Nanoscale

COMMUNICATION

View Article Online
View Journal | View Issue

Check for updates

Cite this: *Nanoscale*, 2019, **11**, 3489

Received 8th January 2019,
Accepted 28th January 2019

DOI: 10.1039/c9nr00224c

rsc.li/nanoscale

Ultraviolet-pumped white light emissive carbon dot based phosphors for light-emitting devices and visible light communication†

Zhen Tian,[a,b] Pengfei Tian,[c] Xiaojie Zhou,[c] Gufan Zhou,[c] Shiliang Mei,[c] Wanlu Zhang,[c] Xutao Zhang,[a,b] Di Li,[a] Ding Zhou,[a] Ruiqian Guo,*[c] Songnan Qu *[a,d] and Andrey L. Rogach [e]

Herein, we report UV-pumped white light emissive carbon dot (CD)-based phosphors to prevent blue light hazard in phosphor-converted WLEDs. Then, UV-pumped WLEDs with a color rendering index exceeding 85 and VLC with a modulation bandwidth of 75 MHz and a data transmission rate of 224 Mbps have been realized.

Introduction

Phosphor-converted white light-emitting devices (WLEDs) as indispensable lighting sources possess many competitive advantages.[1,2] However, blue light hazard from traditional WLEDs which combine a sharp blue emissive LED chip and a green/yellow phosphor[3,4] to generate white light will cause retinal injury and adversely affect human health.[5,6] Thus, ultraviolet (UV)-pumped WLEDs which employ UV-emitting chips to excite white light emissive phosphors are strongly desirable, because the excess UV light can be filtered out without affecting the output white light quality and the blue light hazard of blue-chip-WLEDs can be alleviated.[7] Moreover, UV-pumped WLEDs show great potential in visible light communication (VLC), which can provide healthy white-light illumination when used for data transmission without radio frequency interference.[8–11] However, commercial phosphors in WLEDs are normally rare-earth based materials, whose emission lifetimes are much too long (on the order of several milliseconds) to support high rates of VLC data transmission.[12,13] Some other alternative materials like organic fluorescent materials and lead halide perovskites have also been tested for VLC,[14,15] but the low thermal/optical stability of organic fluorescent materials and the presence of toxic lead in those perovskites hinder practical VLC applications. UV-pumped white light emissive phosphors with short luminescence lifetimes for VLC are scarce. Thus, it is of great importance to exploit environment-friendly UV-pumped white light emissive phosphors with high photoluminescence quantum yields (PLQYs) and short PL lifetimes for healthy lighting and VLC.

Carbon dots (CDs) as a novel luminescent material possess a number of distinct merits such as biocompatibility, high stability, short PL lifetimes on the order of several nanoseconds, low cost and ease of preparation,[16–21] which make them good candidates as color conversion materials for both UV-pumped WLEDs and VLC.[22,23] However, the development of CDs for solid-state lighting applications is hindered by their serious aggregation-induced luminescence quenching.[24–26] Up to now, there have been several reports on highly luminescent solid-state CD-based phosphors by dispersing CDs into an organic/inorganic matrix, such as PVA,[27] starch,[28] NaCl,[29] and $BaSO_4$.[30] In our recent work, we have developed a microwave-assisted treatment of sodium silicate aqueous solutions and CDs allowing us to obtain composite full-color luminescent CD-based phosphors on a large scale. In this synthetic procedure, a dehydrated and solidified sodium silicate forms a 3D glass-like structure immobilizing isolated CDs, which effectively prevents aggregation-induced luminescence quenching.[31] Herein, we have further advanced this method to a one-step production of highly efficient white light emissive CD-based phosphors with tunable color temperatures (CTs) and PLQYs over 30% in the solid state, by homogeneously embedding blue, green and red emissive CDs in a silica matrix. Using these white

