Nanoscale

PAPER



Cite this: Nanoscale, 2019, 11, 14250

Received 17th June 2019, Accepted 8th July 2019 DOI: 10.1039/c9nr05123f

Introduction

Development of phosphorescent materials with tunable emissive properties has attracted great attention in various fields, such as sensing, bioimaging, and last but not least data encryption.^{1–11} Commercially available phosphorescent materials usually employ rare-earth elements such as Yb and Tm,^{12–14} imposing severe restrictions on their applications due to their limited availability and potential environmental issues during their refining and processing.¹⁵

Luminescent carbon dots (CDs), on the other hand, offer several advantages such as ease of synthesis from the readily available cheap precursors, no/low toxicity, and good thermal/

On–Off switching of the phosphorescence signal in a carbon dot/polyvinyl alcohol composite for multiple data encryption[†]

Xin Bao,^{a,b} Elena V. Ushakova, ^b^{c,d} Enshan Liu,^e Zhengjie Zhou,^{a,b} Di Li,^a Ding Zhou,^a Songnan Qu^b*^e and Andrey L. Rogach^{c,d}

Phosphorescence processes in composite systems based on luminescent carbon dots (CDs) are of great fundamental and practical interest. Herein, the control of the phosphorescent signal in a CD/polyvinyl alcohol (PVA) composite is realized. Enhanced green phosphorescence is obtained *via* thermal annealing of the composite under 200 °C, which can be quenched *via* water treatment, and then recovered again, *via* either repeated annealing or near-infrared laser irradiation. Water molecules infiltrating the CD/PVA composite lead to considerable vibrational motions of the CD surface groups through destruction of the rigid composite structure together with an increase in the possibility of the penetration of the phosphorescence quenchers, and thus a decrease in the phosphorescence signal is recovered again. Based on such on–off switching of the phosphorescence signal, a concept of multiple data encryption is realized by using the CD@PVA composite.

photostability, making them promising materials for downconversion light emitting devices and sensors and in bioimaging.¹⁶⁻²⁴ In recent years, phosphorescence phenomena in the CD based composite systems have attracted increasing interest.²⁵⁻³⁰ Deng et al. were the first to demonstrate phosphorescence via embedding CDs in a polyvinyl alcohol (PVA) matrix; they have reported its origin from the aromatic carbonyls on the CD surface, whereas the PVA protected triplet states originate from quenching by intramolecular motions and oxygen.²⁵ Jiang et al. demonstrated CD-based room temperature phosphorescent materials with a long lifetime exceeding one second, attributed to the N and P doping and immobilization of the triplet species.²⁸ Our group demonstrated a thermal-treatment controlled phosphorescence from the blue emissive CD@PVA composites.31 We note that phosphorescence signals from all these systems were rather unstable in an aqueous environment.

In this work, we have used a phosphorescent material based on the green emissive CD@PVA composite, where the emission signal was enhanced after 200 °C annealing. This composite showed a switchable phosphorescent signal, which can be turned off and on by exposing it to water and by subsequent thermal annealing or illumination with a 1532 nm laser, respectively. Based on such processing by applying water, temperature, and near-infrared laser treatments, multiple data encryptions have been demonstrated.



View Article Online

^aState Key Laboratory of Luminescence and Applications, Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Sciences,

Changchun 130033, PR China

^bUniversity of Chinese Academy of Sciences, Beijing 100049, PR China

^cCenter of Information Optical Technologies, ITMO University,

Saint Petersburg 197101, Russia

^dDepartment of Materials Science and Engineering, and Centre for Functional

Photonics, City University of Hong Kong, 83 Tat Chee Avenue, Kowloon, Hong Kong SAR. PR China

^eJoint Key Laboratory of the Ministry of Education, Institute of Applied Physics and Materials Engineering, University of Macau, Taipa, Macau, PR China. F-mail: songrangu@um edu mo

[†]Electronic supplementary information (ESI) available. See DOI: 10.1039/ c9nr05123f

