A Mini Review on the White Light Emission Application of Carbon Based Nanomaterials and their Conjugates with Important Biomolecules

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ARTICLE INFO
Received : 03.04.2023
Revised: 06.06.2023
Accepted: 08.06.2023

Key Words:
Carbon based nanomaterials, carbon dot, fluorescent nanoparticles, white light emission, optoelectronic, biomedical

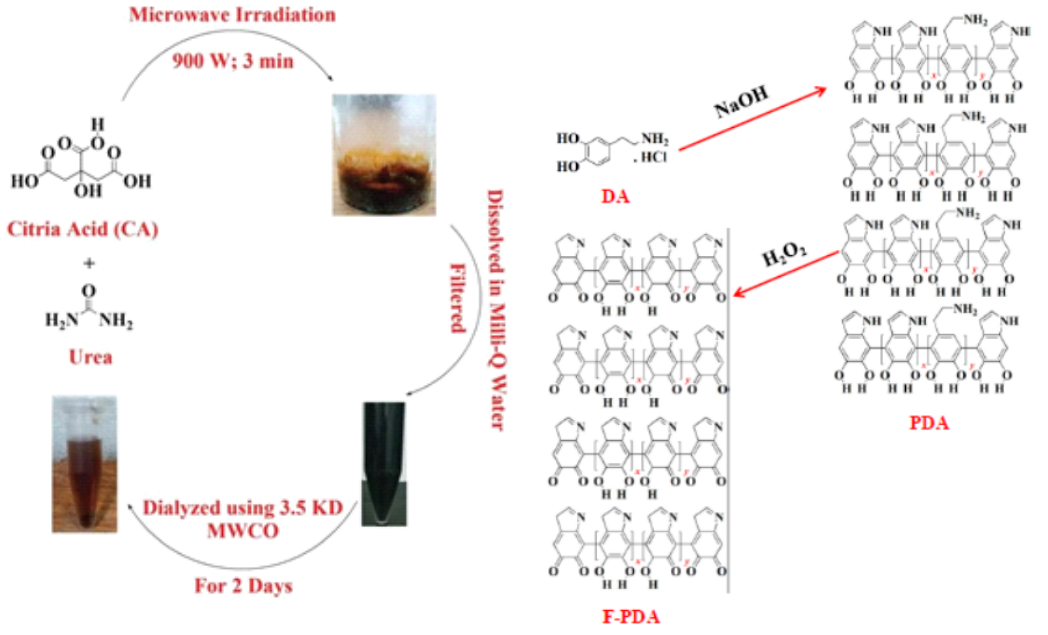
ABSTRACT

Carbon based nanomaterials are very much important due to their versatile nature and wide range of applications in different research fields. In this review, two carbon based nanomaterials, carbon dot and fluorescent nanoparticles have been included and their synthesis, characterizations and interactions with different biomolecules have been discussed. The direct consequence of these nanomaterials-biomolecules interactions have been discussed through the generation as well as modulation of white light emission. This white light emission is extremely important with respect to their optoelectronic as well as biomedical research applications and can be extended to other important nanomaterials and biomaterials systems.

Nanomaterials, one of the most promising and unique material systems, are very much important for their cost effective synthetic strategies, easy characterization procedures, highly tunable optical and photophysical properties and more importantly, their diverse range of applications, covering from biomedical to optoelectronic research areas, make them one of the most widely explored material systems.1-5 Now, these nanomaterial systems, in their family, can have a number of different materials varying the central or core element, however, in this respect, they can be broadly classified into metal based and non-metal based nanomaterials. Nevertheless, the emission or fluorescence property can again subdivide each of the above mentioned nanomaterial systems into fluorescent or emissive and non-fluorescent or non-emissive nanomaterials.6-10 The advantage of the fluorescence property of the nanomaterial system is that it can be modulated through perturbing the energy states of the nanomaterial by changing the composition, structure, morphology, size etc. of the system.6-10 The fluorescence property, upon interaction with suitable foreign molecule, which may be fluorescent or non-fluorescent, can be significantly modulated and the resulting signal can be efficiently employed to serve a wide range of

applications, such as, drug delivery, analysis of important biomolecules, biosensing etc.8-10 However, the other important outcome, in the form of light emitting applications of the nanomaterials as well as their conjugates with suitable biomolecules are also very much important and essential for respective optoelectronic applications.11-14 The most important and common optoelectronic applications include the generation and modulation of white light emission from different molecular systems. White light (WL) emission is the combination of all emission colours that present in the entire visible spectral region and the WL emission can be obtained by equal proportion mixing of the primary emission colours, i.e. blue, green and red as well as sometimes from suitable mixing of other complementary emission colours, such as, cyan and orange. WL emission, which covers the entire visible region spectrum are widely applicable for the light emitting diode (LED) fabrication.11-14 Besides, sensing and analysis of different molecular systems, security ink application etc. can also be achieved by modulating the resulting WL emission. Now, in this present review article, we shall restrict our discussion of WL emission generation and their applications for carbon dot and fluorescent polydopamine nanoparticles as basic nanomaterial systems, although some other nanomaterial systems have also been reported to show significant potential towards efficient WL emission generation.

