

Fluorescence Retention of Organosilane-polymerized Carbon Dots Inverse Opals in CuCl Suspension

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Electronic Supplementary Information

Abstract A novel and fluorescence retention inverse opal has been achieved from organosilane-polymerized carbon dots (SiCDs), which is prepared *via* infiltrating SiCD solution into the interstice of photonic crystal (PC) template, low temperature treatment, heating polymerization and removing the colloidal template. The as-prepared SiCD inverse opals demonstrate close-cell structure, which is completely different from conventional open-cell structure. Then the fluorescence signal of as-prepared sample keeps almost unchanged in CuCl suspension while the fluorescence of SiCD solution can be quenched by CuCl suspension through an effective electron transfer process. This phenomenon can be attributed to the combined effect of high hydrostatic pressure in the pore structure, stable crosslinking network and fluorescence enhancement by PC structure. The SiCD inverse opals have advantages of unique close-cell structure, easy preparation and good repeatability that give an important insight into the design and manufacture of novel and advanced optical devices.

Keywords Carbon dots; Inverse opals; Close-cell structure; Fluorescence retention; Inorganic salt solution

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INTRODUCTION

Typical luminescent material of carbon dots (CDs) has been widely used in the field of bioimaging^[1, 2], light-emitting devices^[3–6] and sensitive detector^[7, 8] owing to the low cost, good biocompatibility, resistance to photobleaching and broadband optical absorption^[9–14]. Scientists have synthesized diverse components of CDs and endowed them with multi-functional ability. Especially for sensors, Hg²⁺^[15], Cr³⁺^[16], Cu²⁺^[17] and Fe³⁺^[18] could be successfully detected by CDs based on the selective fluorescence quenching of CDs towards specific ions. Fluorescence quenching of CDs toward specific ions is a basic function for its sensing applications, but this intrinsic property also reflects the instability of CD fluorescence. To our best knowledge, few papers focus on how to eliminate the quenching effect of CD materials. In this work, we put forward a unique approach to improve the stability of CDs, *i.e.*, eliminating its fluorescent quenching phenomenon upon contacting of metal ions by combining CDs and photonic crystal (PC) structure. It is known that PCs

can be applied in sensing detecting^[19–22], photocatalysis^[23–26] and novel optical devices^[27–37] owing to the periodic structure on optical scale^[38, 39]. At present, few papers have reported the combination of CDs and PCs and it is expected that this approach will endow material with unprecedented properties and applications^[40, 41]. Typically, enhanced Raman scattering^[42], high detection performance for Hg²⁺^[43] and improved photoelectrochemical performance^[44] could be achieved by CDPCs. In this paper, organosilane-polymerized CD inverse opals (SiCDIOs) were obtained by infiltrating a well-designed organosilane^[13, 45] modified CD material into the interstice of PC template, low temperature treatment, thermal polymerization and subsequent template removal. As-fabricated SiCDIOs demonstrated close-cell structure, water-impermeable property and fluorescence retention in diverse inorganic salt (IS) solutions/suspension, such as CuCl suspension, FeCl₃, KCl, Pb(NO₃)₂ and *etc.* This phenomenon can be attributed to the combined effect of high hydrostatic pressure in the pore structure, stable crosslinking network and fluorescence enhancement by PC structure. This unique fluorescence retention property makes it more extensive for applications in multi-functional optical devices, especially for the optical devices requiring stable and persistent fluorescence. For example, SiCDIOs can be used in light

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emitting diode with good performance based on stable fluorescence towards external environment stimulation.

RESULTS AND DISCUSSION

Figure 1 shows a fabrication process of close-cell SiCDIOs from “sacrificial template” method by thermal polymerization. Here, SiCDs (Fig. 1A1) indicated graphene quantum dots modified by organosilanes^[13, 45]. In details, citric acid (0.5 g), *N*-(β -aminoethyl)- γ -aminopropyl methyldimethoxy silane (AEAPMS) (10 mL) and water (10 mL) were sealed into a Teflon equipped stainless steel autoclave and placed in a drying oven with hydrothermal treatment at 180 °C for 12 h. After the reaction, the autoclave was cooled to room temperature. The resulting light brown solution was purified by washing with hexane three times and extracted to obtain yellow brown SiCD fluid. Then the prepared SiCDs were dissolved in ethanol with the volume ratio of 3:1. Finally, the SiCD solution was kept in the refrigerating chamber (3 °C) prior to use. Firstly, the ethanol solution of SiCDs ($V_{\text{CDs}}:V_{\text{ethanol}} = 3:1$) was carefully dropped into a hydrophilic, poly(styrene-methyl methacrylate-acrylic acid) (poly(St-MMA-AA)) PC template (treated by plasma

for 60 s), and the infiltrated sample was kept at 3 °C for 3 h to facilitate a full infiltration of viscous SiCD fluids into the interstice. Subsequently, the sample was put at 80 °C for 24 h. The polymer networks of crosslinked organosilane chain formed *via* thermal polymerization (Fig. 1B) in this process. As a result, a transparent, yellowish brown and hard material formed in the interstice of PC template as shown in Fig. 1(B). Finally, the close-cell SiCDIOs were obtained after dissolving the PC template by tetrahydrofuran (THF). Notably, the close-cell structure could be attributed to the low-temperature process, which induced a shrinkage of soft PAA shell of latex spheres (Figs. 1B1 and 1B2), accompanied with a simultaneous infiltration of SiCD fluids into the shrinkage part (Fig. 1B2). Meantime, the low-temperature infiltration ensured low viscosity and longer evaporation time of SiCD fluids, resulting in a full infiltration of SiCD fluids into the interstice of the latex spheres, contributing to the formation of a complete encapsulation of latex spheres by SiCD fluids shell. The thickness of soft PAA shell of a latex sphere was *ca.* 41 nm (calculated from TEM image in Fig. S1, in the electronic supplementary information, ESI), indicating a larger space for shrinking. Furthermore, the reflectance spectra

