

Red-Emissive Carbon Dots for Fingerprints Detection by Spray Method: Coffee Ring Effect and Unquenched Fluorescence in Drying Process

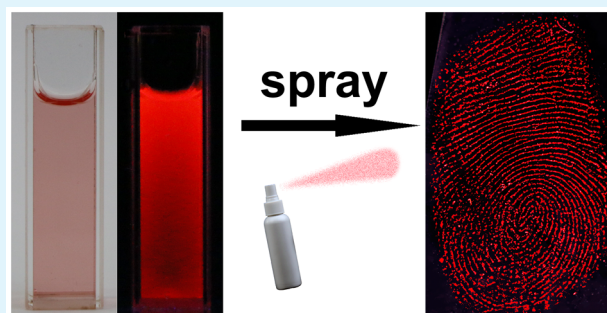
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S Supporting Information

ABSTRACT: Brightly red fluorescent carbon dots are synthesized hydrothermally and dissolved in diluted hydrochloric acid solution. Such carbon dots exhibit excitation-independent emission at about 620 nm with quantum yield over 10%, which is visible in daylight. After the carbon dots solution is sprayed to the fingerprints on various solid substrates and dried in air, clear fingerprints can be seen under an ultraviolet lamp and stay stable for 1 day. Detailed characterizations suggest that during the drying process, the coffee-ring effect and the electrostatic interactions between the carbon dots and the fingerprint residues prevent the typical aggregation-induced fluorescence quenching of carbon dots.

KEYWORDS: carbon dot, fluorescence, fingerprint, visualization, coffee ring effect



Fingerprints analyses have provided reliable evidence for criminal investigations for more than a century.^{1,2} When a finger touches a solid surface, eccrine sweat and oily sebum will leave an imprint of the finger's ridge patterns. Such an imprint is named latent fingerprint (LFP) because it cannot be seen clearly by the naked eyes, and thus the goal of fingerprints detection is to enhance the visualization of LFPs.³ To date, various methods have been developed on the basis of chemical or physical interactions between the chosen reagents with the fingerprint residues.^{4–7} These methods include powder dusting, fluorescent dye staining, cyanoacrylate/iodine fuming, and vacuum metal deposition.⁸ Among them, fluorescence staining is a general approach for LFPs detection with high sensitivity.⁵ Typical fluorescent materials, such as organic dyes,⁹ conjugated polymers,¹⁰ quantum dots,¹¹ and rare earth complexes,¹² have been reported for this application.

Fluorescent carbon dots (CDs) have attracted much attention in the past decade because of their low cost, green synthesis, stable luminescence, good biosafety, and environmental friendliness.¹³ Although CDs have been widely applied in bioimaging, drug delivery, fluorescence sensing, and analyses,^{14–19} there are few reports involving the LFPs detection by CDs.^{20–23} In fact, several obstacles are hindering CDs application in LFP detection. First, most CDs are blue-green emitting, so that their fluorescence is interfered with by self-fluorescence from substrates like paper and plastic. Second, the fluorescence of CDs is always quenched by their aggregation in the solid state,²⁰ and thus the spraying method

has not been performed successfully before. Third, only CD-based hybrid powders have been reported for LFPs detection,²¹ but their fluorescence are too weak to be seen by naked eyes, and brushing nanoparticles powder will destroy the fingerprint details and risk the health of the examiners.⁵ Finally, as for the CD dispersion mediums, water usually cannot adhere stably on many glossy surfaces, whereas organic solvents often destroy LFPs. Therefore, it is still a challenge to light up LFPs by CDs in a simple, portable, safe, clear, and compatible way.

In the present research, we synthesized red-emissive fluorescent CDs (R-CDs) hydrothermally and applied them to visualize LFPs by a simple spraying method. The background fluorescence interference is minimized by the red-emission, and the typical aggregation-induced fluorescence quenching of CDs was overcome and utilized ingeniously. After careful investigations on the enhanced LFPs, we found the R-CDs were extracted into the tiny water droplets which located at the edges of fingerprints. Such an extraction process can be ascribed to the coffee-ring effect during water vaporization and the electrostatic interactions between R-CDs and the fingerprint residues. Our R-CDs are able to detect LFPs on many kinds of solid surfaces, and thus they are promising for practical criminal investigations as a simple, fast, portable, and accurate tool.