The nanomaterial systems, in general, can be synthesized using top-down or bottom-up approaches. In top-down synthetic strategy, large precursor molecule(s) has been decomposed to obtain small nanomaterials; whereas, in the bottom-up approach, small precursor molecule (s) produce comparatively large nanomaterial systems. For the synthesis of carbon dot, both top-down and bottom up approaches have been followed. In this respect, Pan *et* al.15 have synthesized graphene quantum dots starting from the hydrothermal oxidation of graphene sheet, which can be enlisted as the top-down synthetic strategy. On the other hand, Liu and his co-workers16 showed the synthesis of carbonized polymer dots employing the hydrothermal synthetic procedure from the mixture of ortho-phenylene diamine and nitric acid. However, the quantum yield of the CDs synthesized using the "top-down" routes are relatively lower compared to that obtained from the "bottom-up" synthetic routes.17,18 In this context, we synthesized CD in our laboratory through microwave heating of a mixture of citric acid and urea in 1:3 molar ratio and further purified employing dialysis against milli-Q water using 3.5 kD MWCO dialysis membrane for 50 h.19



Scheme 1. Synthetic strategy for the fluorescent nanomaterial, carbon dot (CD). Image (a) and (b) are reproduced with permission from ref 19 (Copyright 2019 Royal Society of Chemistry) and ref 20 (Copyright 2021 American Chemical Society), respectively.

This synthetic process of the CD system has been shown in the Scheme 1 (a). On the other hand, the fluorescent polymeric nanoparticles were synthesized from dopamine hydrochloride and 3, 4-dihydroxy - L - phenylalanine upon alkaline oxidation and further neutralization based synthetic strategy, 20, 21 which has been illustrated in the following Scheme 1 (b). All the nanomaterials, either carbon dots or polymeric fluorescent nanoparticles were extensively characterized employing a series of different spectroscopic and microscopic characterization techniques and this has been shown in the following Figure 1. The spectroscopic characterization results, which primarily contain uv-visible absorption, steady state emission and excitation as well as Fourier transformed infrared (FT-IR) spectra, provide idea about the formation, composition and optical properties of the nanomaterials, whereas, from the microscopic characterization based outcomes from transmission electron microscopy (TEM), scanning electron microscopy (SEM), atomic force microscopy (AFM) and fluorescence lifetime imaging microscopy (FLIM), we can get a clear idea about the morphological information of the nanomaterial system.

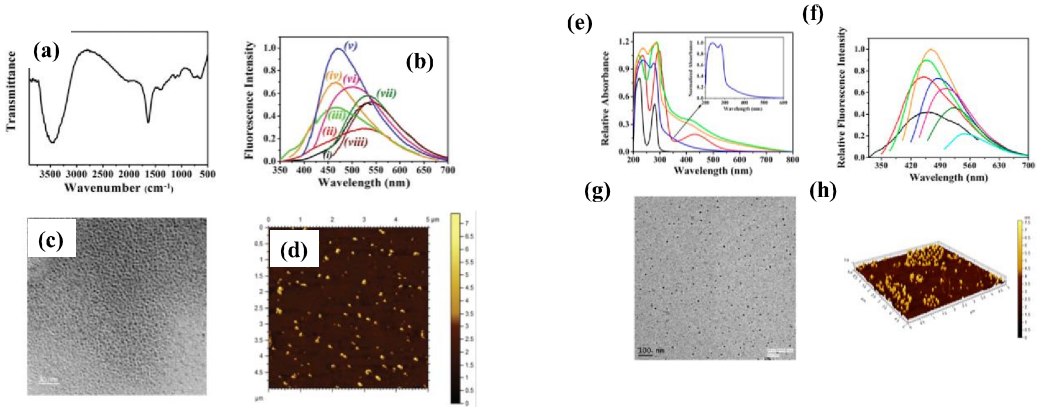


Figure 1. Spectroscopic characterization using (a) FT-IR, (c) steady-state emission (i, ii, iii, iv, v, vi, vii and viii indicate emission spectra corresponding to 280, 300, 330, 350, 375, 400, 420 and 440 nm excitation wavelengths, respectively) spectra and microscopic analysis employing

(c) HR-TEM (scale bar is for 20 nm) and (d) AFM images of the synthesized and purified CD solution; on the other hand, (e) relative UV-vis absorption spectra (inset shows the normalized absorption spectrum of the F-PDA nanoparticle); (f) relative excitation-dependent emissionresults with 300 (black), 330 (red), 350 (green), 375 (orange), 400 (blue), 420 (pink), 440 (olive), and 480 (cyan) nm excitation wavelengths give optical characterization results; whereas, (g)TEM image and (h) 3D AFM image provide morphological understanding about the synthesized F-PDA nanoparticle system. Figures (a-d) are reproduced with permission from ref 19 (Copyright 2019 Royal Society of Chemistry) and Figures (e-h) are reproduced with permission from ref 20 (Copyright 2021 American Chemical Society), respectively.