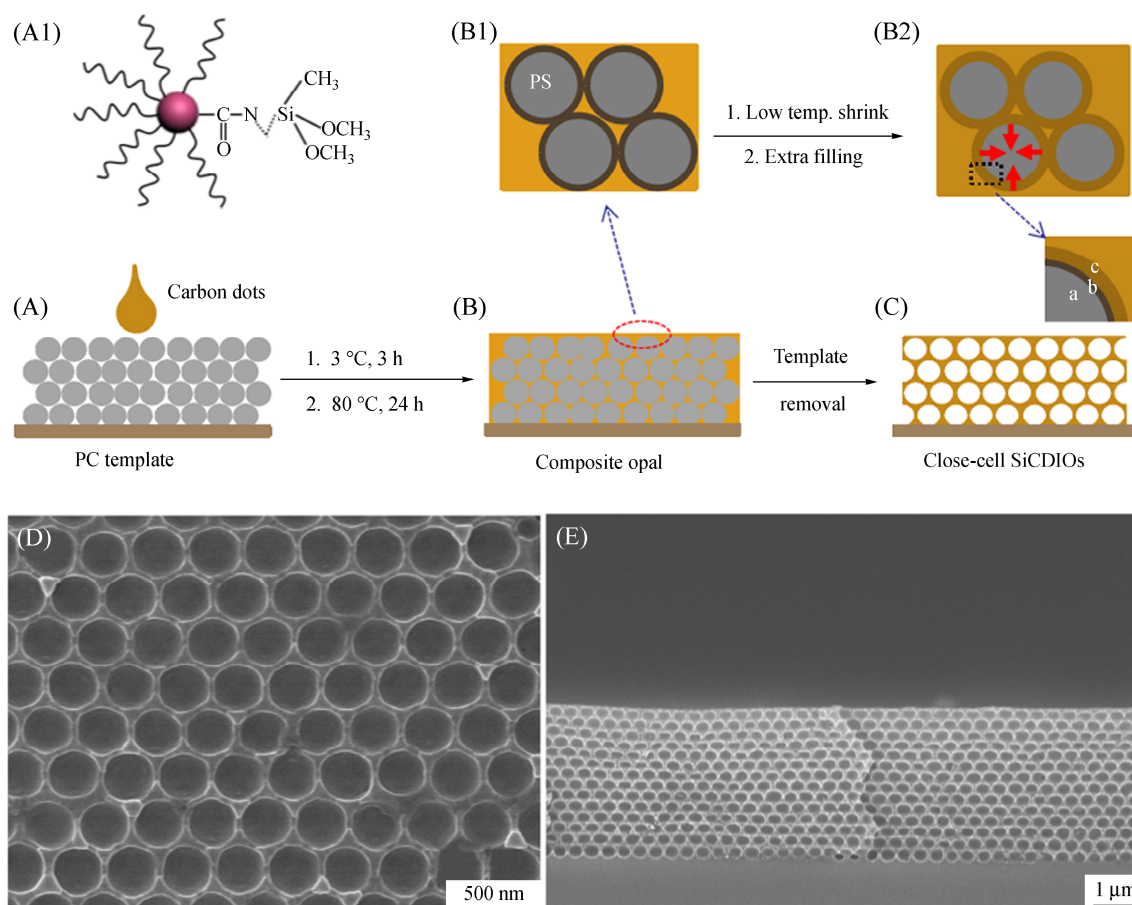


Fig. 1 (A–C) Schematic illustration for the fabrication process of close-cell SiCDIOs: (A) organosilane-CD solution infiltrating into hydrophilic PC template, (A1) chemical structure of organosilane-CDs, (B) thermopolymerization of organosilane-CDs in the interstice of latex spheres to form a composite opal at 80 °C for 24 h, (B1) core-shell latex spheres assembly infiltrated by SiCD solution, (B2) the shrink process of latex spheres in low temperature environment, which caused a further infiltration of SiCD fluids into the shell layer of latex spheres (a, b, c indicate the polystyrene, poly(methyl methacrylate-acrylic acid) and SiCDs respectively.), (C) as-fabricated close-cell SiCDIOs after removing PC template; (D, E) SEM images of as-prepared sample: (D) top view, (E) side view

(Fig. S2, in ESI) of PC template (assembled by latex spheres) during heating or cooling process were recorded to confirm the swelling/shrinking ability of soft PAA shell. Obviously, the bandgap of sample varied from 536, 539 nm to 541 nm when the sample was heated from room temperature to 100 °C, indicating the swelling of latex spheres in the heating process. In contrast, a shrinking of latex spheres occurred with the sample's bandgap changed from 541, 539 nm to 533 nm when the sample was cooled from 100 °C to room temperature. Clearly, the sample showed well-ordered periodic arrangement with pore dimension of *ca.* 290 nm (Fig. 1D), indicating a successful fabrication of inverse opal structure. The width of the reflectance peaks (Fig. S3, in ESI) was narrow and reflectance intensity of samples was up to 60%, indicating a good PC structure. In the top-view and side-view SEM images (Figs. 1D and 1E) of close-cell SiCDIOs, the internal structure could not be seen from the outermost layer, indicating the formation of close-cell structure with pores separated from each other, which had great difference from the traditional inverse opal structure.

Figures 2(a) and 2(b) demonstrate TEM images of as-prepared SiCDIOs. Clearly, the existence of graphene quantum dots with a dimension of *ca.* 5 nm in the inverse opal

framework could be proven from TEM images (Figs. 2a and 2b) and Figs. S4(c) and S4(d) (in ESI), indicating a polymer network of SiCDs was formed. Pore structure observed in TEM images was similar to that in SEM images (Fig. 1d). XPS analysis (at different detecting angles, Fig. 2c) was performed to clarify the chemical component distribution of the close-cell SiCDIOs from the surface to the interior of the film. Different detecting angles indicated the different detecting depth of sample. Clearly, Si and N mainly existed in the organosilane chain while C was primarily found in graphene quantum dots. The Si and N contents reduced firstly and then increased with the observing angle shifting from 30° to 90° during XPS test. That is, silane chain mainly existed in the upper and lower layers. In comparison, the C content increased firstly and then decreased when varying observing angle from 30° to 90°. That meant C mainly existed in the middle of the close-cell SiCDIOs structure. Figure 2(dI) presents an optical image of SiCDIOs under ordinary white light, indicating its red structure color, large area and relatively smooth surface. Figures 2(dII, dIII and dIV) are the fluorescent images of SiCDIOs when being excited at laser of 375, 480 and 560 nm respectively. Obviously, SiCDIOs presented a high-intensity fluorescence