[a] State Key Laboratory of Luminescence and Applications, Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Sciences, Changchun 130033, China
[b] University of Chinese Academy of Sciences, Beijing 100049, China
[c] Engineering Research Center of Advanced Lighting Technology, Ministry of Education, Institute of Future Lighting, Academy for Engineering and Technology, Fudan University, Shanghai 200433, China. E-mail: rqguo@fudan.edu.cn
[d] Joint Key Laboratory of the Ministry of Education, Institute of Applied Physics and Materials Engineering, University of Macau, Avenida da Universidade, Taipa, Macau, China. E-mail: songnanqu@um.edu.mo
[e] Department of Materials Science and Engineering, Centre for Functional Photonics (CFP), City University of Hong Kong, Kowloon, Hong Kong SAR, China

† Electronic supplementary information (ESI) available: Fig. S1–S6 and Table S1. See DOI: 10.1039/c9nr00224c

light emissive CD-based phosphors as color converters, UV-pumped WLEDs with tunable Commission Internationale de L'Eclairage (CIE) coordinates and a color rendering index (CRI) exceeding 85 have been realized. The PL lifetimes of these CD-based phosphors were short, namely 6.8–8.8 ns all over the visible color range. Using white light emissive CD-based phosphors as color converters, VLC with a modulation bandwidth of 75 MHz and a data transmission rate of 224 Mbps has been demonstrated.

Experimental section

Materials

Citric acid (99.5%) and urea (99%) were purchased from Macklin and Aladdin, respectively. Sodium silicate ($Na_2SiO_3 \cdot 9H_2O$, Baume degree 40) was purchased from Usolf. Polydimethylsiloxane (PDMS) elastomer kits (Sylgard 184) were purchased from Dow Corning (Midland, MI, USA). The InGaN LED chips (emission peak at 375 nm, operating under a voltage of 3.0 V) were purchased from Great Shine Semiconductor Technology Company Ltd (China). All chemicals were used as received without further purification.

Synthesis of CDs

Citric acid (1 g) and urea (2 g) were allowed to react at 160 °C for 4 h under hydrothermal or solvothermal conditions in 10 mL of solvent. Blue, green or red emissive CDs were produced by changing the solvent from water to glycerol to dimethylformamide (DMF) as previously reported,[31] and the resulting samples were denoted as B-CDs, G-CDs, and R-CDs, respectively. Colloidal solutions of CDs were mixed with 20 mL of ethanol and centrifuged at 8000 rpm for 10 min. Then, the precipitates were collected, dissolved in ethanol and centrifuged twice to remove all the residual solvents and eventually low molecular weight by-products. The samples were freeze-dried to provide CDs for further use.

Preparation of CD-based phosphors

10 mg of CDs (B-CDs, G-CDs and R-CDs) and 1 mL of deionized water were mixed under stirring with 2 mL of sodium silicate to form a homogeneous solution. The mixture was treated under 550 W microwave irradiation for 2 min to form swelled solid foams, which were subsequently ground into powders. CD-based composite phosphors were washed with ethanol through repeated centrifugation at 2000 rpm for 5 min, three times.

Fabrication of WLEDs from CD-based phosphors

Commercially available UV (375 nm) emissive InGaN LED chips were used as the excitation light source of WLEDs. CD-based phosphors were mixed with PDMS in a mass ratio of 1 : 1, and covered on InGaN chips followed by curing at 80 °C for 1 h. Similarly, resin films with CD-based phosphors were obtained *via* covering the mixtures on glass slides, followed by curing at 80 °C for 1 h.

Characterization

UV-visible absorption spectra were obtained on a Shimadzu UV-3101PC spectrophotometer. PL spectra were collected on a Hitachi F-7000 spectrophotometer. PLQYs of CDs in aqueous solutions and of CD-based phosphors were measured in a calibrated integrating sphere using a FLS920 spectrometer (Edinburgh Instruments Ltd). PL lifetimes of CD-based phosphors were measured *via* time correlated single-photon counting using an FLS920 spectrometer under excitation at 405 nm. Transmission electron microscopy (TEM) was performed on an FEI Tecnai-G2-F20 TEM at 200 kV. Scanning electron microscopy (SEM) was performed on a JEOL FESEM 6700F electron microscope with a primary electron energy of 3 kV. X-ray photoelectron spectroscopy (XPS) analysis was done on an ESCALAB MK II spectrometer using Mg as the excitation source. Fluorescence microscopy images were obtained on a C2+ confocal microscope system (Nikon confocal instruments), with an attached Ocean Optics Maya 2000 Pro fiber optic spectrometer. The emission spectra of CD-based WLEDs were obtained on a Fu Xiang NOVA-EX fiber optic spectrometer.