The nanomaterials were in general observed to be extremely stable against various external stimuli that include temperature, different solvent, solution ionic strength and also various foreign amphiphilic molecules. Pyne et al.19 reported the prominent stability of the synthesized carbon dot solution in presence of increased temperature of the solution, power of excitation light source, foreign amphiphilic molecules, such as, salt, protein and hydrogen peroxide and this has been illustrated from the Figure 2. However, due to the presence of several pH sensitive functional groups, like –COOH, -OH, -NH2 etc. in the skeleton of the nanomaterial systems, the above mentioned nanomaterials showed excellent alterations upon change in pH of the solution and this has also been shown (Figure 2) for our synthesized CD system. Again, the neurotransmitter derived fluorescent

nanoparticles were synthesized using subsequent alkaline pH mediated oxidation and therefore, these nanoparticles will also show significant pH dependence of their formation as well as optical behaviours.

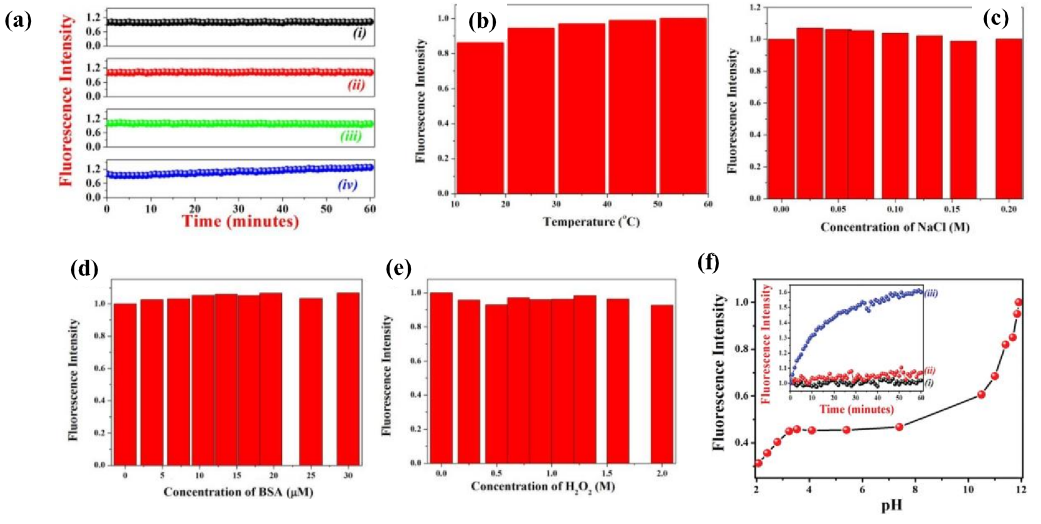


Figure 2. Solution stability of the synthesized CD solution shown against (a) exposure time of excitation light at 400 nm (i) and other foreign molecules, like salt (ii), protein (iii) and H2O2(iv); (b) temperature, (c) salt, NaCl, (d) BSA protein; (e) H2O2 and (f) steady-state emission intensity measurement of the CD solution at different pH values of the medium (inset shows the time-dependent changes in the emission intensities for the CD solution in water (i), at pH 2 (ii) and at pH 12 (iii)). Figures (a-d) are reproduced with permission from ref 19 (Copyright 2019 Royal Society of Chemistry).

The interaction of biologically important molecules, i.e. biomolecules with a nanomaterial system is extremely important and useful from their application point of respect. These biomolecules may be small biomolecules, like single amino acids, nucleobases, osmolites (urea, trimethyl-N-oxide, different sugars etc.), large macromolecules, like proteins, nucleic acids and also some life-saving drug molecules (5-fluorouracil, doxorubicin hydrochloride etc.). Now, the resulting outcomes are very much essential, mainly with respect to their biomedical applications, such as, drug delivery, bioimaging, qualitative as well as quantitative analysis of several essential as well as toxic molecules and so on. However, the other less explored applicative outcome as light emitting response or more preciously optoelectronic outcomes as a result of the above discussed interaction between the biomolecules and nanomaterial systems are also equally important and currently has been

explored to a large extent. In this respect, Pyne et al. explored the light emitting responses of the citric acid / urea derived CD nanomaterial and the well accepted anticancer drug molecule Dox conjugate and reported that the CD-Dox solution showed cyan emission at pH 12, which gradually shifted to excellent WL emission with reducing the pH from 12 to 2. This observation was justified using the steady state emission spectra and further from respective chromaticity diagrams. The chromaticity diagram is also known as Commission Internationale de l'Eclairage (CIE) diagram and this diagram along with associated parameters i.e. CIE coordinates, colour rendering index (CRI) and correlated colour temperature (CCT) are essentially important to analyze the formation and quality of the WL emission. In this scenario, the CIE coordinate for pure WL emission has been assigned as (0.33, 0.33).