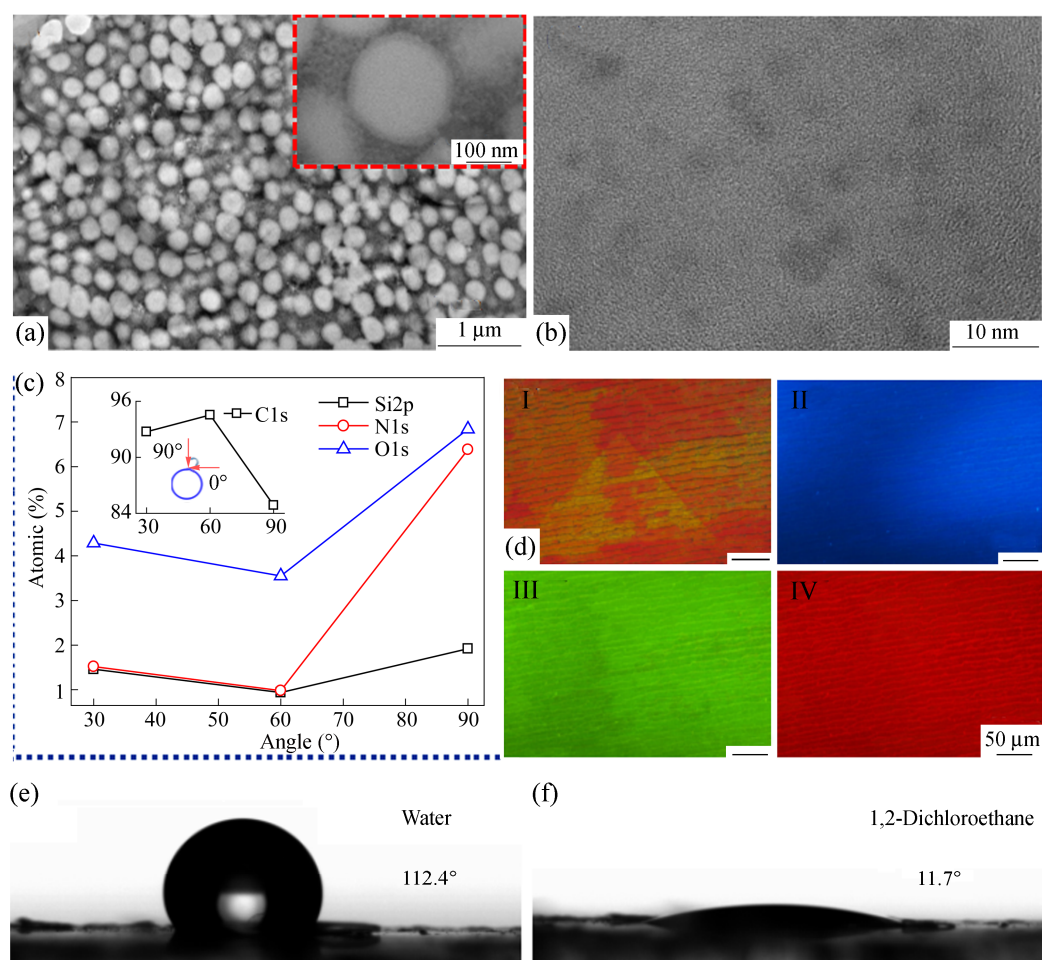


Fig. 2 (a, b) TEM images of close-cell SiCDIOs; (c) XPS results for the composition of Si, N, O, C on the as-prepared close-cell SiCDIOs with varying observing angle from 30° to 90°; (d) Optical image (I) and corresponding fluorescent images (II, III and IV) of close-cell SiCDIOs, which were excited by laser at (II) 375, (III) 480 and (IV) 560 nm respectively; (e, f) CAs of (e) water and (f) 1,2-dichloroethane on the surface of sample

of blue, green and red respectively, indicating an excellent inheritance of the “tricolor-fluorescence” property from SiCDs. The contact angles (CAs) of water/1,2-dichloroethane on the surface of sample were $112.4^\circ/11.7^\circ$ respectively, showing a hydrophobic and lipophilic surface owing to existence of organosilane on the sample's surface. The surface of the sample also demonstrated a high adhesion and water droplet did not roll away from the surface when the sample inclined to a certain angle or even vertical, as shown in Fig. S5 (in ESI).

Figures 3(a1/a2/a3)–3(e1/e2/e3) and Fig. S6 (in ESI) demonstrate fluorescent images of SiCDs (l), $V_{\text{CDs}}:V_{\text{ethanol}} = 3:1$ and mixtures of SiCDs (l) with different IS solutions/suspensions. Obviously, original SiCDs (l) showed fluorescent colors of blue, green and red when being excited by laser at 375, 480 and 560 nm, respectively. Meanwhile, all the mixtures had fluorescence except the mixture of SiCDs (l) with CuCl suspension. The phenomenon of mixing SiCDs (l) with different IS solutions/suspensions could be seen in Table S1 and Fig. S7 (in ESI). For example, when mixing SiCDs (l) with different IS solutions/suspensions, no obvious phenomenon was observed for KCl and Na_2SO_4 , white precipitation formed, subsequently precipitation disappeared and the mixture was clarified for $\text{Pb}(\text{NO}_3)_2$ and ZnSO_4 , while the color of the mixture became dark blue for CuCl. Notably, the mixture of SiCD (l) and CuCl suspension had no fluorescence when being excited at 375, 480 and 560 nm, respectively, as shown in Figs. 3(b1)–3(b3). UV-Vis spectroscopy (Fig. S8, in ESI) was conducted to find out the reason of this phenomenon. The SiCD solution had a strong

absorption at wavelength of 358 nm while peaks at 236/291, 226, 293 and 300 nm for FeCl_3 , $\text{Pb}(\text{NO}_3)_2$, Na_2SO_4 solutions and CuCl suspension. Then the mixtures of SiCD (l) and diverse IS solutions/suspensions were investigated and it was found that all the mixtures had a peak located at 358 nm, which was attributed to the absorption of SiCDs, but a peak at 566 nm occurred for the mixture of SiCD (l) and CuCl suspension. It may be this unique phenomenon that resulted in the fluorescence quenching of SiCDs (l). It is known that luminescence emission of SiCDs arises from the radiative recombination of excitons, which is similar to other quantum dots. Then it is deduced that Cu^+ can quench the fluorescence of SiCDs (l) owing to facilitating non-radiative electron/hole recombination annihilation through an effective electron transfer process^[46, 47]. Furthermore, photoluminescence and photoinduced electron transfer properties of SiCDs (l) were investigated to further understand the fluorescence quenching mechanism. The fluorescence intensity (375 nm excitation) was reduced by 96.2% when SiCDs (l) and CuCl suspension were fully mixed, as shown in Fig. 4(c). Figure 4(d) shows the luminescence decays (375 nm excitation) of the SiCDs (l) before and after being mixed with CuCl suspension. It could be obviously observed that the fluorescence lifetime of the SiCDs (l) was 20.48 ns after fitting, reflecting a fast exciton recombination process. After being mixed with CuCl suspension, the lifetime decreased to 1.08 ns with a percentage reduction of 94.7%. The significantly reduced lifetime indicated that a dynamics quenching occurred, and further confirmed that there was an ultrafast electron transfer process in the SiCDs (l)-CuCl system^[46].