Measurements of the VLC system

A white light-emitting system was obtained by putting the CD-based phosphors in front of the 405 nm emissive laser diode. The experimental setup was designed as a laser diode based white-light real-time communication system with CD-based phosphors as a color converter. The 405 nm emissive laser diode was driven by pseudo-random binary sequences (PRBS) produced by a pulse pattern generator (PPG) module from an Anritsu MP1800 signal quality analyzer, which was combined with a direct current *via* a bias-tee. A clock signal was produced using an Agilent network analyzer for the PPG. CDot-based phosphors were excited with a 405 nm laser diode to generate white light, which was then collimated and focused by a transmitter lens and a receiver lens, while the redundant light from the laser diode was filtered out by a 420 nm long-pass optical filter. An avalanche photodiode (APD 12702) was used to record the optical signal from the transmitter and convert it into an electrical signal for further measurements. The frequency response was analyzed using an N5225A network analyzer, and the bit error rate was measured by an error detector module in the MP1800 signal quality analyzer. An 86100A wide-bandwidth oscilloscope was used to gain eye diagrams.

Results and discussion

CDs emitting in three primary colors, blue, green and red (B-CDs, G-CDs and R-CDs), were synthesized by a previously reported facile hydrothermal/solvothermal route,[31] through the carbonization of citric acid and urea at 160 °C temperature in three different solvents, namely water, glycerol and DMF. Fig. 1a–c show the TEM images of CDs, with corresponding size histograms, illustrating well separated particles with gradually increasing average diameters of 2 ± 0.3 nm, 3 ±

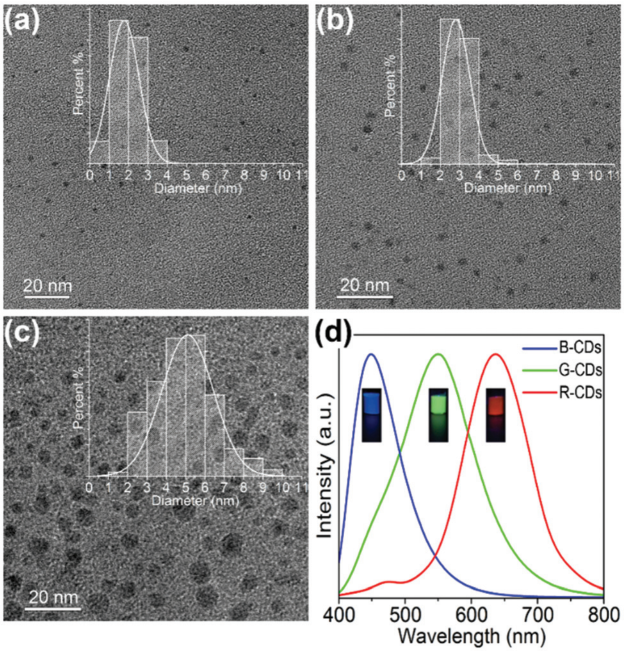

Fig. 1 TEM images of (a) B-CDs, (b) G-CDs, and (c) R-CDs; insets show the size histograms of the respective particles. (d) PL spectra of B-CDs, G-CDs and R-CDs in aqueous solutions under 365 nm excitation; insets show the photographs of the corresponding CD solutions under UV light.