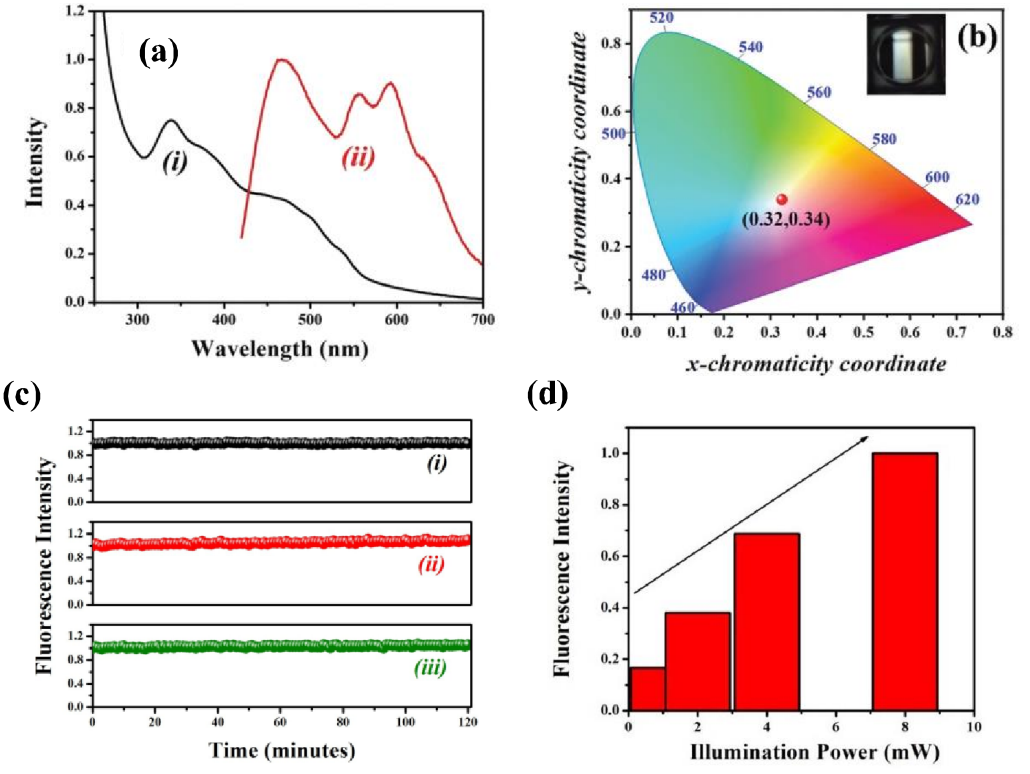


Figure 3. (a) UV-visible absorption (i) and steady-state emission (ii) spectra; (b) CIE plot for the CD–Dox WL system having the concentration of Dox around 21 μM (inset shows the digital photograph of the resulting WL emission); (c) Effect of constant

exposure of 400 nm excitation light in steady state fluorimeter for the CD-Dox WL system at (i) 471 nm, (ii) 555 nm and (iii) 592 nm emission wavelengths; (d) fluorescence intensity histogram of the WL emissive system with increasing illumination power from 1 to 8 mW. Figures (a-d) are reproduced with permission from ref 19 (Copyright 2019 Royal Society of Chemistry).

The CIE parameters for the above mentioned CD-Dox WL emission, as discussed in the work of Pyne et al. are (0.32, 0.34) as CIE coordinates, CRI value as 88 and CCT value as 5799 K were reported, which strongly established the generation of excellent WL emission. In this respect, the resulting WL emission observed to show significant stability against stimuli like exposure to excitation light and increasing power of excitation light source (Figure 3).

