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Carbon Dot-Metal Nano Particle Integrated Composites as Sensors for Biologically Significant Molecules

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Introduction

The sensing of biologically significant small molecules and metal ions is vitally important in the areas of health, environment, food and safety. The development of sensors for these important analytes involves precise architectural design for binding of analytes that induces a change in optical or electrochemical behavior of the sensing component. Although, development of molecular sensors has attracted tremendous attention for selective and sensitive detection, their performance under variable conditions of pH, temperature, solvents, ionic strength along with photo stability and biocompatibility restricts their practical utilization [1]. Use of nano materials has emerged as a viable alternative to molecular sensors due to ease of synthesis, physicochemical malleability, high surface area and possibilities of coupling with molecules of known bio recognition capability [2].

Peculiar properties such as quantum confinement in semiconductor nano crystals, surface plasmon resonance in metal nano particles and tuneable magnetism in magnetic materials have been taken advantage of for development of sensors [2]. The zero dimensional form of carbon nano material family, carbon dots (C-dots) has emerged as an important class of material for diverse applications owing to their splendid fluorescence property, good biocompatibility, water solubility, photo stability and energy conversion abilities [3]. Easy methods of synthesis from low-cost carbon sources coupled with tunability of surface functionalization as desired, makes C-dots vastly applicable in biomedical field such as sensors, imaging, nano vehicles, etc [4]. The integration of two or more type of nanostructures leads to composites which might have superior properties than their individual counterparts resulting in possibility of multimodal sensing [5-7].

Although, several C-dot-metal composites have been developed for applications in photo catalysis, electronics, solar cells, etc., there has been limited investigation into using them as sensors for biologically significant molecules [8,9]. In this perspective, we have explored the developments in the field of carbon dot- metal nano composites as sensors for a range of molecules and ions. We have focused on the developments related to only C-dot and metal nano particle composites eliminating the developments involving only C-dots or other C-dot composites.

Keywords: Carbon dots; Metal nanoparticle; Composite; Sensors; Optical; Electrochemistry

Optical sensors

Optical sensors based on principles such as absorbance, fluorescence, reflectance etc. are senstitive, inexpensive and do not require sophisticated instrumentation. The intrinsic optical properties of C-dot-metal composites such as fluorescence of C-dots and surface plasmon resonance of metal nano particles have been utilized for sensing a host of analytes. Zhu et al [10] fabricated CdSe@C nano hybrid where the core consisted of red emitting CdSe/ZnS quantum dots embedded in silica shell and blue emitting C-dots on the outer sphere. This hybrid showed dual emission bands centered at 485 and 644nm, respectively, under single wavelength excitation of 400 nm. The C-dots were functionalized with an organic molecule specific for Cu^{2+} ions, N-(2-aminoethyl)-N, N, N'tris (pyridin-2-ylmethyl)ethane-1,2-diamine (AE-TPEA). In presence of cellular concentration of Cu^{2+}, the fluorescence owing to C-dots was quenched and the variation of the two fluorescence intensities (I_{485}/I_{644}) served as the ratio metric probe for Cu^{2+}.

The ligand exchange chemistry has been exploited for "off-on" sensing of biothiols using Au-C-dot nano composite. Mandani et al. [5] demonstrated that the inherent fluorescence of C-dots was quenched during their participation as reducing and stabilizing agent for the synthesis of gold nanoparticles (Au NPs). Addition of biothiols like cysteine and glutathione (GSH) to the Au@C-dot nano composite resulted in the recovery of fluorescence inherent to C-dots. Here, the Au NPs were well stabilized by C-dots with a surface plasmon resonance (SPR) band at 528 nm which shifted to higher wavelengths in presence of thiol due to aggregation. On the other hand, the physical mixture of citrate stabilized Au NPs with NC-dots (nitrogen doped C-dots) developed by Deng et al. [6] was purple in color with SPR around 700nm. Upon addition of cysteine, this aggregated system gets dispersed leading to enhancement in fluorescence of C-dots and shifting of SPR of Au NPs to 525nm. In this case, GSH was shown to be ineffective for deaggregation of NC-dots/Au NP composite due to its larger size as compared to cysteine.

In both these studies, the affinity of –SH for Au was exploited for designing the sensors. A similar turn on fluorescence approach for sensing of glutathione was developed by Yang et al. [11]. They synthesized C-dot-MnO_2 nano composites where the fluorescence of C-dots was quenched but upon the addition of GSH, the emission of C-dots could be restored. A further example of colorimetric and fluorometric dual-signal sensor based on Au NPs and C-dots was reported by Liu et al [7]. Arginine is positively charged at pH 7.4 and can electrostatically interact with $AuCl_4$- and carboxyl group of C-dots. This interaction restrained the formation of Au NP/CQD composite resulting in changes in the UV-Vis and emission spectrum as compared to those in absence of arginine. Dong et al. [12] demonstrated the use of C-dot-Pt nano composite as visual and colorimetric sensor for H_2O_2 and glucose owing to the superior peroxidase mimetic activity of C-dot–Pt nano composites which relies on synergistic effects.