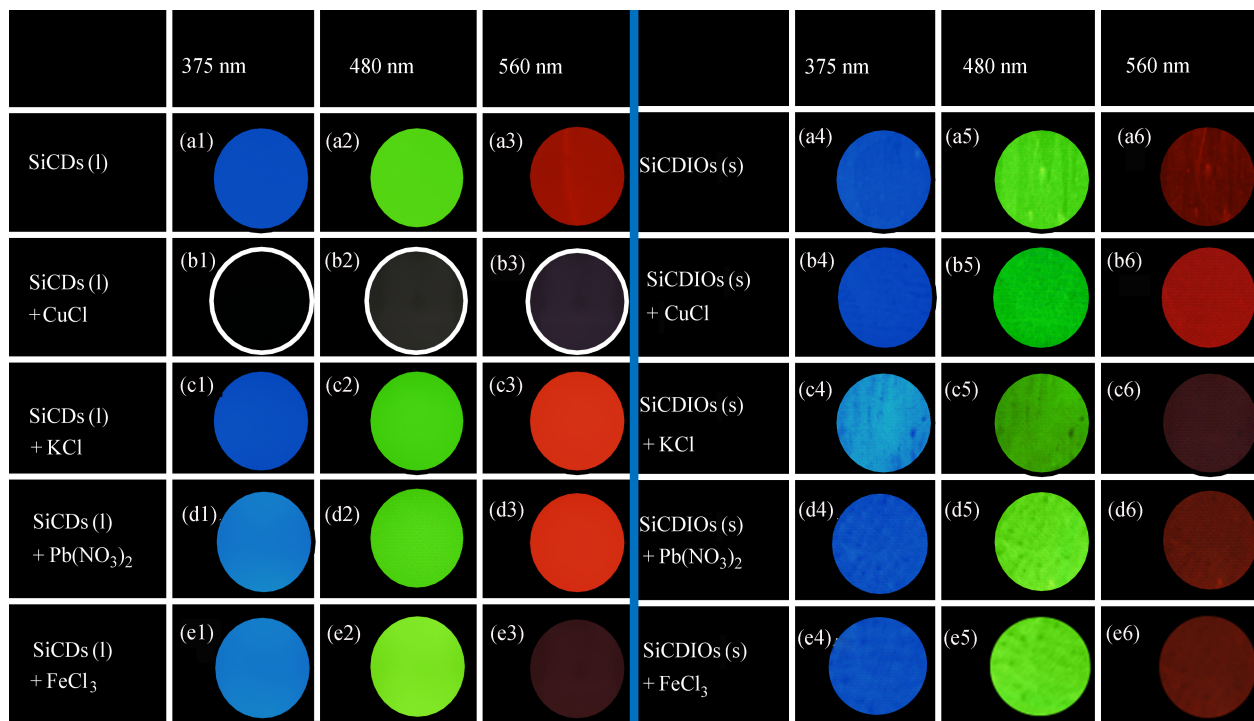


Fig. 3 The fluorescent images of (a1–a3) SiCDs (l) and mixtures of SiCDs (l) with different IS solutions/suspensions, such as (b1–b3) CuCl suspension, (c1–c3) KCl, (d1–d3) $\text{Pb}(\text{NO}_3)_2$, and (e1–e3) FeCl_3 ; The fluorescent images of SiCDIOs (a4–a6) before and after being immersed in different IS solutions/suspensions for 15 min, such as (b4–b6) CuCl suspension, (c4–c6) KCl, (d4–d6) $\text{Pb}(\text{NO}_3)_2$, and (e4–e6) FeCl_3 . Fluorescent images of (a1–e1 and a4–e4), (a2–e2 and a5–e5) and (a3–e3 and a6–e6) were excited by laser at 375, 480 and 560 nm respectively. The concentration of the solution was all 0.1 mol/L.