Results and discussion

CDs were synthesized in water from citric acid and urea precursors, using the microwave assisted treatment according to our previous work.³² As shown in Fig. 1a, CDs have sizes of 1–3 nm as revealed by transmission electron microscopy (TEM). And according to high-resolution electron microscopy (HRTEM) results, CDs exhibited clearly visible lattice fringes with 0.21 nm spacing (Fig. 1b), corresponding to the graphene (100) planes.³³ To produce the CD@PVA composite, 0.5 mg of powdered CDs were dissolved in 2.5 mL of an aqueous solution of PVA (10 wt%), dried at room temperature, and annealed at different temperatures as discussed below. Thermal gravimetric analysis (TGA) curves (Fig. 1c) indicate a minor weight loss for both CDs and PVA and the CD@PVA composite when heated over 100 °C, which is due to the starting dehydration processes affecting the CD surface (carboxyl and hydroxyl groups) and the PVA chains (hydroxyl groups). At temperatures over 200 °C, the weight loss of both CDs and PVA and the CD@PVA composite increases considerably, due to the ongoing dehydration and carbonization processes. Changes in the chemical structure of the CD@PVA composite at different temperatures were studied by Fourier transform-infrared spectroscopy (FT-IR), as shown in Fig. 1d. Broad absorption bands at 3430–3650 cm⁻¹ are assigned to the hydroxyl groups;³⁴ their intensity decreases with an increase in temperature up to 200 °C, which is in accord with the TGA data suggesting a reduction of the hydroxyl groups in the CD@PVA composite through dehydration and carbonization processes. It can be inferred that the annealing of the CD@PVA composite at 200 °C results in the appearance of additional chemical bonds and strengthening of the existing bonds between CDs and the PVA matrix.



Fig. 1 (a) TEM image of CDs. (b) HRTEM image of CDs. (c) TGA curves of CDs, PVA and CD@PVA composites. (d) FT-IR spectra of CD@PVA composites annealed at different temperatures.

Absorption spectra of the CD@PVA composites, CDs, and PVA after 60 °C and 200 °C annealing are shown in Fig. 2a. After annealing at 200 °C, the absorption of the CD@PVA composite becomes significantly enhanced at 340 nm to 360 nm as compared to that of the sample annealed at 60 °C. From the analysis of the absorption spectra of CDs and PVA after the same thermal treatment, it can be seen that this absorption enhancement is mainly caused by the thermal-induced processes in PVA. Fluorescence spectra of the CD@PVA composites after 60 °C and 200 °C annealing were measured under 360 nm excitation and are shown in Fig. 2b; for both the same intensity. The PLQY of the CD@PVA composite after 60 °C annealing was 37%, and slightly decreased to 34% after 200 °C annealing.

Green phosphorescence can be easily observed with the naked eye from the 200 °C annealed CD@PVA composite films (Fig. 2c). Time-resolved phosphorescence decay curves of the CD@PVA composites annealed at different temperatures are shown in Fig. 2d. On increasing the annealing temperature from 60 °C up to 200 °C, the average luminescent lifetime increases from 176 ms to 292 ms. The phosphorescence spectra of the CD@PVA composites annealed at 502 nm (Fig. 2b) that can be attributed to the radiative relaxation from the triplet state of the PVA-embedded CDs, which becomes enhanced due to the



Fig. 2 (a) Absorption spectra of 60 °C and 200 °C annealed CD@PVA composites (top), 60 °C and 200 °C annealed CDs (middle), and 60 °C and 200 °C annealed PVA (bottom). (b) Fluorescence spectra of 60 °C and 200 °C annealed CD@PVA composites excited at 360 nm, and normalized phosphorescence spectra of 60 °C and 200 °C annealed CD@PVA composites measured with a time delay of 90 ms. (c) Bright field, fluorescence and phosphorescence images of CD@PVA composite films annealed at 60 °C and 200 °C. (d) Luminescence decay curves monitored at 480 nm (360 nm excitation) of CD@PVA composites annealed at 60 °C, 150 °C, and 200 °C.

suppression of the vibrational motions of the surface groups on CDs through the dehydration processes between CDs and the PVA.³¹