Electrochemical sensors

In recent years, electrochemical methods have attracted significant attention of the scientists because of their fast response, low-cost, high sensitivity and selectivity. A few examples of metal/ carbon dot nano composites have been reported for electrochemical sensing of various analytes [13]. Xi et al. [14] designed Pd nano particles decorated N-doped graphene quantum dots@N-doped carbon hollow nano spheres which showed high electrochemical performance due to the synergistic effect derived from their unique structure and extraordinary electrocatalytic properties. This biosensor could specifically detect H_2O_2 secreted from living cancer cells. A multifunctional electrochemical platform for hydrogen peroxide (H_2O_2) and nitrite (NO_2-) based on silver/carbon nano-composite (Ag/CNC) was proposed by Zhang and group [15]. In this work, C-dots were used as efficient stabilizers to prevent aggregation of silver nano particles resulting in a better electrocatalytic material for sensing applications. In another scheme, Au NPs and graphene quantum dots (GQDs) co-modified glassy carbon electrode have been designed for catechol sensing by Zhao et al. [16].

They reported that synergistic cooperation between Au NPs and C-dots can increase specific surface area and enhance electronic and catalytic properties of glassy carbon electrode for sensing applications. A similar approach for electrochemical detection of catechol and hydroquinone has been reported by Yan et al. [17] who synthesized C-dots-ZnO/multi walled carbon nano tubes (MWCNT) through microwave assisted technique. They have exploited the carboxyl rich surface of C-dots for enhanced interactions with catechol and hydroquinone which results in improved redox response required for efficient sensing. A bimetallic nano composite incorporating Au-Pt NPs along with GQDs has been fabricated by Yola et al. [18] for simultaneous determination of ascorbic acid, dopamine (DA), uric Acid and tryptophan. Huang et al. [19] developed Au@C-dot-chitosan composite for sensitive detection of dopamine. Here, the negative charge on C-dots imparted by carboxyl functionalities could attract the amine functional groups in DA through electrostatic interaction and Au nano particle made the surface highly conductive. The resultant nano composite could detect even 1nM DA. Arvand et al. [20] fabricated Fe_3O_4@GQD based system for electrochemical detection of progesterone which proved to be a cost-effective, convenient, rapid and selective platform for sensing in human serum samples.

Electrochemiluminescence (ECL) sensors

In addition to optical and electrochemical approaches, sensors based on the electro chemiluminescence property of C-dots have also been reported [21,22]. Deng et al [23] demonstrated the use of Pt/Fe@C-dots as signal labels in sensitive ECL immunosensor for carcinoembryonic antigen (a tumor marker) detection. Here, the nano tubular mesoporous Pt/Fe nano particles provided high surface area for immobilization of more C-dots resulting in enhanced ECL response as compared to only C-dots. Another significant development relying on the similar principle of using bimetallic nano particles as support for C-dots was reported by Wu et al. [24]. A paper-based electrochemiluminescence electrode as an aptamer-based cyto sensor using PtNi@carbon dots as nano labels was used for detection of cancer cells and for in-situ screening of anticancer drugs. In a different work, Wu et al. [25] proposed Ag@C-dots as electro chemiluminescent label for detection of prostate protein antigen (PSA). The nano porous silved used had high surface area to attach abundant antibodies on one hand and loading large number of C-dots on other.

Conclusion and Outlook

Carbon dots have emerged as excellent sensors owing to their tuneable functionalized surface which results in robust optical and electronic properties. C-dots when integrated with metal/ metal oxide nano particles, the resulting nano composites show superior behavior compared to individual components that could function as highly reliable and sensitive biosensors. Considering the ease of synthesis and biocompatibility of C-dots, such nano composites offer great potential for optical imaging and studying bio molecular events in vivo. Going forward, the C-dot composites have great potential for widespread integration into devices for routine sensing.