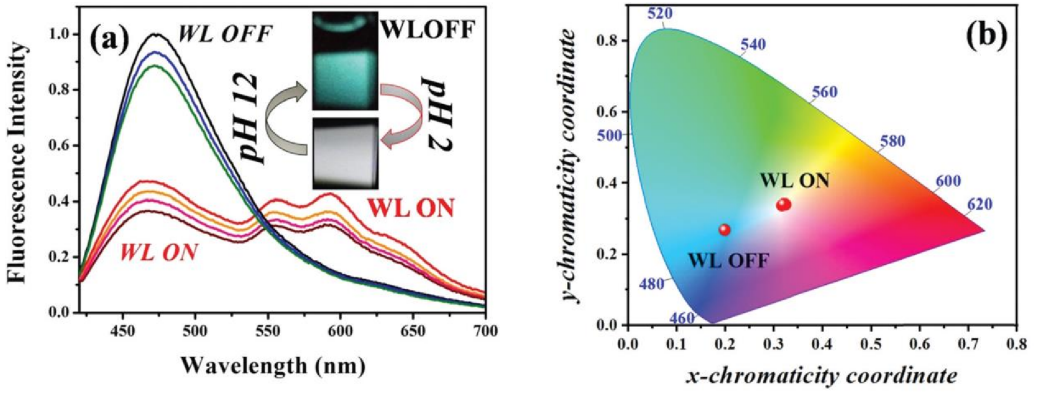


Figure 4. pH-mediated reversible photoswitching of the CD–Dox WL system between extreme pH values, 2 and 12 established using (a) Steady-state emission (inset shows the blue and white emission colours of the pH-dependent CD-Dox system) and (b) Corresponding chromaticity diagram. Figures (a-b) are reproduced with permission from ref 19 (Copyright 2019 Royal Society of Chemistry).

Moreover, the efficient switching between blue and WL emission (Figure 4) upon changing solution pH from 12 to 2 provided an excellent application as pH mediated reversible photoswitching behaviour for a nanomaterial-biomolecule conjugate. The CIE coordinates for the blue emission reported as (0.20, 0.27), whereas, for the WL emission, the CIE coordinate shifted to (0.32, 0.34) and thus, the "WL ON-OFF" photoswitching can be easily traced out by looking into the change in the CIE parameters and also from the visual observation (Figure 4).

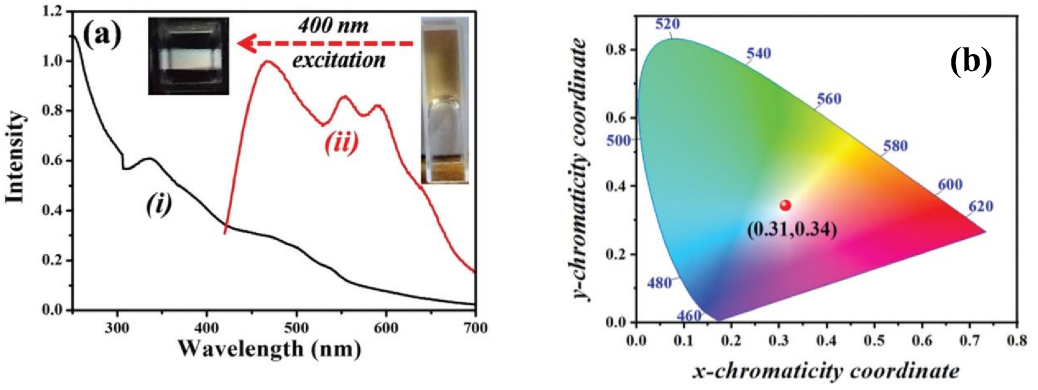


Figure 5. (a) UV-visible absorption (i) and steady-state emission (ii) spectra with the inset shows the digital micrographs of WL@agarose gel under day light and 400 nm excitation light; (b) CIE plot for the CD–Dox WL system in agarose gel. Figures (a-d) are reproduced with permission from ref 19 (Copyright 2019 Royal Society of Chemistry).

Finally, the optical retainment of the WL emission from the solution phase to the agarose gel matrix (Figure 5) provided a firm foundation towards the possible future application of the discussed nanomaterial-drug based luminescent assembly for solid state based light emitting diode (LED) fabrication.The polymeric nanoparticles derived from neurologically important biomolecules, dopamine hydrochloride (DA) and 3,4-dihydroxy-L-phenylalanine (L-Dopa), on the other hand, undergo auto-oxidation to melanine like polydopamine nanoparticles, which can be converted into respective fluorescent analogues upon applying suitable reaction condition. In this respect, Pyne et al. showed the alkaline oxidation and subsequent neutralization of DA using hydrogen peroxide (H2O2) produced fluorescent polydopamine (F-PDA) nanoparticles. In another work, Pyne et al. synthesized fluorescent polymeric nanoparticles from DA, L-Dopa and their mixture under alkaline oxidation, following acid neutralization. In both these scenario (shown in Scheme 1 (b)), the synthesized nanoparticles were well characterized employing different spectroscopic and microscopic characterization tools and this has been shown in the given Figure 1 (e-h). Now, since, these nanoparticles are fluorescent with large number of polar functional groups, they can effectively undergo interaction with various biomolecules and also can be employed as an emission center for WL emission generation.