We found that the phosphorescence of the 200 °C annealed CD@PVA composite is quenched upon contact with water, but can be recovered again as a result of subsequent heating, which results in the removal of the adsorbed water molecules. As shown in Fig. 3a, fluorescence and phosphorescence can be observed from the 200 °C annealed CD@PVA composites subjected to UV light on and off conditions, respectively. The phosphorescence vanished after water was spraved on the surface of the composites, and then was recovered after 100 °C annealing. The fluorescence of the composites has no obvious change under these treatments. Fig. 3b shows the changes in the phosphorescence decay curves for the 200 °C annealed CD@PVA film before and after spraying water, and on further 100 °C annealing. The phosphorescence signal can be observed in the 200 °C annealed CD@PVA composites, and vanished after spraving water on the composites. However, after 100 °C annealing, the phosphorescence was almost fully recovered in the CD@PVA composites. Such an erasable/recovered phosphorescence signal provides a useful tool for data encryption. As shown in Fig. 3c, a character "C" can be handwritten with a pen using water as ink on the 200 °C annealed CD@PVA film. Upon turning off the UV light, the water trace shows no phosphorescence signal, and can be clearly distinguished from the phosphorescence background. Importantly, this water-written character "C" can be erased by subsequent 100 °C annealing of the CD@PVA composite to recover the phosphorescence. The water mediated on-off phosphorescence switching exhibits good repeatability, as demonstrated in Fig. S1.†

The energy dispersive X-ray spectra of the CD(a)PVA composite before and after 200 °C annealing as well as after water spraying were collected. As shown in Fig. S2,† the amount of the O element decreased after 200 °C annealing, but showed an obvious increase after subsequent water spraying. The highresolution O_{1s} X-ray photoelectron spectroscopy (XPS) data further revealed that the intensity of the C–O/OH bond greatly decreased after 200 °C annealing, but was recovered after the water spraying (Fig. S3†).

Possible mechanisms for the thermal and water mediated on-off switching of the phosphorescence signal in the CD@PVA composite are illustrated in Scheme 1. The phosphorescence originates from radiative transitions from the triplet state (T) in the CDs followed by the absorption and relaxation through the intersystem crossing (ISC) from the singlet state (S). The relaxation process from the T state in most cases is non-radiative and passes through the vibrational dissipations (Vib. in Scheme 1) occurring in the composite. At the same time, as demonstrated previously, the non-radiative processes deactivating the T state in the CD@PVA composite may be caused by the presence of molecules, such as oxygen, which play the role of a strong phosphorescence quencher.²⁷ During 200 °C annealing, dehydration processes take place between the hydroxyl and carboxyl groups in the CD and PVA



Fig. 3 (a) Fluorescence ("UV on") and phosphorescence ("UV off") images of 200 °C annealed CD@PVA composite films before and after being water sprayed, and those of films further annealed at 100 °C. (b) Phosphorescence decay curves of the 200 °C annealed CDs@PVA before and after being water sprayed, and those of films further annealed at 100 °C. All curves were collected at 480 nm under 360 nm excitation. (c) Fluorescence ("UV on") and phosphorescence ("UV off") images of CD@PVA composite films which were annealed at 200 °C; a character "C" was written using water, and then the films were subjected to annealing at 100 °C.

composite, which covalently bind the CDs within the PVA matrix, resulting in the formation of a rigid matrix. This, in turn, leads to a decrease in the vibrational motions of the CD surface groups together with the formation of a protection layer from the phosphorescence quenchers, such as oxygen, resulting in enhanced phosphorescence. After spraying, the



Scheme 1 Proposed mechanism of the photophysical processes taking place in CD@PVA composites (a) annealed at 60 °C, (b) annealed at 200 °C, and (c) after being water sprayed. "S", "ISC", "T", "Fluo.", "Phosp.", and "Vib." represent "singlet state", "intersystem crossing", "triplet state", "fluorescence", "phosphorescence", and "vibrational relaxation" processes, respectively.

water molecules infiltrate the composite and introduce additional hydroxyl groups bonded with the CD surface groups, as shown in Scheme 1c, accompanied by the breaking of the composite rigid structure. This leads to considerable vibrational motions of the hydroxyl groups and increases the possibility of the penetration of the phosphorescence quenchers in the composite, thus decreasing the phosphorescence intensity. After annealing, the water molecules are heated and the nonradiative transitions are restricted, and the phosphorescence signal is recovered again.