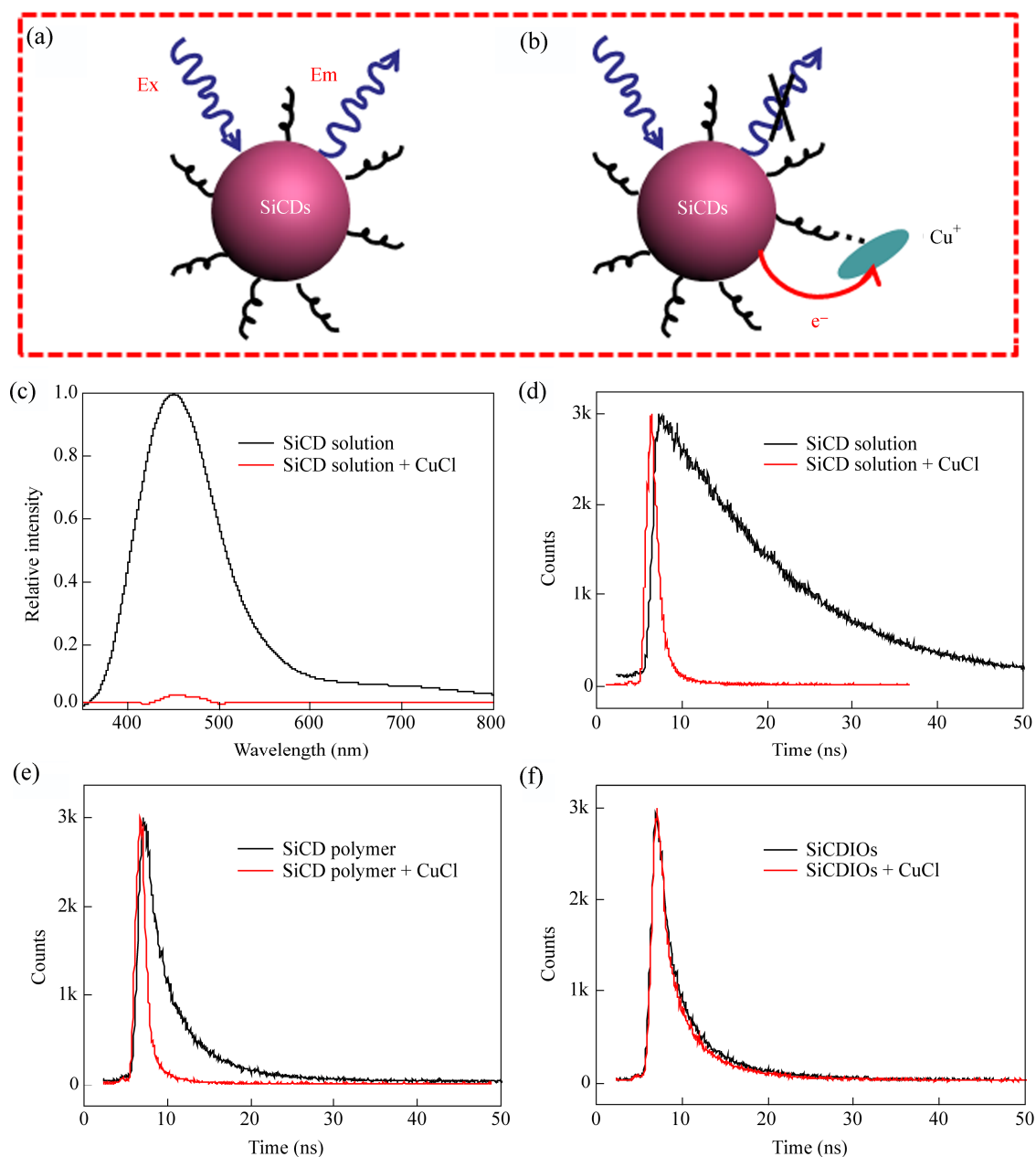


Fig. 4 Schematic illustration of the fluorescence quenching mechanism of the SiCDs (I) in the (a) absence and (b) presence of Cu^+ ; (c) Luminescence emission spectra (375 nm excitation) of the SiCDs (I) in the presence and absence of CuCl suspension; Luminescence decays (375 nm excitation) of (d) SiCDs (I), (e) SiCD polymer and (f) SiCDIOs in the presence and absence of CuCl suspension

In comparison, fluorescent signal of SiCD polymer after being immersed in different IS solutions/suspensions for 15 min was investigated, as shown in Fig. S9 (in ESI). Obviously, SiCD polymer still had faint fluorescence even being soaked in CuCl suspension for 15 min. This phenomenon was attributed to the stable structure formed by crosslinking network^[13]. It could be confirmed by luminescence decays spectra in Fig. 4(e). After being immersed in CuCl suspension for 15 min, the lifetime decreased to 0.87 ns from original 4.56 ns with the percentage of the reduction as 79.6%, confirming a reduced electron transfer process in SiCD polymer-CuCl system based on a stable crosslinking structure^[46]. Figures 3(a4/a5/a6)–3(e4/e5/e6)

and Fig. S10 (in ESI) demonstrate fluorescent images of close-cell SiCDIOs after being immersed in different IS solutions/suspensions for 15 min. Obviously, original close-cell SiCDIOs showed fluorescent color of blue, green and red when being excited with laser at 375, 480 and 560 nm, respectively. In comparison, the most fluorescence phenomena of close-cell SiCDIOs after being soaked in different IS solutions/suspensions for 15 min were similar to corresponding mixtures of SiCDs (I) and diverse IS solutions/suspensions. Notably, close-cell SiCDIOs still had fluorescence even being soaked in CuCl suspension for 15 min. The lifetime (Fig. 4f) was 3.44 ns for close-cell SiCDIOs after being immersed in CuCl suspension for 15 min,

which was similar to original lifetime (3.95 ns). This phenomenon indicated that almost no electron transfer process occurred in close-cell SiCDIOs-CuCl system^[46]. In comparison, the fluorescence signal of open-cell SiCDIOs was investigated, as shown in Fig. S11 (in ESI). Open-cell SiCDIOs presented weaker fluorescence intensity than close-cell SiCDIOs while stronger than SiCD polymer because the internal structure could be infiltrated by liquid.

The fluorescence retention of SiCDIOs after being immersed in CuCl suspension for 15 min can be attributed to three factors: high hydrostatic pressure in the closed pore structure, stable structure formed by crosslinking network and fluorescence enhancement by PC structure. When a liquid is dropped on the surface of traditional open-cell inverse opal structure, liquid infiltrates into the pore and takes place of the air owing to the interconnected structure^[48, 49]. In contrast, the pore of close-cell inverse opal (Fig. 5a) cannot be infiltrated by liquid owing to the high pressure in the pore and the separated pore structure. The pressure (P) in the pore can be calculated by Eq. (1)^[50, 51]

$$P = -l\gamma_v(\cos\theta_A)/A \quad (1)$$

In Eq. (1), γ_v is the surface tension of the liquid-vapor interface, l is the circumference of a pore, A is the cross-sectional area of a pore and θ_A is the advancing angle of water on the sample's surface. In our experiments, it can be calculated from the cross-section SEM image (Fig. 5c) that l is 910 nm, A is $6.6 \times 10^4 \text{ nm}^2$ and $\gamma_{\text{water-air}}$ is $72.2 \times 10^{-3} \text{ N/m}$. The advancing angle of water on the sample's surface is 109.8° . Equation (1) predicts the hydrostatic pressure in the

pore to be $3.5 \times 10^5 \text{ Pa}$. As a result, internal structure still has strong fluorescence because the internal structure of the sample cannot be infiltrated by CuCl suspension based on the high hydrostatic pressure in pores. Besides this factor, stable structure formed by crosslinking network also plays a significant role in the fluorescence retention phenomenon^[13, 45]. The stable crosslinking network structure of SiCDIOs is determined by the formation of Si—O—Si bonding. In details, SiCDIOs can keep uniformly dispersed and stable owing to the connection and support of Si—O—Si bonding^[13, 45]. Here, SiCDs (Fig. 1A1) indicates graphene quantum dots modified by organosilanes. The organosilanes in the free states are easily infected by CuCl suspension, thus resulting in fluorescence quenching through an effective electron transfer process. However, stable structure is achieved by crosslinking network (Fig. 5b) between organosilanes. That is, organosilanes cannot contact with CuCl suspension owing to the existence of the polymer network, thus avoiding the quenching of fluorescence. Finally, fluorescence intensity can be effectively enhanced by PC structure owing to periodic arrangement interacts with excitation laser, the resulted high-intensity near field efficiently excites the fluorescence of SiCDIOs^[52, 53]. The fluorescence enhancement of SiCDIOs with different overlapping between the reflection band and fluorescent peak has been investigated in detail in our previous study^[54]. In summary, the as-prepared sample can keep original fluorescence based on the high hydrostatic pressure in the pore structure, stable structure formed by crosslinking network and fluorescence enhancement by PC structure.