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Experimentally, the R-CDs were synthesized by hydrothermal treatment of p-phenylenediamine and phosphorus acid. After purification, 10 mg of R-CDs was dissolved in 10 mL of 0.1 M hydrochloric acid aqueous solution. The solution was sealed into a little spray bottle and sprayed onto the fingerprints. In general, the developing time for R-CDs stained finger prints is about half an hour at room temperature, while the optimal record time for taking photos is about several hours. To clarify structures and surface properties, which is crucial for developing fingerprints, the as-prepared R-CDs were characterized by various methods.

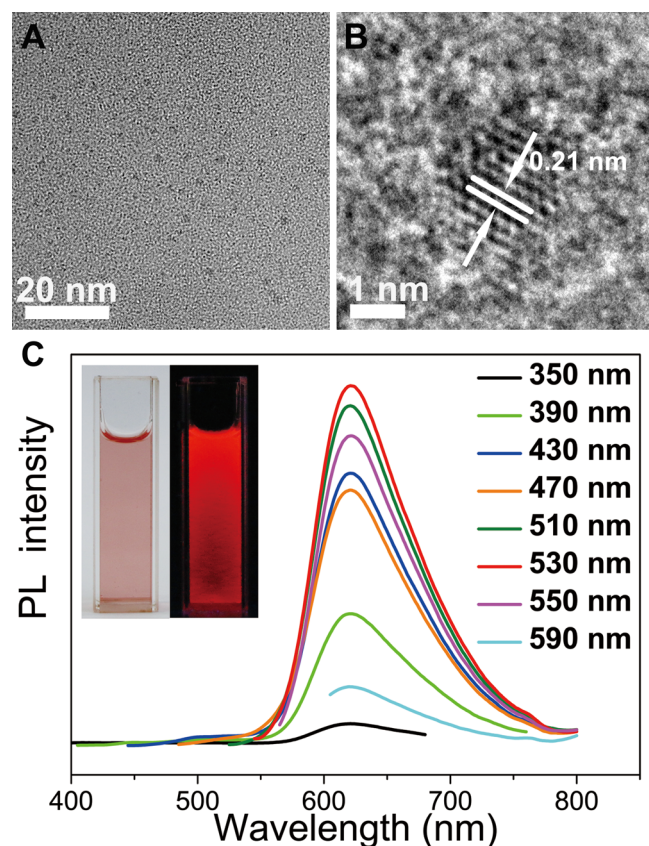


Figure 1. (A) TEM and (B) HRTEM images of R-CDs, and (C) photoluminescent (PL) emission spectra of R-CDs under excitation light of different wavelengths (the inset legends). The inset photos are the sample in room light (left) and under a UV lamp (right), respectively.

The TEM image (Figure 1A) shows that the R-CDs are uniform and well dispersed with an average diameter of 2.4 nm, whereas the HRTEM image of R-CDs (Figure 1B) presents the lattice fringes with an average interplanar spacing of 0.21 nm, corresponding to the (101) lattice space of graphite.²⁴ X-ray photoelectron spectra (XPS) in the full range (Figure S1A) prove the existence of C 1s (285 eV), N 1s (400 eV), O 1s (532 eV) and Cl 2p (198 eV).²⁵ We can obtain from the XPS spectra that the element contents are 69.79, 12.51, 9.91, and 7.80% for C, O, N, and Cl, respectively. In the high-resolution XPS spectra (Figure S1B–D), the C 1s band can be deconvoluted into two peaks corresponding to sp² carbons (C=C, 284.6 eV) and sp³ carbons (C–O/C–N, 285.6 eV). Unlike most of the reported CDs, carbonyl carbons (C=O, 287.8 eV) and