0.5 nm and 5 ± 0.8 nm, respectively. Fig. S1† shows the XPS spectra of B-CDs, G-CDs and R-CDs, with three peaks at 284.0, 400.0, and 530.6 eV, attributed to C_{1s}, N_{1s}, and O_{1s}, respectively.[32] High-resolution XPS C_{1s} spectra of three CDs can be deconvoluted into three peaks at 284.5, 285.8 and 287.8 eV, which are attributed to the C–C/C=C, C–N and C–O/C=O groups, respectively (Fig. S2†).[33,34] High-resolution XPS N_{1s} and O_{1s} spectra also confirmed the presence of C–C/C=C, C–N and C–O/C=O bonds (Fig. S3 and S4†). Under UV excitation, aqueous solutions of B-CDs, G-CDs and R-CDs show bright luminescence, with emission peaks at 450 nm, 550 nm and 640 nm, respectively (Fig. 1d).

To realize white light-emitting CD-based phosphors, we have chosen an aqueous solution of sodium silicate as a transparent matrix to prevent aggregation-induced luminescence quenching.[31] Sodium silicate is an ideal transparent matrix and surface agent for the fabrication of inorganic CD based composite phosphors, due to its good water solubility and the ability to dehydrate and solidify at elevated temperatures forming 3D glass-like structures.[35,36] Fig. S5† illustrates the formation process of the white light emissive CD-based phosphors. White light emissive phosphors were prepared by combining B-CDs, G-CDs and R-CDs in different mass ratios with sodium silicate, followed by subsequent microwave heating. After 550 W microwave irradiation for 2 min, solutions were dehydrated and solidified to form swelled solid foams (Fig. S6†), which were subsequently ground into powders, thoroughly washed with ethanol, and dried at 60 °C to obtain powdered CD-based phosphors. The PL spectral profiles of the white light emissive CD-based phosphors could be adjusted by varying the mass ratios of B-CDs, G-CDs and R-CDs. As summarized in Table S1,† cold white CD-based phosphors with a PLQY of 31% were prepared at a mass ratio of 20 : 10 : 1 (B-CDs : G-CDs : R-CDs), and named P-1. Pure white CD-based phosphors with a PLQY of 33% were prepared at a mass ratio of 10 : 10 : 1, and named P-2. Warm white CD-based phosphors with a PLQY of 31% were prepared at a mass ratio of 5 : 5 : 1, and named P-3. Fluorescence microscopy images of the prepared white light emissive CD-based phosphors demonstrate their uniform cold, pure or warm white color emissions (Fig. 2), indicating that the B-CDs, G-CDs and R-CDs were homogeneously embedded in the silica matrix. Fig. 2 also shows the PL spectra and photographs (taken under UV light) of the corresponding CD-based powdered phosphors.

Phosphor-converted WLEDs were fabricated by deposition of white light emissive CD-based phosphors onto UV emissive InGaN LED chips (emission peak centered at 375 nm). As shown in Fig. 3, the resulting CD-based WLEDs possess the advantage of tunable CIE coordinates and CTs. In detail, a cold white LED (D-1) with CIE coordinates of (0.27, 0.31), a CT of 9927 K, a CRI of 85, and a luminous efficiency of 7.8 lm W^{-1} was realized by using P-1. A pure white LED (D-2) with CIE coordinates of (0.32, 0.33), a CT of 6109 K, a CRI of 88, and a luminous efficiency of 6.3 lm W^{-1} was realized by using P-2. A warm white light device (D-3) with CIE coordinates of (0.41, 0.41), a CT of 3510 K, a CRI of 86 and a luminous efficiency of 5.2 lm W^{-1} was realized by using P-3.