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References

1. Baptista FR, Belhout SA, Giordani S, Quinn SJ (2015) Recent developments in carbon nano material sensors. Chem Soc Rev 44: 4433-4453.
2. Doria G, Conde J, Veigas B, Giestas L, Almeida C, et al. (2012) Noble metal nano particles for biosensing applications. Sensors 12(2): 1657-1687.
3. Lim SY, Shen W, Gao Z (2015) Carbon quantum dots and their applications. Chem. Soc Rev 44(1): 362-381.
4. Zheng XT, Ananthanarayanan A, Luo KQ, Chen P (2015) Glowing graphene quantum dots and carbon dots: properties, syntheses, and biological applications. Small 11(14): 1620-1636.
5. Mandani S, Sharma B, Dey D, Sarma TK (2015) Carbon nanodots as ligand exchange probes in Au@ C-dot nanobeacons for fluorescent turn-on detection of biothiols. Nano scale 7(5): 1802-1808.
6. Deng J, Lu Q, Hou Y, Liu M, Li H, et al. (2015) Nanosensor composed of nitrogen-doped carbon dots and gold nano particles for highly selective detection of cysteine with multiple signals. Anal Chem 87(4): 2195-2203.
7. Liu T, Li N, Dong JX, Zhang Y, Fan YZ, et al. (2017) A colorimetric and fluorometric dual-signal sensor for arginine detection by inhibiting the growth of gold nano particles/carbon quantum dots composite. Biosens Bioelectron 87: 772-778.
8. Liu R, Huang H, Li H, Liu Y, Zhong J, et al. (2013) Metal nanoparticle/ carbon quantum dot composite as a photocatalyst for high-efficiency cyclohexane oxidation. ACS Catal 4(1): 328-336.
9. De B, Karak N (2017) Recent progress in carbon dot-metal based nanohybrids for photochemical and electrochemical applications J Mater. Chem A 5: 1826-1859.
10. Zhu A, Qu Q, Shao X, Kong B, Tian Y (2012) Carbon-dot-based dual-emission nano hybrid produces a ratiometric fluorescent sensor for *in-vivo* imaging of cellular copper ions. Angew Chem Int Ed 51(59): 7185-7189.
11. Yang C, Deng W, Liu H, Ge S, Yan M (2015) Turn-on fluorescence sensor for glutathione in aqueous solutions using carbon dots-MnO_2 nano composites. Sens. Actuators B: Chem 216: 286-292.
12. Dong Y, Zhang J, Jiang P, Wang G, Wu X, et al. (2015) Superior peroxidase mimetic activity of carbon dots–Pt nanocomposites relies on synergistic effects. New J Chem 39: 4141-4146.
13. Jahanbakhshi M, Habibi B (2016) A novel and facile synthesis of carbon quantum dots via salep hydrothermal treatment as the silver nano particles support: Application to electro analytical determination of H_2O_2 in fetal bovine serum. Biosens. Bioelectron 81: 143-150.
14. Xi J, Xie C, Zhang Y, Wang L, Xiao J, et al. (2016) Pd Nanoparticles Decorated N-Doped Graphene Quantum Dots@ N-Doped Carbon Hollow Nanospheres with High Electrochemical Sensing Performance in Cancer Detection. ACS Appl Mater Interfaces 8(4): 22563-22573.
15. Zhang S, Liu X, Huang N, Lu Q, Liu M, et al. (2016) Sensitive detection of hydrogen peroxide and nitrite based on silver/carbon nano composite synthesized by carbon dots as reductant via one step method. Electrochim. Acta 211: 36-43.
16. Zhao X, He D, Wang Y, Hu Y, Fu C (2016) Au nanoparticles and graphene quantum dots co-modified glassy carbon electrode for catechol sensing. Chem Phys Lett 647: 165-169.
17. Yan Y, Huang Q, Wei C, Hu S, Zhang H, et al. (2016) Microwave-assisted synthesis of carbon dots–zinc oxide/multi-walled carbon nanotubes and their application in electrochemical sensors for the simultaneous determination of hydroquinone and catechol. RSC Adv 6: 115317-115325.
18. Yola ML, Atar N (2016) Functionalized Graphene Quantum Dots with Bi-Metallic Nanoparticles Composite: Sensor Application for Simultaneous Determination of Ascorbic Acid, Dopamine, Uric Acid and Tryptophan. J Electrochem Soc 163(14): B718-B725.
19. Huang Q, Zhang H, Hu S, Li F, Weng W, et al. (2014) A sensitive and reliable dopamine biosensor was developed based on the Au@ carbon dots-chitosan composite film. Biosens Bioelectron 52: 277-280.
20. Arvand M, Hemmati S (2017) Magnetic nanoparticles embedded with graphene quantum dots and multiwalled carbon nanotubes as a sensing platform for electrochemical detection of progesterone. Sens. Actuators B: Chem 238: 346-356.
21. Zhang M, Liu H, Chen L, Yan M, Ge L, et al. (2013) A disposable electrochemiluminescence device for ultrasensitive monitoring of K562 leukemia cells based on aptamers and ZnO @ carbon quantum dots. Biosens Bioelectron 49: 79-85.
22. Wu L, Wang J, Ren J, Li W, Qu X (2013) Highly sensitive electrochemiluminescent cytosensing using carbon nanodot @ Ag hybrid material and graphene for dual signal amplification. Chem Commun 49: 5675-5677.
23. Deng W, Liu F, Ge S, Yu J, Yan M et al. (2014) A dual amplification strategy for ultrasensitive electrochemiluminescence immunoassay based on a Pt nanoparticles dotted graphene-carbon nanotubes composite and carbon dots functionalized mesoporous Pt/Fe. Analyst 139(7): 1713-1720.
24. Wu L, Zhang Y, Wang Y, Ge S, Liu H, et al. (2016) A paper-based electrochemiluminescence electrode as an aptamer-based cytosensor using PtNi@ carbon dots as nanolabels for detection of cancer cells and for *in-situ* screening of anticancer drugs. Microchim Acta 183(6): 1873-1880.
25. Wu L, Li M, Zhang M, Yan M, Ge S, et al. (2013) Ultrasensitive electrochemiluminescence immunosensor for tumor marker detection based on nanoporous sliver@carbon dots as labels. Sens and Actuators B: Chem 186: 761-767.