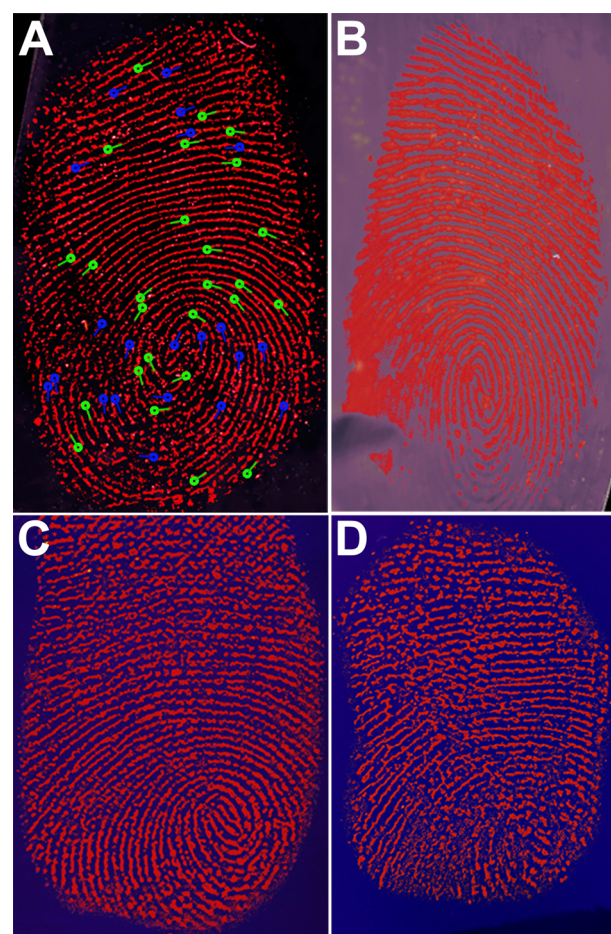


Figure 2. Photographs of R-CDs stained fingerprints on (A) glass sheet, (B) aluminum foil, (C) leather, and (D) plastic pieces under UV light, respectively. The ridge termination points (green) and the bifurcation points (blue) are marked in A.

carboxyl carbons (COOH, 289.0 eV) are not observed in the XPS of our sample. The O 1s band contains two peaks at 532.4 and at 536.2 eV for C–O and the absorbed oxygen or H₂O, respectively. The N 1s band can be deconvoluted into three peaks at 399.2, 400.3, and 401.4 eV, representing amino N, pyrrolic N, and graphite N, respectively, which indicates that the R-CDs have good dispersibility in acidic solution. The Fourier transform infrared (FTIR) spectra (Figure S2) show O–H or N–H stretching vibrations at 3414 cm^{−1}, C=C or C=N vibrations at 1630 cm^{−1}, and a broad band representing oxygen-related groups like –OH and C–O at 1380–1290 cm^{−1}.²⁶ The sharp peak at 1500 cm^{−1} results from the –NH₃⁺, indicating the R-CDs are apt to accept H⁺ ions in acidic solutions to form positive nanoparticles. Such CDs have a zeta potential of 18.7 mV, distinguished from those conventional CDs with negatively charged surfaces. The positive surface charge is very important for the fingerprints detection, because the residues of sweat and sebum are negatively charged.²⁷

The UV–visible absorption and fluorescence spectra of the R-CDs are shown in Figure S3. In the UV region, two absorption maxima at 240 and 283 nm are corresponding to the π – π^* transitions of C=C and C=N bonds of the aromatic rings, respectively. In the visible region, a broad absorption band within 360–600 nm can be assigned to the complicated surface states of R-CDs. In Figure 1C, the emission peak at 622 nm is independent of the excitation wavelengths, and its highest