Based on the above results, the concept of multiple data encryption is proposed *via* the water treatment and the subsequent step-by-step thermal annealing at different temperatures, as shown in Fig. 4. Firstly, a symbol "□" was assembled on a glass slide, in which the "[" part was written on a 200 °C annealed CD@PVA composite, and the "]" part was written on



Fig. 4 Schematic presentation of a multiple data encryption using 60 °C and 200 °C annealed CD@PVA composites *via* water spraying and step by step thermal annealing.

a 60 °C annealed CD@PVA composite. When the UV light was turned on, the symbol "□" showed a green fluorescence. Upon turning off the UV light, only the symbol "[" could be observed through its green phosphorescence, which is the first encryption level. In the next step, after the water spraying, the phosphorescence was quenched and the encrypted character "[" was hidden, which is the second encryption level. To decrypt the information, the slide was annealed at 100 °C for 5 min, and the character "[" recovered its green phosphorescence. Finally, the slide was annealed at 200 °C for 5 min, and the whole symbol "□" could be observed again through its phosphorescence, which is the third encryption level. We note that the fluorescence ("UV on" in Fig. 4) of the CD@PVA composite experienced no obvious change during all these treatments.

Water has a strong absorption and the PVA matrix has a negligible absorption in the spectral region of 1400 nm–1600 nm (Fig. 5a), which means that a high power laser beam with such wavelengths can quickly heat and evaporate water from the PVA-based films. Bearing this in mind, a near-infrared laser (1532 nm) beam was used for the contactless removal of adsorbed water molecules from the CD@PVA film, in order to write information visible in the phosphorescence mode, as demonstrated in the inset of Fig. 5a. Laser written green phos-



Fig. 5 (a) Absorption spectra of water and PVA in the infrared region, with an inset presenting the processes of writing on the water sprayed 200 °C annealed CD@PVA film using a focused 1532 nm laser beam. (b) Fluorescence/phosphorescence images of the IR laser written "CD" characters in the 200 °C annealed CD@PVA composite film after being water sprayed under UV light on and off conditions, respectively.

phorescent "CD" characters can be clearly seen with the naked eye (Fig. 5b).

Experimental section

Materials

Citric acid (99.5%) and urea (99%) were purchased from Aladdin. PVA was purchased from Macklin.

Synthesis of CDs

CDs were synthesized in the same way as reported in our previous work.³² Citric acid (3 g) and urea (3 g) were co-dissolved in 10 mL of distilled water, and the mixture was heated in a microwave oven (750 W) for 5 min, which resulted in the formation of a dark-brown solid, which was re-dispersed in water and then purified by centrifugation (3000 rpm, 10 min) to remove the agglomerated particles. A clear brownish supernatant was collected, freeze-dried, and ground into a powder.

Fabrication of CD@PVA composites

0.5 mg of CD powder was dissolved in 2.5 mL of aqueous solution containing 10 wt% PVA, and the mixture was coated onto quartz plates and dried at room temperature, followed by annealing at different temperatures (60–200 $^{\circ}$ C).

Characterization

TEM images were obtained on an FEI Tecnai-G2-F20 transmission electron microscope with an acceleration voltage of 200 kV. UV-visible absorption and PL spectra were collected on a Shimadzu UV-3101PC spectrophotometer and a Hitachi F-7000 spectrophotometer, respectively. TGA was performed on an American TA Q500 analyzer under a nitrogen atmosphere, with a flow rate of 100 mL min⁻¹. FT-IR spectra were obtained with a Perkin–Elmer spectrometer. Time-resolved PL spectra and phosphorescence spectra were recorded on a Life Spec-II lifetime spectrophotometer. Phosphorescence spectra were collected with a time delay of 90 ms. XPS analysis was performed on an ESCALAB MK X-ray photoelectron spectrometer using Mg as the excitation source.

Emission lifetimes

Time-resolved phosphorescence decay curves were collected at 480 nm, under 360 nm excitation. Average luminescence life-times were calculated using the following equation (1):

$$\tau_{\rm avg} = \frac{\sum a_i \tau_i^2}{\sum a_i \tau_i} \tag{1}$$

Time-resolved luminescence decay curves shown in Fig. 2d were fitted with tri-exponential functions. For the CD@PVA composite films annealed at 60 °C, the lifetime components were 2.9 ms (17%), 25.8 ms (31%), and 186.2 ms (52%). For the films annealed at 150 °C, the lifetime components were 4.5 ms (18%), 34.8 ms (27%) and 299.6 ms (55%). For the films annealed at 200 °C, the lifetime components were 3.8 ms (26%), 31.1 ms (20%) and 303.4 ms (54%).