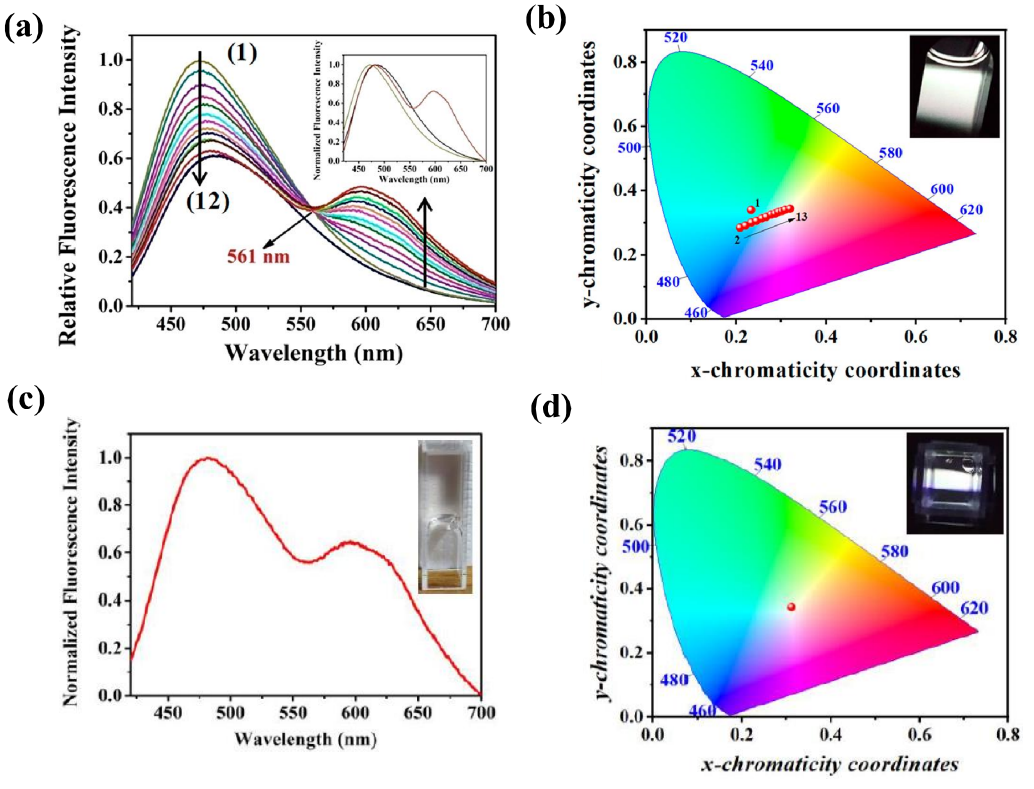


Figure 6. (a) Relative steady state emission spectra of F-PDA (black), DAPI in F-PDA (blue), DAPI-ct-DNA (1), and DAPI-ct-DNA in the presence of increasing concentrations of EtBrfrom 1.3 µM (2; dark cyan colored curve) to 15.3 µM(12; wine colored curve) in F-PDA with the inset showing the normalized emission spectra for F-PDA (black), DAPI-ct-DNA in F- PDA (dark yellow), and DAPI-ct-DNA-15.3 µM EtBr in F-PDA, i.e., the WL system (wine) show FRET from DAPI-ct-DNA to EtBr in F-PDA; (b) Respective chromaticity diagram for the generation of the WL emission with inset shows the digital photograph of DAPI-ct-DNA- 15.3 µM EtBr/F-PDA WL emission; (c) Steady state emission spectrum (inset shows the digital photograph under day light) and (d) corresponding CIE plot (inset shows the digital photograph under 400 nm excitation). Figures (a-d) are reproduced with permission from ref 20 (Copyright 2021 American Chemical Society), respectively.

The synthesized F-PDA nanoparticle was employed by Pyne et al. for modulating the photophysics of simultaneous binding of two deoxyribonucleic acid (DNA) binding probe molecules, 4',6-Diamidino-2-phenylindole dihydrochloride (DAPI) and

ethidium bromide (EtBr). The photophysics behind the simultaneous binding of DAPI and Etbr to calf-thymus DNA (ct-DNA) was reported as Förster based resonance energy transfer (FRET) and the control over the FRET efficiency for DAPI/ct-DNA/EtBr in presence of F-PDA nanoparticles produced excellent WL emission with CIE coordinate (0.32, 0.34), CRI and CCT values 89 and 6080 K respectively in case of the DNA bound probe mixture with 15.3 µM EtBr (Figure 6). Finally, the application in the solid agarose based gel matrix (Figure 6) were also reported to establish the possibility of this luminescent mixture to be upgraded in future as solid state based lightening applications.