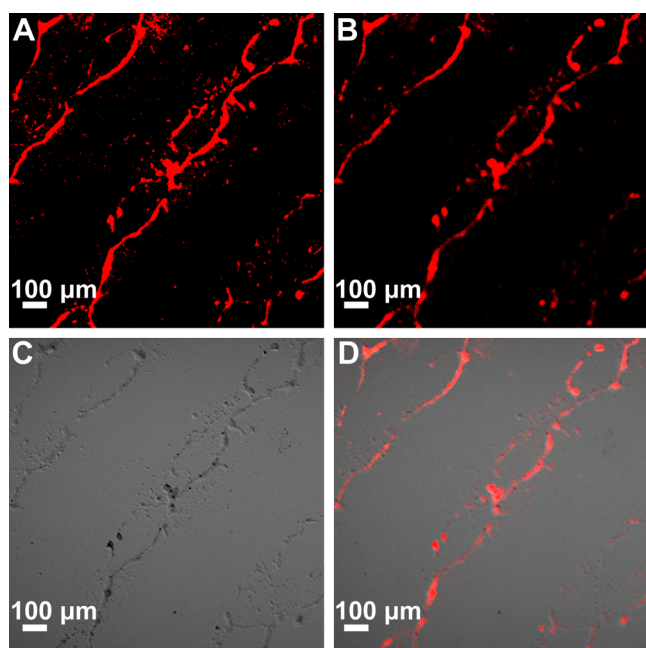


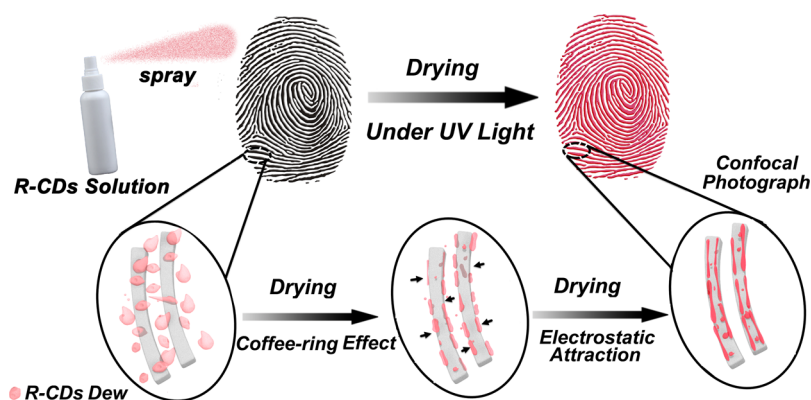
Figure 3. Confocal fluorescence images of the R-CDs stained fingerprints on glass (A) in dark field after 30 min drying, and in (B) dark field and (C) bright field after 60 min drying, respectively. (D) Merged picture of B and C.

emission intensity is observed when the excitation wavelength is set at 530 nm. The fluorescence excitation spectrum of R-CDs can be well overlapped with the absorption curve in the visible region (Figure S3), indicating that the surface structures and states are responsible for the red emission. The corresponding luminescent mechanism may be ascribed to the surface molecular state fluorescence.²⁸ The so-called surface molecular state fluorescence is regarded as one of the supposed origins of CDs fluorescence, which is related to the surface molecular groups on CDs and shows excitation-independent PL emission. Our R-CDs possess strong red fluorescence under UV light, and they can even emit red fluorescence in daylight at lab. Their optimal quantum yield in aqueous solution is measured to be 11.2% by an integrating sphere, which is outstanding among the reported R-CDs. Therefore, both the excitation-independent red fluorescence and the positively charged surface states of our R-CDs are beneficial to the following LFPs detection.

After one drop of R-CDs aqueous solution is dried on a clean flat surface, a red circular stamp appears. This phenomenon is the so-called “coffee-ring effect”, which discloses that as liquid evaporation proceeds, the capillary flow outward from the center of the liquid will bring the suspended particles to the edge until almost all particles deposit to form a ring pattern.²⁹ Further drying the substrate will cause the solid-state R-CDs lose their red fluorescence due to the well-known aggregation induced fluorescence quenching of CDs. However, if the substrate is touched by fingers beforehand, the situation will change dramatically. In Figure 2 A, although the R-CDs are sprayed homogeneously on the glass sheet, only the ridges of fingerprints show bright red patterns after drying, while the regions in the fingerprint furrows and outside LFPs are not fluorescent. The second-level details, such as the ridge termination and bifurcation, can be also recognized. These details form the basis of fingerprint identification in principle, and they are critical in practical identification.⁷ The red fluorescence of fingerprints are so strong that it can even overcome the reflection light from the aluminum foil (Figure 2B) and the blue background fluorescence from leather (Figure 2C) and plastic (Figure 2D).

