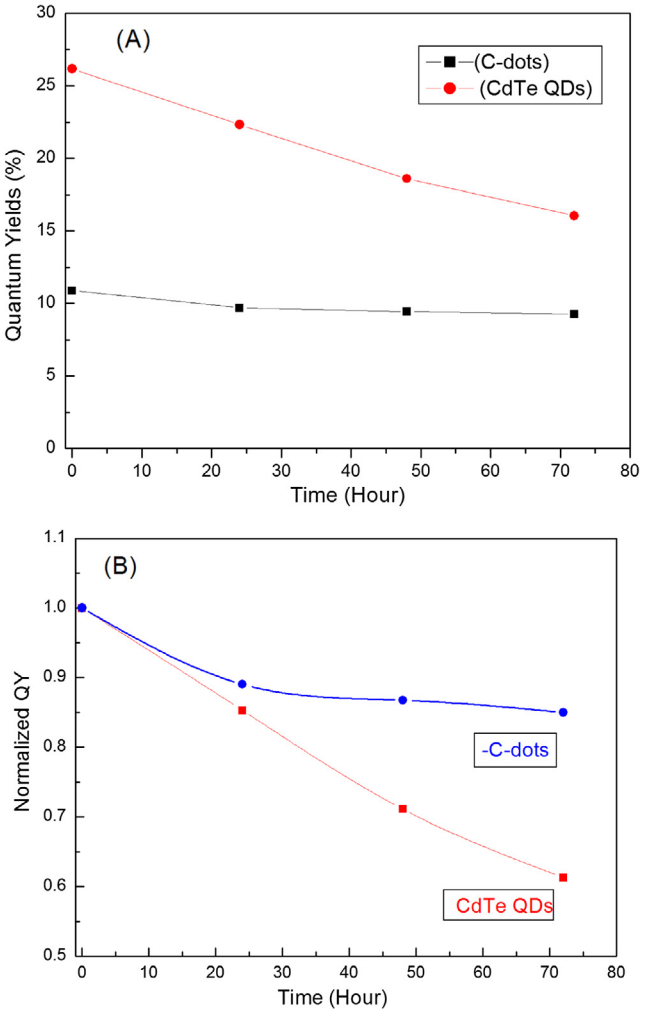

Fig. 6. The comparisons of quantum yields-time plot curves (A) and the normalized quantum yields (B) for the carbon dots and CdTe QDs.

most important aspects that could influence the performance of the resultant fluorescent films in the display devices. Fig. 4 shows the tensile modulus of C-dots composite film were 4.6, 4.9, 6.4, 7.8 MPa respectively with corresponding 0%, 1%, 2% and 5% mass fraction of C-dots, which indicates that the tensile modulus of the composite film escalates with the increased quantity of C-dots. Compared with C-dots composite film, the tensile modulus of the film with different mass faction of CdTe QDs showed in Fig. 5. Results showed that they were nearly 4.6 MPa, which indicates that the quantity of CdTe QDs has almost no impact on the mechanical strength of the composite film. These results elucidate C-dots are better to make the membrane which has good mechanical strength and flexibility for displays.

The quantum yield tests were carried out by the Steady State Fluorescence Spectrometer to analyze the situations of C-dots and CdTe QDs equally added into the membrane respectively. The curve of C-dots showed in Fig. 6(A) indicates a quantum yield decay rate of 1% calculated averagely for 72 h of continuous irradiations, while the decay rate of CdTe QDs was more than 10%, which is much higher than C-dots. According to the vividly contrast (Fig. 6B), we can find that the decay curve of CdTe QDs descends in a much larger amplitude than the curve of C-dots. The results elucidate that C-dots in the membrane decays in a much lower rate than the CdTe QDs, which means C-dots are more photostable in the membrane.