PL lifetimes of the powdered CD phosphors were measured by time correlated single-photon counting using an FLS920

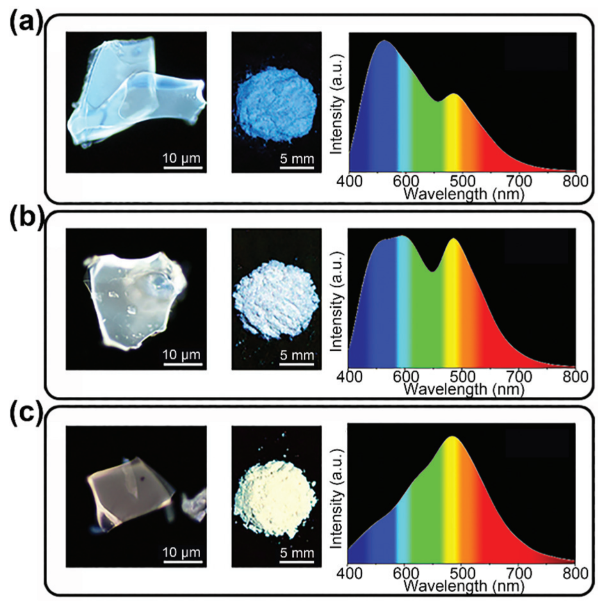

Fig. 2 White light emissive CD-based phosphors (a) P-1, (b) P-2, and (c) P-3: Fluorescence images of fragments (left), photographs of the respective powdered samples (middle), and their PL spectra under 375 nm excitation (right).

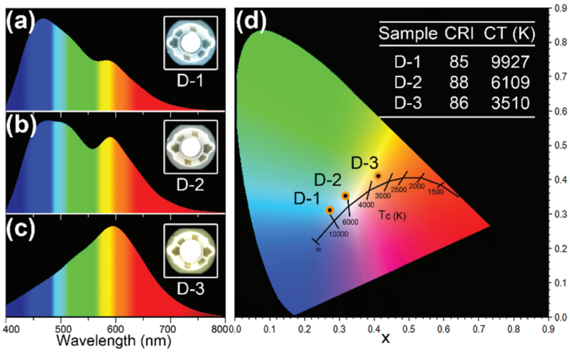

Fig. 3 Emission spectra of CD-based WLEDs (a) D-1, (b) D-2, and (c) D-3; insets show the photographs of the operating devices. (d) CIE coordinates of the CD-based devices D-1, D-2, and D-3; insets show their respective CRI and CT.

spectrometer with excitation at 405 nm. The PL lifetimes of P-1 were collected from 430 nm to 700 nm. The PL decay curves can be fitted with a single-exponential function, and provide relatively constant, short PL lifetimes in the range of 6.8–8.8 ns (Fig. 4a). PL lifetimes of single color CD-based phosphors B-CDs, G-CDs and R-CDs also remain relatively constant over the range of the scanned wavelengths, but differ significantly from each other, giving average values of 12 ns, 7 ns and 3 ns, respectively (Fig. 4b). These data further confirmed that the white light emissive CD-based composite phosphors should be in a homogeneous phase rather than a simple mechanical mixture of the three RGB emissive CD-based phosphors.

To demonstrate the application of the white light emissive CD based phosphors for VLC, the experimental setup (Fig. 5a) was used to measure the frequency response. The direct current of 89 mA from the Yokogawa GS610 current source and the small signal from the Agilent N5225A network (10 MHz–50 GHz) were combined to drive a laser diode which was used to excite the plate of the PDMS/P-1 composite. The violet light generated by a 405 nm laser was cut off by a 420 nm filter. Thus, the generated white light originated exclu-

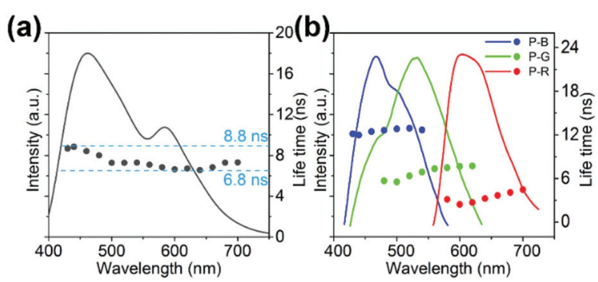

Fig. 4 (a) PL spectrum of the white light emissive CD-based phosphors used as a color converter for VLC (solid line). PL lifetimes collected for the different spectral points over the PL profile (excitation wavelength 405 nm) from 430 nm to 700 nm are indicated by black dots. (b) PL spectra (solid lines) and the corresponding PL lifetimes (dots) of the P–B, P–G and P–R (excitation wavelength 405 nm) collected for the different spectral points over the PL profiles.