To study these interesting results deeply, we employed a laser scanning confocal microscope to observe the R-CD stained fingerprints on a glass sheet. After the glass sheet was sprayed and dried in air for 30 min, the dark-field image (Figure 3 A) clearly shows numerous tiny red droplets, whereas the majority of fluorescent droplets are aggregated to the edges of fingerprints. This phenomenon can be explained by the coffee-ring effect, that as water vaporizes, R-CDs sprayed into the other regions are forced to the edges of fingerprints where there is separation between the sebum-covering region and the no-sebum region. More interestingly, after another 30 min drying, most tiny red droplets disappeared, whereas the R-CDs at the edges of fingerprints remained luminescent (Figure 3B). The bright-field image (Figure 3C) confirms some liquids are located at the edges of fingerprints, which can overlap perfectly with the dark-field image (Figure 3 D). Therefore, the final results are ascribed to the fluorescence quenching of CDs when they changed from the liquid phase to the solid state. On one hand, because the lipid compounds in the fingerprint residues are able to prevent water evaporation, those R-CDs solution sprayed into the fingerprints will be protected by lipids from evaporation. On the other, the R-CDs solution sprayed into the gaps between fingerprints and the blank area outside fingerprints will dry gradually, but during the drying process some R-

Scheme 1. Fluorescence Staining Process and Mechanism of R-CDs toward the Fingerprints on Solid Substrates



CDs will be pushed to fingerprint edges due to the coffee-ring effect, while the other R-CDs aggregate in the blank area and lose their fluorescence. It is known that the fingerprint residues contain the negatively charged fatty acids, which might have electrostatic interactions^{27,30} with the positive R-CDs so as to coat the tiny water droplets by sebum. As a result, the sebum coating prevents water evaporation and maintains the fluorescence of the R-CDs for a few days at room temperature. Scheme 1 illustrates the fluorescence staining process and the unquenched fluorescence mechanism of our R-CDs, which are based on the coffee-ring effect and the electrostatic interactions.

In summary, we synthesized a new kind of CDs with strong red fluorescence and positive surface charges in water. They can be sprayed onto various solid surfaces to show the LFPs clearly under UV light. Although the aggregation-induced fluorescence quenching is a universal problem for CDs, the LFPs stained by our R-CDs remained luminescence in air for a long time. Detailed characterizations disclosed the coffee-ring effect during water evaporation and the electrostatic interactions between R-CDs and the fingerprint residues, which prevented the red fluorescence at the fingerprint edges from quenching. Our present research provides an effective, rapid, portable, and user-friendly method for fingerprint detection.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.7b03917.

Details of the experiments and characterization results of XPS, FTIR, DLS, UV-vis, Raman, PL spectra, and CLSM images (PDF)

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

- (1) Oden, S.; Von Hofsten, B. Detection of Fingerprints by the Ninhydrin Reaction. *Nature* **1954**, *173*, 449–450.
- (2) Jickells, S. M. Fingerprinting: Into the Future. *Meas. Control* **2008**, *41*, 243–247.
- (3) Hazarika, P.; Russell, D. A. Advances in Fingerprint Analysis. *Angew. Chem., Int. Ed.* **2012**, *51*, 3524–3531.
- (4) Leggett, R.; Lee-Smith, E. E.; Jickells, S. M.; Russell, D. A. "Intelligent" Fingerprinting: Simultaneous Identification of Drug Metabolites and Individuals by Using Antibody-functionalized Nanoparticles. *Angew. Chem., Int. Ed.* **2007**, *46*, 4100–4103.
- (5) Xu, L.; Zhang, C.; He, Y.; Su, B. Advances in the Development and Component Recognition of Latent Fingerprints. *Sci. China: Chem.* **2015**, *58*, 1090–1096.
- (6) Jie, Y.; Zhu, H. R.; Cao, X.; Zhang, Y.; Wang, N.; Zhang, L. Q.; Wang, Z. L. One-Piece Triboelectric Nanosensor for Self-Triggered