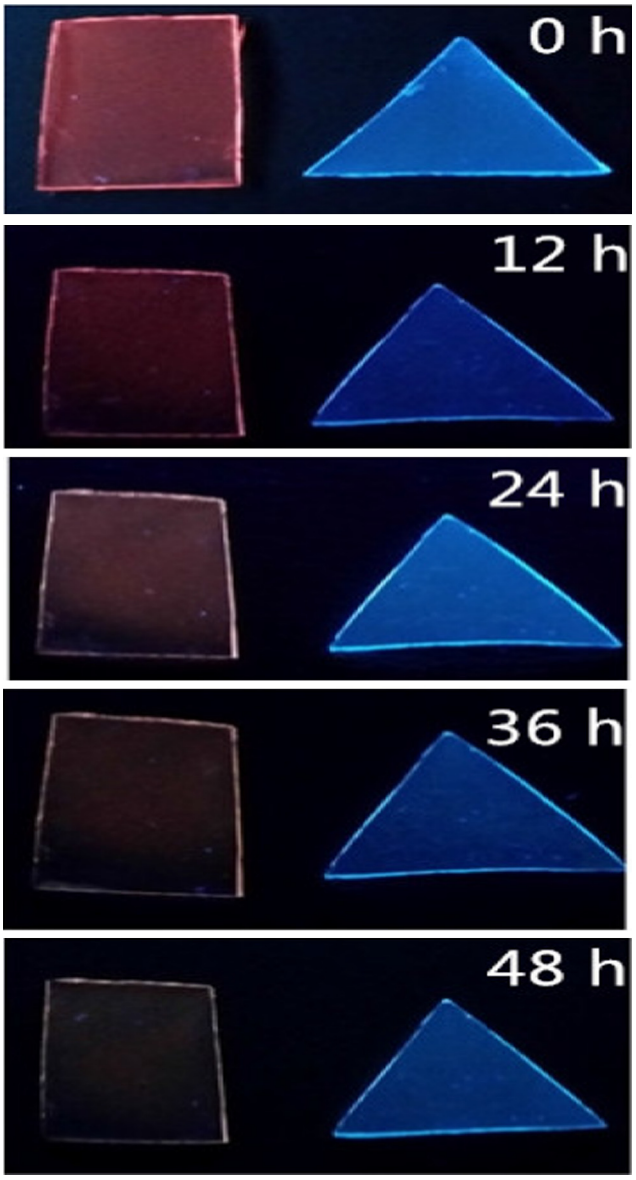

Fig. 7. The fluorescent graphics of C-EPO and CdTe-EPO membrane under UV within different times.

The pictures taken in 48 h with an interval of 12 h show a clearly fluorescence intensity of C-dots EPO (Fig. 7, right) and CdTe-EPO (Fig. 7, left) membrane under UV. An obvious descending fluorescence intensity of CdTe-EPO membrane can be observed from the pictures, while the C-dots EPO membrane's fluorescence intensity changes slightly which coincides with the result showed in Fig. 6. The results indicate that C-dots as the fluorophore for the fluorescent enhancement films are much more photostable than CdTe QDs.

Conclusions

Compared with traditional semiconductor quantum dots, Carbon quantum dots (C-dots) attracts scientists' attention due to their advantages of solubility, low toxicity, and photostability, so C-dots are deemed as a kind of promising candidate to replace the conventional semiconductor quantum dots (QDs). The fluorescent membrane combined with epoxy resin and C-dots have a good transparency and mechanical properties. And the C-dots which are

very compatible with the resin have distinct and stable fluorescence properties in the membrane. This kind of material is a better choice to apply into some advanced display devices in the future.