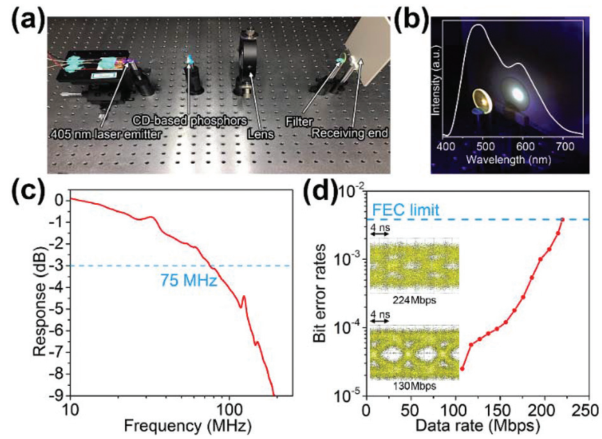

Fig. 5 (a) Experimental setup of the VLC link. (b) Photograph and the corresponding spectrum of the VLC generated white light using a 405 nm laser diode, CD-based phosphor (P-1), and a cut-off 420 nm filter. (c) Frequency response of the −3 dB modulation bandwidth of the output white light cut off by a 420 nm filter. The dashed line represents the −3 dB bandwidth of the system. (d) BER at different data rates using OOK of the white-light. The dashed line stands for the FEC limit of 3.8×10^{-3}. Inset: eye diagrams of the white light converted by CD-based phosphors (P-1) at data rates of 224 Mbps and 130 Mbps.

sively from the CD-based P-1 phosphor, thus effectively preventing blue light hazard. Fig. 5b provides the PL spectrum and the photograph of the produced white light, with CIE coordinates of (0.34, 0.32) and a CT of 5092 K. The frequency response and the characteristics of the −3 dB modulation bandwidth of the output white light are presented in Fig. 5c. Compared with traditional nitride-based phosphors (∼12.4 MHz) and commercial YAG-based phosphors (3–12 MHz),[37] the bandwidth of the white-light system with CD-based phosphors as the color converter can attain 75 MHz. Furthermore, we used a high-sensitivity APD (C12702, 100 MHz) to receive optical pulses, and detected the data transmission of the phosphor-converted VLC through a nonreturn-to-zero on–off keying (NRZ-OOK) modulation. The curve of the bit error rate (BER) is depicted in Fig. 5d, and the BER is below the forward error correction (FEC), which is the maximum BER to achieve error-free data transmission. The "open eye" in the eye diagrams (Fig. 5d) illustrates that the difference between zero and one bit is clearly resolved at the data rate of 224 Mbps and 130 Mbps, indicating that the achievable data rate of the CD-based phosphor-converted VLC is up to 224 Mbps.

Conclusions

In summary, we demonstrated a convenient method which allowed the one-step fabrication of highly efficient, UV-pumped white light emissive CD-based phosphors with PLQYs over 30% in the solid state, by homogeneously embedding B-CDs, G-CDs and R-CDs in a silica matrix. The PL spectral profiles of these phosphors can be conveniently adjusted by varying the mass ratios of B-CDs, G-CDs and R-CDs. UV-pumped WLEDs were obtained by depositing the CD-based phosphors on UV emissive InGaN LED chips, and have shown the advantage of tunable CIE coordinates and a high CRI exceeding 85. Due to the short PL lifetimes of the CD-based phosphors in the range of 6.8–8.8 ns, VLC with a modulation bandwidth of 75 MHz and a data transmission rate of 224 Mbps have been realized only based on the white light from the CD-based phosphors. As the UV light can be filtered out without affecting the quality of the output white light, the blue light hazard of WLEDs and VLC demonstrated here can be efficiently alleviated, making white light emissive CD-based phosphors prospective for both healthy lighting and VLC applications.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (projects No. 51602304, 61675049), the Youth Innovation Promotion Association of CAS, the Jilin Province Science and Technology Research Projects No. 20180101190JC, 20170101191JC, 20170101042JC, 20160520008JH, 20150519003JH, Fudan University – CIOMP Joint Fund (FC 2017-004), and by NPRP grant No. 8-878-1-172 from the Qatar National Research Fund (a member of the Qatar Foundation).