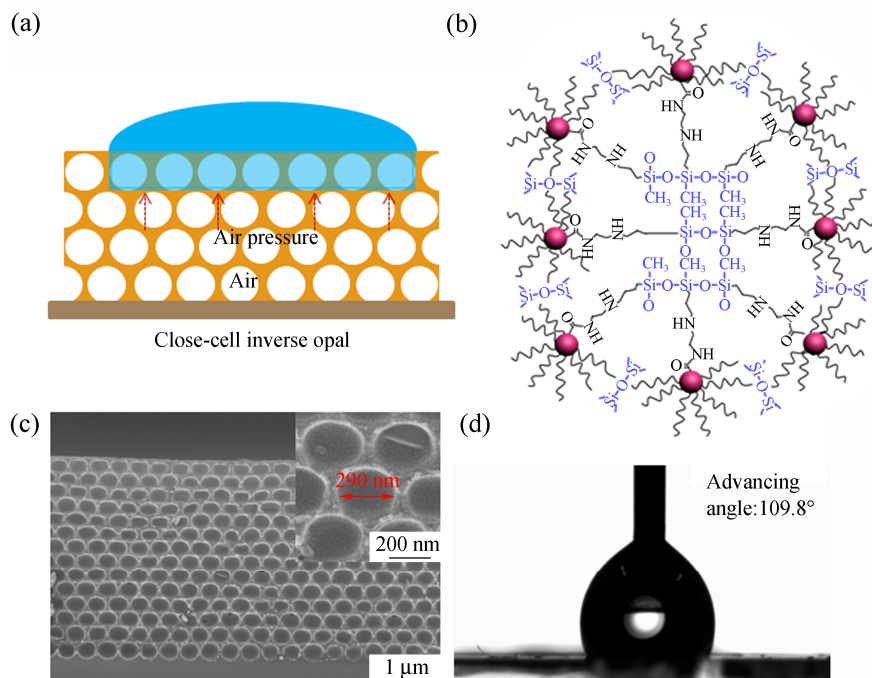


Fig. 5 (a) Scheme for the immersion process of a liquid into a close-cell inverse opal structure (The pores could not be infiltrated by liquid owing to the existence of high pressure in the pore structure.); (b) The chemical structure of the polysiloxane after self-polymerization of organosilane functionalized CDs; (c) Cross-section SEM image of close-cell SiCDIOs and (d) corresponding advancing angle on the sample's surface (The diameter of pore was *ca.* 290 nm and advancing angle was 109.8° .)

CONCLUSIONS

In conclusion, a multi-functional PC material can be achieved from SiCDs *via* “sacrificial template” method through thermal polymerization. The as-prepared sample demonstrates unique close-cell structure and original strong fluorescence intensity even being soaked in the CuCl suspension for 15 min owing to high hydrostatic pressure in the pore structure, stable structure formed by crosslinking network and fluorescence enhancement by PC structure, which gives an important insight into the design of novel and advanced optical devices.

Electronic Supplementary Information

Electronic supplementary information (ESI) includes experimental and characterization, which is available free of charge in the online version of this article at <http://dx.doi.org/10.1007/s10118-018-2126-7>.