Alarm System and Latent Fingerprint Detection. *ACS Nano* **2016**, *10*, 10366–10372.

(7) Xu, L. R.; Li, Y.; Wu, S. Z.; Liu, X. H.; Su, B. Imaging Latent Fingerprints by Electrochemiluminescence. *Angew. Chem., Int. Ed.* **2012**, *51*, 8068–8072.

(8) Sodhi, G. S.; Kaur, J. Powder Method for Detecting Latent Fingerprints: A Review. *Forensic Sci. Int.* **2001**, *120*, 172–176.

(9) Wang, K. R.; Yang, Z. B.; Li, X. L. High Excimer-State Emission of Perylene Bisimides and Recognition of Latent Fingerprints. *Chem. - Eur. J.* **2015**, *21*, S680–S684.

(10) Yoon, J. H.; Jin, Y. J.; Sakaguchi, T.; Kwak, G. Visualization of Sweat Fingerprints on Various Surfaces Using a Conjugated Polyelectrolyte. *ACS Appl. Mater. Interfaces* **2016**, *8*, 24025–24029.

(11) Ryu, S. J.; Jung, H. S.; Lee, J. K. Latent Fingerprint Detection Using Semiconductor Quantum Dots as a Fluorescent Inorganic Nanomaterial for Forensic Application. *Bull. Korean Chem. Soc.* **2015**, *36*, 2561–2564.

(12) Wang, M.; Li, M.; Yu, A.; Wu, J.; Mao, C. Rare Earth Fluorescent Nanomaterials for Enhanced Development of Latent Fingerprints. *ACS Appl. Mater. Interfaces* **2015**, *7*, 28110–28115.

(13) Lim, S. Y.; Shen, W.; Gao, Z. Q. Carbon Quantum Dots and Their Applications. *Chem. Soc. Rev.* **2015**, *44*, 362–381.

(14) Jiang, K.; Sun, S.; Zhang, L.; Lu, Y.; Wu, A.; Cai, C.; Lin, H. Red, Green, and Blue Luminescence by Carbon Dots: Full-Color Emission Tuning and Multicolor Cellular Imaging. *Angew. Chem., Int. Ed.* **2015**, *54*, 5360–5363.

(15) Cao, L.; Wang, X.; Meziani, M. J.; Lu, F. S.; Wang, H. F.; Luo, P. J. G.; Lin, Y.; Harruff, B. A.; Veca, L. M.; Murray, D.; Xie, S. Y.; Sun, Y. P. Carbon dots for multiphoton bioimaging. *J. Am. Chem. Soc.* **2007**, *129*, 11318–11319.

(16) Zheng, M.; Liu, S.; Li, J.; Qu, D.; Zhao, H. F.; Guan, X. G.; Hu, X. L.; Xie, Z. G.; Jing, X. B.; Sun, Z. C. Integrating Oxaliplatin with Highly Luminescent Carbon Dots: An Unprecedented Theranostic Agent for Personalized Medicine. *Adv. Mater.* **2014**, *26*, 3554–3560.

(17) Li, G. L.; Fu, H. L.; Chen, X. J.; Gong, P. W.; Chen, G.; Xia, L.; Wang, H.; You, J. M.; Wu, Y. N. Facile and Sensitive Fluorescence Sensing of Alkaline Phosphatase Activity with Photoluminescent Carbon Dots Based on Inner Filter Effect. *Anal. Chem.* **2016**, *88*, 2720–2726.