References

1 E. F. Schubert and J. K. Kim, *Science*, 2005, **308**, 1274–1278.
2 X. Li, J. D. Budai, F. Liu, J. Y. Howe, J. Zhang, X. Wang, Z. Gu, C. Sun, R. S. Meltzer and Z. Pan, *Light: Sci. Appl.*, 2013, **2**, e50.
3 V. Bachmann, C. Ronda and A. Meijerink, *Chem. Mater.*, 2009, **21**, 2077–2084.
4 T. Senden, R. J. A. van Dijk-Moes and A. Meijerink, *Light: Sci. Appl.*, 2018, **7**, 8.
5 L. Bellia, F. Bisegna and G. Spada, *Build. Environ.*, 2011, **46**, 1984–1992.
6 H. Ji, J. Su and Y. Do, *Light: Sci. Appl.*, 2014, **3**, e141.
7 B. Chen, A. S. Susha, C. J. Reckmeier, S. V. Kershaw, Y. Wang, B. Zou, H. Zhong and A. L. Rogach, *Adv. Mater.*, 2017, **29**, 1604284.
8 P. Pathak, X. Feng, P. Hu and P. Mohapatra, *IEEE Commun. Surv. Tuts.*, 2015, **17**, 2047–2077.
9 H. Elgala, R. Mesleh and H. Haas, *IEEE Commun. Mag.*, 2011, **49**, 56–62.
10 S. Rajbhandari, H. Chun, G. Faulkner, K. Cameron, A. V. N. Jalajakumari, R. Henderson, D. Tsonev, M. Ijaz, Z. Chen and H. Haas, *IEEE J. Sel. Area. Comm.*, 2015, **33**, 1750–1757.
11 M. T. Sajjad, P. P. Manousiadis, C. Orofino, D. Cortizo-Lacalle, A. L. Kanibolotsky, S. Rajbhandari, D. Amarasinghe, H. Chun, G. Faulkner, D. C. O'Brien, P. J. Skabara, G. A. Turnbull and I. D. W. Samuel, *Adv. Opt. Mater.*, 2015, **3**, 536–540.
12 A. M. Khalid, G. Cossu, R. Corsini, P. Choudhury and E. Ciaramella, *IEEE Photonics J.*, 2012, **4**, 1465–1473.
13 H. Chun, P. Manousiadis, S. Rajbhandari, D. A. Vithanage, G. Faulkner, D. Tsonev, J. D. Mckendry, S. Videv, E. Xie and E. Gu, *IEEE Photonics Technol. Lett.*, 2014, **26**, 2035–2038.
14 M. T. Sajjad, P. P. Manousiadis, H. Chun, D. A. Vithanage, S. Rajbhandari, A. L. Kanibolotsky, G. Faulkner, D. O'Brien, P. J. Skabara and I. D. W. Samuel, *ACS Photonics*, 2015, **2**, 194–199.
15 S. Mei, X. Liu, W. Zhang, R. Liu, L. Zheng, R. Guo and P. Tian, *ACS Appl. Mater. Interfaces*, 2018, **10**, 5614.
16 K. Hola, Y. Zhang, Y. Wang, E. P. Giannelis, R. Zboril and A. L. Rogach, *Nano Today*, 2014, **9**, 590–603.
17 Y. Xiong, J. Schneider, E. V. Ushakova and A. L. Rogach, *Nano Today*, 2018, **23**, 124–139.
18 H. Ding, S. Yu, J. Wei and H. Xiong, *ACS Nano*, 2016, **10**, 484–491.