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REFERENCES

- Lu, S. Y.; Sui, L. Z.; Liu, J. J.; Zhu, S. J.; Chen, A. M.; Jin, M. X.; Yang, B. Near-infrared photoluminescent polymer-carbon nanodots with two-photon fluorescence. *Adv. Mater.* 2017, 29, 1603443.
- Wang, L.; Wang, Y. L.; Xu, T.; Liao, H. B.; Yao, C. B.; Liu, Y.; Li, Z.; Chen, Z. W.; Pan, D. Y.; Sun, L. T.; Wu, M. H. Gram-scale synthesis of single-crystalline graphene quantum dots with superior optical properties. *Nat. Commun.* 2014, 5, 5357.
- Mahesh, S.; Lekshmi, C. L.; Renuka, K. D.; Joseph, K. Simple and cost-effective synthesis of fluorescent graphene quantum dots from honey: application as stable security ink and white-light emission. *Part. Part. Syst. Charact.* 2016, 33, 70–74.
- Zhang, F.; Feng, X. T.; Zhang, Y.; Yan, L. P.; Yang, Y. Z.; Liu, X. J. Photoluminescent carbon quantum dots as a directly film-forming phosphor towards white LEDs. *Nanoscale* 2016, 8, 8618–8612.
- Zhu, L. L.; Yin, Y. J.; Wang, C. F.; Chen, S. Plant leaf-derived fluorescent carbon dots for sensing, patterning and coding. *J. Mater. Chem. C* 2013, 1, 4925–4932.
- Liu, S. S.; Wang, C. F.; Li, C. X.; Wang, J.; Mao, L. H.; Chen, S. Hair-derived carbon dots toward versatile multidimensional fluorescent materials. *J. Mater. Chem. C* 2014, 2, 6477–6483.
- Liu, S.; Tian, J. Q.; Wang, L.; Zhang, Y. W.; Qin, X. Y.; Luo, Y. L.; Asiri, A. M.; Al-Youbi, A. O.; Sun, X. P. Hydrothermal treatment of grass: a low-cost, green route to nitrogen-doped, carbon-rich, photoluminescent polymer nanodots as an effective fluorescent sensing platform for label-free detection of Cu(II) ions. *Adv. Mater.* 2012, 24, 2037–2041.
- Xu, Y.; Chen, X.; Chai, R.; Xing, C. F.; Li, H. R.; Yin, X. B. A magnetic/fluorometric bimodal sensor based on a carbon dots-MnO₂ platform for glutathione detection. *Nanoscale* 2016, 8, 13414–13421.
- Miao, X.; Qu, D.; Yang, D. X.; Nie, B.; Zhao, Y. K.; Fan, H. Y.; Sun, Z. C. Synthesis of carbon dots with multiple color emission by controlled graphitization and surface functionalization. *Adv. Mater.* 2018, 30, 1704740.
- Liu, J. J.; Lu, S. Y.; Tang, Q. L.; Zhang, K.; Yu, W. X.; Sun, H. C.; Yang, B. One-step hydrothermal synthesis of photoluminescent carbon nanodots with selective antibacterial activity against *porphyromonas gingivalis*. *Nanoscale* 2017, 9, 7135–7142.
- Lu, S. Y.; Xiao, G. J.; Sui, L. Z.; Feng, T. L.; Yong, X.; Zhu, S. J.; Li, B. J.; Liu, Z. Y.; Zou, B.; Jin, M. X.; Tse, J. S.; Yan, H.; Yang, B. Piezochromic carbon dots with two-photon fluorescence. *Angew. Chem. Int. Ed.* 2017, 129, 6283–6287.
- Liu, X. J.; Liu, L. T.; Hu, X. J.; Zhou, S. Y.; Ankri, R.; Fixler, D.; Xie, Z. Multimodal bioimaging based on gold nanorod and carbon dot nanohybrids as a novel tool for atherosclerosis detection. *Nano Res.* 2017, DOI: 10.1007/s12274-017-1739-4
- Xie, Z.; Wang, F.; Liu, C. Y. Organic-inorganic hybrid functional carbon dot gel glasses. *Adv. Mater.* 2012, 24, 1716–1721.
- Huang, J. J.; Zhong, Z. F.; Rong, M. Z.; Zhou, X.; Chen, X. D.; Zhang, M. Q. An easy approach of preparing strongly luminescent carbon dots and their polymer based composites for enhancing solar cell efficiency. *Carbon* 2014, 70, 190–198.
- Lu, W. B.; Qin, X. Y.; Liu, S.; Chang, G. H.; Zhang, Y. W.; Luo, Y. L.; Asiri, A. M.; Al-Youbi, A. O.; Sun, X. P. Economical, green synthesis of fluorescent carbon nanoparticles and their use as probes for sensitive and selective detection of Mercury(II) ions. *Anal. Chem.* 2012, 84(12), 5351–5357.
- Zheng, M.; Xie, Z. G.; Qu, D.; Li, D.; Du, P.; Jing, X. P.; Sun, Z. C. On-off-on fluorescent carbon dot nanosensor for recognition of Chromium(VI) and ascorbic acid based on the inner filter effect. *ACS Appl. Mater. Interfaces* 2013, 5, 1078–1083.
- Dong, Y. Q.; Wang, R. X.; Li, G. L.; Chen, C. Q.; Chi, Y. W.; Chen, G. N. Polyamine-functionalized carbon quantum dots as fluorescent probes for selective and sensitive detection of copper ions. *Anal. Chem.* 2012, 84, 6620–6624.
- Lu, W. J.; Gong, X. J.; Nan, M.; Liu, Y.; Shuang, S. M.; Dong, C. Comparative study for N and S doped carbon dots: synthesis, characterization and applications for Fe³⁺ probe and cellular imaging. *Anal. Chim. Acta* 2015, 898, 116–127.
- Luo, W.; Yan, J. D.; Tan, Y. L.; Ma, H. R.; Guan, J. G. Rotating 1-D magnetic photonic crystal balls with a tunable lattice constant. *Nanoscale* 2017, 9, 9548–9555.
- Wu, Y. N.; Li, F. T.; Zhu, W.; Cui, J. C.; Tao, C. A.; Lin, C. X.; Hannam, P. M.; Li, G. T. Metal-organic frameworks with a three-dimensional ordered macroporous structure: dynamic photonic materials. *Angew. Chem. Int. Ed.* 2011, 50, 12518–12522.
- Liu, J. C.; Wan, L.; Zhang, M. B.; Jiang, K. J.; Song, K.; Wang, J. X.; Ikeda, T.; Jiang, L. Electrowetting-induced morphological evolution of metal-organic inverse opals toward a water-lithography approach. *Adv. Funct. Mater.* 2017, 27, 1605221.
- Chen, K.; Fu, Q. Q.; Ye, S. Y.; Ge, J. P. Multicolor printing using electric-field-responsive and photocurable photonic crystals. *Adv. Funct. Mater.* 2017, 27, 1702825.
- Pang, F.; Jiang, Y. T.; Zhang, Y. Q.; He, M. Y.; Ge, J. P. Synergetic enhancement of photocatalytic activity with a photonic crystal film as a catalyst support. *J. Mater. Chem. A* 2015, 3, 21439–21443.
- Waterhouse, G. I. N.; Wahab, A. K.; Al-Oufi, M.; Jovic, V.; Anjum, D. H.; Sun-Waterhouse D.; Liorca, J.; Idriss, H. Hydrogen production by tuning the photonic band gap with the electronic band gap of TiO₂. *Sci. Rep.* 2013, 3, 2849.
- Rahul, T. K.; Sandhyarani, N. Nitrogen-fluorine co-doped titania inverse opals for enhanced solar light driven photocatalysis.