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References

[1] Kim TH, Chung DY, Ku JY, Song I, Sul S, Kim DH, Cho KS, Choi BL, Kim JK, Hwang S, Kim K. Heterogeneous stacking of nanodot monolayers by dry pick-and-place transfer and its applications in quantum dot light-emitting diode. Nat Comm 2013;4:453–64.
[2] Bera D, Qian L, Tseng TK, Holloway PH. Quantum dots and their multimodal applications: a review. Materials 2010;3:2260–345.
[3] Li Y-Q, Wang H-Q, Wang J-H, Guan L-Y, Liu B-F, Zhao Y-D, Chen H. A highly efficient capillary electrophoresis-based method for size determination of water-soluble CdSe/ZnS core-shell quantum dots. Anal Chim Acta 2009;647:219–25.
[4] Baker SN, Baker GA. Luminescent carbon nanodots: emergent nanolights. Angew Chem Int Ed 2010;49:6726–44.
[5] Wei W, Liu C, Liu J, Liu X, Zou L, Cai S, Shi H, Cao Y-C. Do the cations in clay and the polymer matrix affect quantum dot fluorescent properties? Luminescence 2016;31:1020–4.
[6] Cao Y-C, Wang Z, Yang R, Zou L, Zhou Z, Mi T, Shi H. Quantum dots encoded Au coated polystyrene bead arranged micro-channel for multiplex arrays. Talanta 2016;146:749–53.
[7] Wang X, Cao L, Lu F, Meziani MJ, Li H, Qi G, Zhou B, Huarruf BA, Kermarrec F, Sun Y-P. Photoinduced electron transfers with carbon dots. Chem Comm 2009;25:3774–6.
[8] Li Y, Hu Y, Zhao Y, Shi G, Deng L, Hou Y, Qu L. An electrochemical avenue to green-luminescent graphene quantum dots as potential electron-acceptors for photovoltaics. Adv Mater 2011;23:776–80.
[9] Tang L, Ji R, Cao X, Lin J, Jiang H, Li X, Teng KS, Luk CM, Zeng S, Hao J, Lau SP. Deep ultraviolet photoluminescence of water soluble self-passivated graphene quantum dots. ACS Nano 2012;6:5102–10.
[10] Lu J, Yeo PS, Gan CK, Wu P, Loh KP. Transforming C_{60} molecules into graphene quantum dots. Nat Nanotechnol 2011;6:247–52.
[11] Xu X, Ray R, Gu Y, Ploehn HJ, Gearheart L, Raker K, Scrivens WA. Electrophoretic analysis and purification of fluorescent single-walled carbon nanotube fragments. J Am Chem Soc 2001;126:12736–7.
[12] Bottini M, Balasubramanian C, Dawson MI. Isolation and characterization of fluorescent nanoparticles from pristine and oxidized electric produced single-walled carbon nanotubes. J Phys Chem B 2006;110:831–6.
[13] Peng J, Gao W, Gupta BK, Liu Z, Romero-Aburto R, Ge L, Song L, Alemany LB, Zhan X, Gao G, Vithayathil SA, Kaipparettu BA, Marti AA, Hayashi T, Zhu J-J, Ajayan PM. Graphene quantum dots derived from carbon fibers. Nano Lett 2012;12:844–9.
[14] Selvi BR, Jagadeesan D, Suma BS, Nagashankar G, Arif M, Balasubramanyam K, Eswaramoorthy M, Kundu TK. Intrinsically fluorescent carbon nanosphere as a nuclear targeting vector: Delivery of membrane-impermeable molecule to modulate gene expression in vivo. Nano Lett 2008;8:3182–8.
[15] Yang S-T, Cao L, Luo PG, Lu FS, Wang X, Wang HF, Meziani M, Liu YF, Qi G, Sun Y-P. Carbon dots for optical imaging in vivo. J Am Chem Soc 2009;131:08–11309.
[16] Pan D, Zhang J, Li Z, Wu M. Hydrothermal route for cutting graphene sheets into blue-luminescent graphene quantum dots. Adv Mater 2010;21:734–8.
[17] Wang X, Qu K, Xu B, Ren J, Qu X. Microwave assisted one-step green synthesis of cell-permeable multicolor photoluminescent carbon dots without surface passivation reagents. J Mater Chem 2011;21:2445–50.
[18] Boverzac K. Quantum dots go on display. Nature 2013;493. 283-283.
[19] Kim T-H, Cho K-S, Lee EK, Lee SJ, Chae J, Kim JW, Kim DH, Kwon J-Y, Amaratunga G, Lee SY, Choi BL, Kim JM, Kim K. Full-color quantum dots displays fabricated by transfer printing. Nat Photonics 2011;5:176–82.
[20] Reineke S. Hydroxyl-terminated CuInS2 based quantum dots: toward efficient and bright light emitting diodes. Nat Mater 2015;14:459–62.
[21] Bai Z, Ji W, Han D, Chen L, Chen B, Shen H, Zou B, Zhong H. Complementary LED technologies. Chem Mater 2016;28:1085–91.
[22] Wei WJ, Xu H, Cao YC. Preparation of quantum dot luminescent materials through the ink approach. Mater Design 2016;91:165–70.
[23] Deng Z, Pi XD, Zhao JJ, Yang D. Photoluminescence from silicon nanocrystals in encapsulating materials. J Mater Sci Technol 2013;3:221–4.