In another study, Pyne et al. introduced the fluorescent nanoparticles derived from DA, L-Dopa and their mixture and used them to study interaction between these nanoparticles separately with well known protein matrices, namely bovine serum albumin (BSA), albumin obtained from hen egg, lysozyme obtained from hen egg white and pepsin. The protein specific responses of the nanoparticles (Figure) were well utilized to produce efficient WL emission upon incorporation of anticancer drug molecule, Dox in the nanoparticle-protein matrices. In each set of nanoparticle-protein-Dox assembly, WL emission was generated, however, the best quality WL emission was produced from F-PDA nanoparticle-BSA-Dox combination (Figure 7). Furthermore, the WL emission obtained was largely observed to depend on the nature of protein matrix as well as the nature of the nanoparticle system and from the Figure 7, it has been clear that for DA derived nanoparticle, no protein specificity on the generation and qualityof the WL emission was observed, whereas, for the other two nanoparticles, derived from L- Dopa and DA/L-Dopa mixture, significant protein specificity upon the quality of WL emission was obtained.

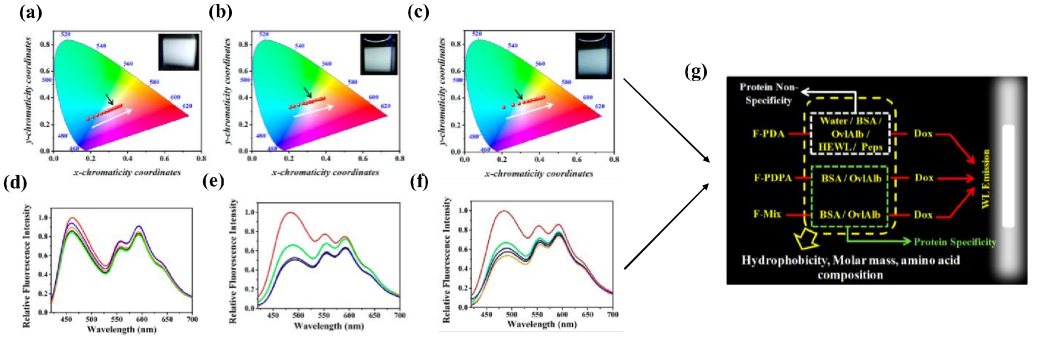


Figure 7. (a-c) CIE plots with insets show corresponding digital photographs taken for the WL generation in the BSA matrix in case

of (a) F-PDA, (b) F-PDPA, and (c) F-Mix NPs in addition of increasing concentrations of Dox; (d-f) Relative steady state emission spectra for protein specificity of the WL emission generation in (d) F-PDA, (e) F-PDPA, and (f) F-Mix NPs in the presence of water (black), BSA (red), OvlAlb (green), HEWL (orange), pepsin (blue), and corresponding WL emitting concentration of Dox for each set and (g) Schematic illustration for the protein specificity of such WL emission generation. Figures (a-g) are reproduced with permission from ref 21 (Copyright 2022 American Chemical Society), respectively.

Therefore, in conclusion, in this review article, we have only restricted our discussion for two specific nanomaterial systems, i.e. carbon dot and fluorescent nanoparticles for their interaction with different biologically important molecular systems (proteins, DNA and drug molecule). However, a large number of other nanomaterial systems (like metal nanoclusters, pervoskites etc.) are also potentially important for their interaction with biomolecules and subsequent WL emission generation. Therefore, the optoelectronic applications for nanomaterials and subsequent nano-bio conjugates are relatively less explored research area, however, due to the wide range of variations of the nanomaterials present, their easy synthetic procedures, stronginteraction with various biomolecules and tunable optical properties bring this application in the lime light and make it acceptable towards a large number of research communities.

References.

1. Baig, N.; Kammakakam, I.; Falath, W. Nanomaterials: A Review of Synthesis Methods, Properties, Recent Progress, and Challenges. Mater. Adv. 2021, 2, 1821-1871.
2. Mackey, M. A.; Ali, M. R. K.; Austin, L. A.; Near, R. D.; ElSayed, M. A. The Most Effective Gold Nanorod Size for Plasmonic Photothermal Therapy: Theory and In Vitro Experiments. J. Phys. Chem. B 2014, 118, 1319-1326.
3. Guan, G.; Wu, M.; Han, M. Y. Stimuli-Responsive Hybridized Nanostructures. Adv. Funct. Mater. 2020, 30 (2), 1903439.
4. Zeineldin, R. Nanotechnology for Cancer Screening and Diagnosis: From Innovations to Clinical Applications. Biomaterials for Cancer Therapeutics 2020, 261-289.
5. Yakavets, I.; Francois, A.; Guiot, M.; Lequeux, N.; Fragola, A.; Pons, T.; Bezdetnaya, L. NIR Imaging of the Integrin-Rich Head and Neck Squamous Cell Carcinoma Using Ternary Copper Indium Selenide/Zinc Sulfide-Based Quantum Dots. Cancers 2020, 12, 3727.
6. Liu, J.; Li, R.; Yang, B. Carbon Dots: A