(18) Chen, H.; Xie, Y. J.; Kirillov, A. M.; Liu, L. L.; Yu, M. H.; Liu, W. S.; Tang, Y. A Ratiometric Fluorescent Nanoprobe Based on Terbium Functionalized Carbon Dots for Highly Sensitive Detection of an Anthrax Biomarker. *Chem. Commun.* **2015**, *51*, 5036–5039.

(19) Baptista, F. R.; Belhout, S. A.; Giordani, S.; Quinn, S. J. Recent Developments in Carbon Nanomaterial Sensors. *Chem. Soc. Rev.* **2015**, *44*, 4433–4453.

(20) Xu, M.; He, G.; Li, Z.; He, F.; Gao, F.; Su, Y.; Zhang, L.; Yang, Z.; Zhang, Y. A Green Heterogeneous Synthesis of N-doped Carbon Dots and Their Photoluminescence Applications in Solid and Aqueous States. *Nanoscale* **2014**, *6*, 10307–10315.

(21) Fernandes, D.; Krysmann, M. J.; Kelarakis, A. Carbon Dot Based Nanopowders and Their Application for Fingerprint Recovery. *Chem. Commun.* **2015**, *51*, 4902–4905.

(22) Wang, C. L.; Wu, W. C.; Periasamy, A. P.; Chang, H. T. Electrochemical Synthesis of Photoluminescent Carbon Nanodots from Glycine for Highly Sensitive Detection of Hemoglobin. *Green Chem.* **2014**, *16*, 2509–2514.

(23) Dilag, J.; Kobus, H.; Yu, Y.; Gibson, C. T.; Ellis, A. V. Non-toxic Luminescent Carbon Dot/Poly(dimethylacrylamide) Nanocomposite Reagent for Latent Fingerprint Detection Synthesized via Surface Initiated Reversible Addition Fragmentation Chain Transfer Polymerization. *Polym. Int.* **2015**, *64*, 884–891.

(24) Liu, J.; Liu, Y.; Liu, N. Y.; Han, Y. Z.; Zhang, X.; Huang, H.; Lifshitz, Y.; Lee, S. T.; Zhong, J.; Kang, Z. H. Metal-free Efficient Photocatalyst for Stable Visible Water Splitting via a Two-electron Pathway. *Science* **2015**, *347*, 970–974.

(25) Ding, H.; Yu, S. B.; Wei, J. S.; Xiong, H. M. Full-Color Light-Emitting Carbon Dots with a Surface-State-Controlled Luminescence Mechanism. *ACS Nano* **2016**, *10*, 484–491.

- (26) Wei, J. S.; Ding, H.; Zhang, P.; Song, Y. F.; Chen, J.; Wang, Y. G.; Xiong, H. M. Carbon Dots/NiCo₂O₄ Nanocomposites with Various Morphologies for High Performance Supercapacitors. *Small* **2016**, *12*, 5927–5934.
- (27) Gao, F.; Han, J. X.; Zhang, J.; Li, Q.; Sun, X. F.; Zheng, J. C.; Bao, L. R.; Li, X.; Liu, Z. L. The Synthesis of Newly Modified CdTe Quantum Dots and Their Application for Improvement of Latent Fingerprint Detection. *Nanotechnology* **2011**, *22*, 075705.
- (28) Pan, L. L.; Sun, S.; Zhang, L.; Jiang, K.; Lin, H. W. Near-infrared Emissive Carbon Dots for Two-photon Fluorescence Bioimaging. *Nanoscale* **2016**, *8*, 17350–17356.
- (29) Yunker, P. J.; Still, T.; Lohr, M. A.; Yodh, A. G. Suppression of the Coffee-ring Effect by Shape-dependent Capillary Interactions. *Nature* **2011**, *476*, 308–311.
- (30) Wang, F.; Chen, J.; Zhou, H.; Li, W.; Zhang, Q.; Yu, C. Facile Detection of Latent Fingerprints on Various Substrates Based on Perylene Probe Excimer Emission. *Anal. Methods* **2014**, *6*, 654–657.