Phosphorescence via laser irradiation

0.5 mg of powdered CDs were dissolved in 2.5 mL of PVA aqueous solution (10 wt% PVA), and then the mixture was coated onto plastic plates and dried at room temperature. The films could be easily peeled off the plates and showed phosphorescence after being annealed at 200 °C. After spraying water on the films, the phosphorescence signal was quenched. A focused laser beam from an optical fiber near infrared laser (1532 nm, 1 W) generated from MD-N-1532-2W-14037157 was then used to handwrite information on the latter.

Conclusions

In summary, a switchable phosphorescence signal is observed in the CD@PVA composite, where an enhanced green emission is obtained after 200 °C annealing and becomes quenched upon exposing the composite to water. Further phosphorescence recovery can be achieved by annealing at 100 °C, or by a 1532 nm laser treatment resulting in the evaporation of the adsorbed water molecules. Water molecules infiltrating the composite break down the CD@PVA composite rigid structure, which leads to considerable vibrational motions of the hydroxyl groups at the CD surface and the possibility of the penetration of the phosphorescence quenchers inside the matrix, and thus the quenching of the phosphorescence. After annealing, the nonradiative transitions are restricted, and the phosphorescence signal is recovered again. Based on these results, multiple data encryption is realized using the CD@PVA composite, which provides a new material system and method for data encryption.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work has been supported by the National Natural Science Foundation of China (projects No. 51602304), the Jilin Province Science and Technology Research (projects No. 20180101190JC, 20170101191JC, 20170101042JC), and the Ministry of Education and Science of the Russian Federation (Grant 14.Y26.31.0028).

Notes and references

- 1 S. Mukherjee and P. Thilagar, *Chem. Commun.*, 2015, **51**, 10988.
- 2 K.-H. Kim, S. Lee, C.-K. Moon, S.-Y. Kim, Y.-S. Park, J.-H. Lee, J. Woo Lee, J. Huh, Y. You and J.-J. Kim, *Nat. Commun.*, 2014, 5, 4769.
- 3 H. Xu, R. Chen, Q. Sun, W. Lai, Q. Su, W. Huang and X. Liu, *Chem. Soc. Rev.*, 2014, **43**, 3259.

- 4 B. Q. Liu, L. Wang, D. Y. Gao, J. H. Zou, H. L. Ning,
 J. B. Peng and Y. Cao, *Light: Sci. Appl.*, 2016, 5, e16137.
- 5 S. Z. Cai, H. F. Shi, J. W. Li, L. Gu, Y. Ni, Z. C. Cheng, S. Wang, W. W. Xiong, L. Li, Z. F. An and W. Huang, *Adv. Mater.*, 2017, 29, 1701244.
- 6 Z. Chen, K. Y. Zhang, X. Tong, Y. Liu, C. Hu, S. Liu, Q. Yu,
 Q. Zhao and W. Huang, *Adv. Funct. Mater.*, 2016, 26, 4386.
- 7 S. Hirata, Adv. Opt. Mater., 2017, 5, 1700116.
- 8 Z. He, W. Zhao, J. W. Y. Lam, Q. Peng, H. Ma, G. Liang,
 Z. Shuai and B. Z. Tang, *Nat. Commun.*, 2017, 8, 416.
- 9 D. Li, X. Yang and D. Yan, ACS Appl. Mater. Interfaces, 2018, 10, 34377.
- 10 M. S. Kwon, D. Lee, S. Seo, J. Jung and J. Kim, Angew. Chem., Int. Ed., 2014, 53, 11177.
- 11 Z. An, C. Zheng, Y. Tao, R. Chen, H. Shi, T. Chen, Z. Wang, H. Li, R. Deng, X. Liu and W. Huang, *Nat. Mater.*, 2015, 14, 685.
- 12 W. J. Kim, M. Nyk and P. N. Prasad, *Nanotechnology*, 2009, **20**, 185301.
- 13 Y. Lu, J. Zhao, R. Zhang, Y. Liu, D. Liu, E. M. Goldys, X. Yang, P. Xi, A. Sunna, J. Lu, Y. Shi, R. C. Leif, Y. Huo, J. Shen, J. A. Piper, J. P. Robinson and D. Jin, *Nat. Photonics*, 2014, 8, 32.
- 14 D. Tu, C. Xu, Y. Fujio and A. Yoshida, *Light: Sci. Appl.*, 2015, 4, e356.
- 15 P. Wu and X. P. Yan, Chem. Soc. Rev., 2013, 42, 5489.
- 16 S. N. Baker and G. A. Baker, Angew. Chem., Int. Ed., 2010, 49, 6726.
- 17 S. Y. Lim, W. Shen and Z. Gao, *Chem. Soc. Rev.*, 2015, 44, 362.
- 18 X. Miao, D. Qu, D. Yang, B. Nie, Y. Zhao, H. Fan and Z. Sun, Adv. Mater., 2018, 30, 1.
- 19 Y. Xiong, J. Schneider, C. J. Reckmeier, H. Huang, P. Kasak and A. L. Rogach, *Nanoscale*, 2017, 9, 11730.