New Type of Carbon Based Nanomaterial with Wide Applications. ACS Cent. Sci. 2020, 6, 2179-2195.
7. Tan, C.; Yu, P.; Hu, Y.; Chen, J.; Huang, Y.; Cai, Y.; Luo, Z.; Li, B.; Lu, Q.; Wang, L.; et al. High-Yield Exfoliation of Ultrathin TwoDimensional Ternary Chalcogenide Nanosheets for Highly Sensitive and Selective Fluorescence DNA Sensors. J. Am. Chem. Soc. 2015, 137, 10430-10436.
8. Guo, Z.; Park, S.; Yoon, J.; Shin, I. Recent Progress in the Development of Near-Infrared Fluorescent Probes for Bioimaging Applications. Chem. Soc. Rev. 2014, 43, 16-29.
9. Yao, J.; Yang, M.; Duan, Y. Chemistry, Biology, and Medicine of Fluorescent Nanomaterials and Related Systems: New Insights into Biosensing, Bioimaging, Genomics, Diagnostics, and Therapy. Chem. Rev. 2014, 114, 6130-6178.
10. Dolai, B.; Nayim, S.; Hossain, M.; Pahari, P.; Atta, A. K. A Triazole Linked C-Glycosyl Pyrene Fluorescent Sensor for Selective Detection of Au3+ in Aqueous Solution and its Application in Bioimaging. Sens. Actuators, B 2019, 279, 476-482.
11. Chang, H. X.; Wu, H. K. Graphene-Based Nanomaterials: Synthesis, Properties, and Optical and Optoelectronic Applications. Adv. Funct. Mater. 2013, 23, 1984–1997.
12. Jariwala, D.; Sangwan, V. K.; Lauhon, L. J.; Marks, T. J.; Hersam, M. C. Carbon Nanomaterials for Electronics, Optoelectronics, Photovoltaics, and Sensing. Chem. Soc. Rev. 2013, 42, 2824–2860.
13. Yu, J.; Luo, M.; Lv, Z.; Huang, S.; Hsu, H.-H.; Kuo, C.-C.; Han, S.-T.; Zhou, Y. Recent Advances in Optical and Optoelectronic Data Storage Based on Luminescent Nanomaterials. Nanoscale 2020, 12 (46), 23391-23423.
14. Jariwala, D.; Sangwan, V. K.; Lauhon, L. J.; Marks, T. J.; Hersam, M. C. Emerging Device Applications for Semiconducting Two-Dimensional Transition Metal Dichalcogenides. ACS Nano 2014, 8, 1102-1120.
15. Pan, D.; Zhang, J.; Li, Z.; Wu, M. Hydrothermal Route for Cutting Graphene Sheets into Blue-Luminescent Graphene Quantum Dots. Adv. Mater. 2010, 22, 734-738.
16. Liu, J.; Li, D.; Zhang, K.; Yang, M.; Sun, H.; Yang, B. One-Step Hydrothermal Synthesis of Nitrogen-Doped Conjugated Carbonized Polymer Dots with 31% Efficient Red Emission for In Vivo Imaging. Small 2018, 14, 1703919.
17. Zhu, S.; Meng, Q.; Wang, L.; Zhang, J.; Song, Y.; Jin, H.; Zhang, K.; Sun,

H.; Wang, H.; Yang, B. Highly Photoluminescent Carbon Dots for Multicolor Patterning, Sensors, and Bioimaging. Angew. Chem., Int. Ed. 2013, 52, 3953-3957.
18. Yuan, F.; Yuan, T.; Sui, L.; Wang, Z.; Xi, Z.; Li, Y.; Li, X.; Fan, L.; Tan, Z.; Chen, A.; Jin, M.; Yang, S. Engineering Triangular Carbon Quantum Dots with Unprecedented Narrow Bandwidth Emission for Multicolored LEDs. Nat. Commun. 2018, 9, 2249.
19. Pyne, A.; Layek, S.; Patra, A.; Sarkar, N. An easy and smart way to explore the light- emitting responses of carbon dot and doxorubicin hydrochloride assembly: White light generation and pH-dependent reversible photoswitching. J. Mater. Chem. C 2019, 7, 6414-6425.
20. Pyne, A.; Nandi, S.; Layek, S.; Ghosh, M.; Nandi, P. K.; Bera, N.; Sarkar, N. Influence of a Polyneurotransmitter on DNA-Mediated Fo¨rsterBased Resonance Energy Transfer: A Path Leading to White Light Generation. J. Phys. Chem. B 2021, 125, 12637-12653.
21. Pyne, A.; Nandi, P. K.; Layek, S.; Bera, N.; Hazra, R.; Sarkar, N. Deciphering Dual Modes of Parkinsonian Biomolecules Derived Fluorescent Nanoparticles: Protein Specificity and White Light Generation. J. Phys. Chem. Lett. 2022, 13, 7016-7022.