- Nanoscale 2015, 7, 18259–18270.
- 26 Wang, H.; Gu, H. C.; Chen, Z. Y.; Shang, L. R.; Zhao, Z.; Gu, Z. Z.; Zhao, Y. J. Enzymatic inverse opal hydrogel particles for biocatalyst. *ACS Appl. Mater. Interfaces* 2017, 9(15), 12914–12918.
 - 27 Gao, N.; Tian, T.; Cui, J. C.; Zhang, W. L.; Yin, X. P.; Wang, S. Q.; Ji, J. W.; Li, G. T. Efficient construction of well-defined multicompartment porous systems in a modular and chemically orthogonal fashion. *Angew. Chem. Int. Ed.* 2017, 56, 3880–3885.
 - 28 Zhao, Z.; Wang, H.; Shang, L. R.; Yu, Y. R.; Fu, F. F.; Zhao, Y. J.; Gu, Z. Z. Bioinspired heterogeneous structural color stripes from capillaries. *Adv. Mater.* 2017, 29, 1704569.
 - 29 Liu, J. C.; Xie, Z.; Shang, Y. Y.; Ren, J. K.; Hu, R. X.; Guan, B.; Wang, J. X.; Ikeda, T.; Jiang, L. Lyophilic but nonwetttable organosilane-polymerized carbon dots inverse opals with close-cell structure. *ACS Appl. Mater. Interfaces* 2018, 10, 6701–6710.
 - 30 Fu, F. F.; Chen, Z. Y.; Zhao, Z.; Wang, H.; Shang, L. R.; Gu, Z. Z.; Zhao, Y. J. Bio-inspired self-healing structural color hydrogel. *Proc. Natl. Acad. Sci.* 2017, 114, 5900–5905.
 - 31 Guo, D.; Li, C.; Wang, Y.; Li, Y. N.; Song, Y. L. Precise assembly of particles for zigzag or linear patterns. *Angew. Chem. Int. Ed.* 2017, 129, 15550–15554.
 - 32 Hou, J.; Li, M. Z.; Song, Y. L. Patterned colloidal photonic crystals. *Angew. Chem. Int. Ed.* 2018, 57(10), 2544–2553.
 - 33 Xing, H. H.; Li, J.; Shi, Y.; Guo, J. B.; Wei, J. Thermally driven photonic actuator based on silica opal photonic crystal with liquid crystal elastomer. *ACS Appl. Mater. Interfaces* 2016, 8(14), 9440–9445.
 - 34 Wei, W. Y.; Shi, A. S.; Wu, T. H.; Wei, J.; Guo, J. B. Thermo-responsive shape and optical memories of photonic composite films enabled by glassy liquid crystalline polymer networks. *Soft Matter* 2016, 12, 8534–8541.
 - 35 Zhou, J. M.; Yang, J.; Gu, Z. D.; Zhang, G. F.; Wei, Y.; Yao, X.; Song, Y. L.; Jiang, L. Controllable fabrication of noniridescent microshaped photonic crystal assemblies by dynamic three-phase contact line behaviors on superhydrophobic substrates. *ACS Appl. Mater. Interfaces* 2015, 7(40), 22644–22651.
 - 36 Zhou, J. M.; Han, P.; Liu, M. J.; Zhou, H. Y.; Zhang, Y. X.; Jiang, J. K.; Liu, P.; Wei, Y.; Song, Y. L.; Yao, X. Self-healable organogel nanocomposite with angle-independent structural colors. *Angew. Chem. Int. Ed.* 2017, 129, 10598–10602.
 - 37 Liu, J. C.; Shang, Y. Y.; Zhang, D. J.; Xie, Z.; Hu, R. X.; Wang, J. X. Single-material solvent-sensitive fluorescent actuator from carbon dots inverse opals based on gradient dewetting. *Chinese J. Polym. Sci.* 2017, 35(9), 1043–1050.
 - 38 Yablonovitch, E. Inhibited spontaneous emission in solid-state physics and electronics. *Phys. Rev. Lett.* 1987, 58, 2059–2062.
 - 39 John, S. Strong localization of photons in certain disordered dielectric superlattices. *Phys. Rev. Lett.* 1987, 58, 2486–2489.
 - 40 Sun, Y.; Zhang, Z. X.; Xie, A. J.; Xiao, C. H.; Li, S. K.; Huang, F. Z.; Shen, Y. H. An ordered and porous N-doped carbon dot-sensitized Bi₂O₃ inverse opal with enhanced photoelectrochemical performance and photocatalytic activity. *Nanoscale* 2015, 7, 13974–13980.
 - 41 Cheng, J.; Wang, C. F.; Zhang, Y.; Yang, S. Y.; Chen, S. Zinc ion-doped carbon dots with strong yellow photoluminescence. *RSC Adv.* 2016, 6, 37189–37194.
 - 42 Fan, Y. O.; Cheng, H. H.; Zhou, C.; Xie, X. J.; Liu, Y.; Dai, L. M.; Zhang, J.; Qu, L. T. Honeycomb architecture of carbon quantum dots: a new efficient substrate to support gold for stronger SERS. *Nanoscale* 2012, 4, 1776–1781.
 - 43 Eftekhari, E.; Wang, W. T.; Li, X.; Nikhil, A.; Wu, Z. Q.; Klein, R.; Cole, I. S.; Li, Q. Picomolar reversible Hg(II) solid-state sensor based on carbon dots in double heterostructure colloidal photonic crystals. *Sensor Actuat. B-Chem.* 2017, 240, 204–211.
 - 44 Zhang, W. J.; Zhang, X. Z.; Zhang, Z. X.; Wang, W. H.; Xie, A. J.; Xiao, C. H.; Zhang, H.; Shen, Y. H. A nitrogen-doped carbon dot-sensitized TiO₂ inverse opal film: preparation, enhanced photoelectrochemical and photocatalytic performance. *J. Electrochem. Soc.* 2015, 162, H638–H644.
 - 45 Wang, F.; Xie, Z.; Zhang, H.; Liu, C. Y.; Zhang, Y. G. Highly luminescent organosilane-functionalized carbon dots. *Adv. Funct. Mater.* 2011, 21, 1027–1031.
 - 46 Liu, R. H.; Li, H. T.; Kong, W. Q.; Liu, J.; Liu, Y.; Tong, C. Y.; Zhang, X.; Kang, Z. H. Ultra-sensitive and selective Hg²⁺ detection based on fluorescent carbon dots. *Mater. Res. Bull.* 2013, 48, 2529–2534.
 - 47 Xia, Y. S.; Zhu, C. Q. Use of surface-modified CdTe quantum dots as fluorescent probes in sensing mercury (II). *Talanta*. 2008, 75, 215–221.
 - 48 Blanford, C. F.; Schroden, R. C.; Al-Daous, M.; Stein, A. Tuning solvent-dependent color changes of three-dimensionally ordered macroporous (3DOM) materials through compositional and geometric modifications. *Adv. Mater.* 2001, 13, 26–29.
 - 49 Li, H. L.; Wang, J. X.; Yang, L. M.; Song, Y. L. Superoleophilic and superhydrophobic inverse opals for oil sensors. *Adv. Funct. Mater.* 2008, 18, 3258–3264.
 - 50 Tian, D. L.; Chen, Q. W.; Nie, F. Q.; Xu, J. I.; Song, Y. L.; Jiang, L. Patterned wettability transition by photoelectric cooperative and anisotropic wetting for liquid reprography. *Adv. Mater.* 2009, 21, 3744–3749.
 - 51 Heng, L. P.; Li, J.; Li, M. C.; Tian, D. L.; Fan, L. Z.; Jiang, L.; Tang, B. Z. Ordered honeycomb structure surface generated by breath figures for liquid reprography. *Adv. Funct. Mater.* 2014, 24, 7241–7248.
 - 52 Li, H.; Wang, J. X.; Pan, Z. L.; Cui, L. Y.; Xu, L.; Wang, R. M.; Song, Y. L.; Jiang, L. Amplifying fluorescence sensing based on inverse opal photonic crystal toward trace TNT detection. *J. Mater. Chem.* 2011, 21, 1730–1735.
 - 53 Chen, J. I. L.; Freymann, G. V.; Choi, S. Y.; Kitaev, V.; Ozin, G. A. Amplified photochemistry with slow photons. *Adv. Mater.* 2006, 18, 1915–1919.
 - 54 Liu, J. C.; Ren, J. K.; Xie, Z.; Guan, B.; Wang, J. X.; Ikeda, T.; Jiang, L. Multi-functional organosilane-polymerized carbon dots inverse opals. *Nanoscale* 2018, DOI: 10.1039/C7NR09387J