- 20 S. Qu, D. Zhou, D. Li, W. Ji, P. Jing, D. Han, L. Liu, H. Zeng and D. Shen, *Adv. Mater.*, 2016, 28, 3516.
- 21 D. Li, D. Han, S. N. Qu, L. Liu, P. T. Jing, D. Zhou, W. Y. Ji, X. Y. Wang, T. F. Zhang and D. Z. Shen, *Light: Sci. Appl.*, 2016, 5, 1.
- 22 X. Bao, Y. Yuan, J. Chen, B. Zhang, D. Li, D. Zhou, P. Jing, G. X. Y. Wang, K. Hola, C. Wu, L. Song, C. Liu, R. Zboril and S. Qu, *Light: Sci. Appl.*, 2018, 7, 91.
- 23 G. Xu, X. Bao, J. Chen, B. Zhang, D. Li, D. Zhou, X. Wang,
 C. Liu, Y. Wang and S. Qu, *Adv. Healthcare Mater.*, 2018, 1800995.
- 24 S. Qu, D. Shen, X. Liu, P. Jing, L. Zhang, W. Ji, H. Zhao, X. Fan and H. Zhang, *Part. Part. Syst. Charact.*, 2014, 31, 1175–1182.
- 25 Y. Deng, D. Zhao, X. Chen, F. Wang, H. Song and D. Shen, *Chem. Commun.*, 2013, **49**, 5751–5753.
- 26 S. Kalytchuk, Y. Wang, K. Polakova and R. Zboril, ACS Appl. Mater. Interfaces, 2018, 35, 29902.
- 27 K. Jiang, Y. H. Wang, C. Z. Cai and H. W. Lin, Adv. Mater., 2018, 30, 1800783.
- 28 K. Jiang, Y. H. Wang, X. L. Gao, C. Z. Cai and H. W. Lin, Angew. Chem., Int. Ed., 2018, 57, 6216.
- 29 C. J. Lin, Y. X. Zhuang, W. H. Li, T. L. Zhou and R. J. Xie, *Nanoscale*, 2018, **11**, 6584.
- 30 K. Jiang, Y. H. Wang, C. Z. Cai and H. W. Lin, *Chem. Mater.*, 2017, 29, 4866.
- 31 Z. Tian, D. Li, E. V. Ushakova, V. G. Masliv, D. Zhou, P. Jing, D. Shen, S. Qu and A. L. Rogach, *Adv. Sci.*, 2018, 1800795.
- 32 S. Qu, X. Wang, Q. Lu, L. X. Liu and L. Wang, Angew. Chem., 2012, **124**, 12381.
- 33 T. F. Yeh, C. Y. Teng, S. J. Chen and H. Teng, Adv. Mater., 2014, 26, 3297.
- 34 D. Qu, M. Zheng, J. Li, Z. Xie and Z. Sun, *Light: Sci. Appl.*, 2015, 4, e364.