19 S. Zhu, Q. Meng, L. Wang, J. Zhang, Y. Song, H. Jin, K. Zhang, H. Sun, H. Wang and B. Yang, *Angew. Chem., Int. Ed.*, 2013, **52**, 3953–3957.
20 S. Kalytchuk, K. Polakova, Y. Wang, J. P. Froning, K. Cepe, A. L. Rogach and R. Zboril, *ACS Nano*, 2017, **11**, 1432–1442.
21 X. Bao, Y. Yuan, J. Chen, B. Zhang, D. Li, D. Zhou, P. Jing, G. Xu, Y. Wang, K. Holá, D. Shen, C. Wu, L. Song, C. Liu, R. Zboril and S. Qu, *Light: Sci. Appl.*, 2018, **7**, 91.
22 T. Zhang, F. Zhao, L. Li, B. Qi, D. Zhu, J. Lu and C. Lu, *ACS Appl. Mater. Interfaces*, 2018, **10**, 19796–19805.
23 Z. Zhou, P. Tian, X. Liu, S. Mei, D. Zhou, D. Li, P. T. Jing, W. Zhang, R. Guo, S. Qu and A. L. Rogach, *Adv. Sci.*, 2018, **5**, 1800369.
24 Y. Chen, M. Zheng, Y. Xiao, H. Dong, H. Zhang, J. Zhuang, H. Hu, B. Lei and Y. Liu, *Adv. Mater.*, 2016, **28**, 312–318.
25 Y. Wang, S. Kalytchuk, L. Wang, O. Zhovtiuk, K. Cepe, R. Zboril and A. L. Rogach, *Chem. Commun.*, 2015, **51**, 2950–2953.
26 D. Li, D. Han, S. Qu, L. Liu, P. Jing, D. Zhou, W. Ji, X. Wang, T. Zhang and D. Shen, *Light: Sci. Appl.*, 2016, **5**, e16120.
27 S. Qu, W. Wang, Q. Lu, X. Liu and L. Wang, *Angew. Chem., Int. Ed.*, 2012, **51**, 12215–12218.
28 S. Qu, D. Zhou, D. Li, W. Ji, P. Jing, D. Han, L. Liu, H. Zeng and D. Shen, *Adv. Mater.*, 2016, **28**, 3516–3521.
29 Y. Zhai, D. Zhou, P. Jing, D. Li, H. Zeng and S. Qu, *J. Colloid Interface Sci.*, 2017, **497**, 165–171.
30 D. Zhou, Y. Zhai, S. Qu, D. Li, P. Jing, W. Ji, D. Shen and A. L. Rogach, *Small*, 2017, **13**, 1602055.
31 Z. Tian, X. Zhang, D. Li, D. Zhou, P. Jing, D. Shen, S. Qu, R. Zboril and A. L. Rogach, *Adv. Opt. Mater.*, 2017, **5**, 1700416.

32 D. Qu, M. Zheng, J. Li, Z. Xie and Z. Sun, *Light: Sci. Appl.*, 2015, **4**, e364.
33 S. Liu, J. Tian, L. Wang, Y. Zhang, X. Qin, Y. Luo, A. M. Asiri, A. O. Al-Youbi and X. Sun, *Adv. Mater.*, 2012, **24**, 2037–2041.
34 L. Xiao and H. Sun, *Nanoscale Horiz.*, 2018, **3**, 565–597.
35 P. Zhu and R. Jin, *J. Mater. Chem.*, 2008, **18**, 313–318.
36 Y. Li, X. Cheng, W. Cao, L. Gong, R. Zhang and H. Zhang, *Mater. Des.*, 2015, **88**, 1008–1014.
37 D. Tsonev, H. Chun, S. Rajbhandari, J. D. McKendry, S. Videv, E. Gu, M. Haji, S. Watson, A. E. Kelly, G. Faulkner, M. D. Dawson, H. Haas and D. O'Brien, *IEEE Photonics Technol. Lett.*, 2014, **26**, 637–640.