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N-Doped carbon hybrid conjugates as vectors for photocatalytic CS₂ production

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Abstract

PAPER

Nanostructured carbon materials have attracted much attention, because the doping or modification can efficiently induce charge delocalization and tune the work function of carbon. Herein, we report that N-doped carbon hybrid conjugates are highly sensitive in photocatalytic CS₂ production due to the energy transfer and electron transfer between carbon and organic ligands. The key towards success was opening a new avenue for the cheap and rapid release of a potential therapeutic agent using carbon materials as vectors.

1. Introduction

Carbon disulfide (CS₂), a small molecule that causes neurotoxic effects and hepatotoxicity in high concentration [1], is a potential therapeutic agent for cancer, pointed out by fragmentary evidence [2]. It could be produced by the cleavage of 1, 1-dithiooxalate (DTO) or O-t-butyl-1, 1-dithiooxalate ('BuDTO). And it may react with biological amines to form dithiocarbamates, known inhibitors of nuclear factor κ_B (NF- κ_B) [3, 4], a crucial mediator in inflammation-induced tumor growth and progression [5]. Recently many efforts have been taken to develop biosensors to suppress cancer inhibition. For example, a dioxobridged binuclear gold (III) complex bearing two 2, 9-dimethyl-phenanthroline ligands displays excellent biological features *in vitro* against a wide panel of cancer cells [6]. Furthermore, other metal elements, such as Cu, Cd, Zn, Pt, Ag, etc, have been conjugated with some other sulphides as anticancer agents to produce CS₂ by cleavage reactions [7–11]. However, there are some fatal disadvantages, which should not be underestimated. First of all, those heavy metal elements cannot be metabolized normally in the human body. And many unexpected diseases, such as schizophrenia and hereditary diseases caused by gene mutation, would emerge when those metal elements accumulate to a certain concentration, even leading to serious body rejection. Besides, the cost and instability of those heavy metal or metal-doped ligand biosensors make them far from industrialization and practical application *in vivo*.

Fluorophotometry is used widely owing to its operational simplicity and high sensitivity [12–15], which opens a new avenue for the cheap and rapid determination of biosensors. Nanoparticles (NPs) are one of the most popular fluorescence materials in such applications. Traditional semiconductor NPs mostly contain heavy metals, such as CdS, CdSe, PbSe, and Ag₂S. However, most of the previous strategies usually need either complicated surface modification or a harsh detection environment, and these NPs also more or less suffer from the problems of toxicity, hydrophobicity, and high cost, which limit their practical application [16–18]. Thus, it

is still urgent to develop new approaches that allow biosensors functionalized in simple, sensitive, and lowtoxic ways.

As a new type of the nanocarbon family, carbon nanoparticles (CNPs) exhibit many advantages, such as low cytoxicity, high chemical stability, easy preparation, and environmental friendliness [18]. Therefore, more and more attention has been paid to these emerging carbon nanomaterials, including their synthesis, property studies, and applications [19]. In previous work [20–22], N-doped nanostructured carbon materials can efficiently induce charge delocalization and tune the work function of carbon because of the doping of N. Therefore, the introduction of N into CNPs, namely NCNPs, will also be expected to display enhanced performance in this research.

In this report, NCNPs were firstly synthesized from a carbohydrate polymer by a hydrothermal approach, as described previously [21, 22]. DTO and ^tBuDTO were synthesized according to previous reports [23–26], and their structures were conformed by ¹³CNMR analysis (see figure S1 in supporting information). Then, DTO-NCNP/^tBuDTO-NCNP conjugates were prepared by surface conjugation (see preparation in supporting information for details). The as-prepared conjugates could serve as photochemical CS₂ precursors, showing photocatalytic oxidative decomposition under UV light irradiation for the release of CS₂.

2. Results and discussion

Firstly, x-ray photoelectron spectrum (XPS) was utilized to confirm the effective incorporation of nitrogen and surface chemical properties of the obtained NCNPs (see figure S2 in supporting information). The high-resolution C spectrum of the NCNPs reveals the presence of C-H (284.6 eV), C-N (285.2 eV), and C-O (287.2 eV) bonds. The high-resolution N^{1s} spectrum shows the presence of both pyridine-like (398.8 eV) and pyrrolic-like (399.6 eV) N atoms. The high-resolution O spectrum of the NCNPs also displays three peaks at 530.2, 530.6, and 531.1 eV, which are attributed to the C=O, C-O-H, and C-O bonds, indicating that the asprepared NCNPs are rich in hydroxyl, carbonyl, and carboxylic acid groups on their surfaces (see figure S3 in supporting information) [27–31]. This makes the conjugation reactions take place between DTO or ^tBuDTO dianions and polar groups originally terminating the NCNP surface.

Figures 1(a) and (b) show the typical TEM images of DTO-NCNP and ^tBuDTO-NCNP conjugates. The diameter of two conjugates is about 50 nm, which is close to the DLS results, as shown in figure 1(c). Moreover, these conjugates exhibit excellent monodispersity. The polydispersity index of DTO-NCNP and ^tBuDTO-NCNP conjugates is 14.32% and 13.61%, respectively. The quantum yields of DTO-NCNP and ^tBuDTO-NCNP conjugates are up to 23.7% and 27.5% using Rhodamine B as a standard, compared with that of NCNPs at only 2.9% (see table S1 in supporting information) [21, 22]. However, the size of these conjugates is larger than that of the native NCNPs. The possible reason for this phenomenon is the rich polar groups on the surface of DTO-NCNP/^tBuDTO-NCNP conjugates, which provide more opportunities to aggregate together to form larger particles due to the hydrogen bond and electrostatic reactions between the conjugates. The zeta potential of DTO-NCNP and ^tBuDTO-NCNP conjugates are -48.7 and -45.2 mV, compared with -20.9 mV of native NCNPs. It reveals that DTO-NCNP and ^tBuDTO-NCNP conjugates are successfully prepared and easy to aggregate (see figure S3 in supporting information). The high luminescence quantum yields make these NP conjugates stable for optoelectronic and biological applications, especially in fluorescent probes [27]. Figure 1(d) shows the typical UV-vis absorption spectra of DTO-NCNP and ^tBuDTO-NCNP conjugates. The strong absorption bands of DTO-NCNP and ^tBuDTO-NCNP conjugates are observed at 335 nm, 349 nm, with a tail extending to the visible region, while no obvious absorption band appears in the spectra of native NCNPs.

The XPS spectra of DTO-NCNP and ^tBuDTO-NCNP conjugates reveal the prominent peaks of sulfur, with percentages of 2.43%, 3.22%, respectively (see figure S4 in supporting information). The high-resolution O spectrum of DTO-NCNP conjugates displays three peaks at 530.02, 530.75, and 531.24 eV, which are attributed to the C=O, C-O-H, and C-O bonds. The C=O, C-O-H, C-O bonds for ^tBuDTO-NCNP conjugates at 531.06, 531.49, and 532.00 eV also can be observed. These peaks exhibit little difference compared with those in the original NCNPs, due to the hydrogen reactions between the NP conjugates. The high-resolution S spectrum of DTO-NCNP conjugates demonstrates the presence of S-H (167.0 eV), S-C (167.55 eV), and S=C (168.34 eV) bonds. Similarly, the S-H, S-C, and S=C bonds of ^tBuDTO-NCNP conjugates at 168.44, 169.10, and 169.91 eV also can be found. These further indicate that DTO and ^tBuDTO have been successfully linked to the surface of as-prepared NCNPs. Moreover, the conjugation reaction between the DTO/^tBuDTOs and NCNPs are mostly dependent on the hydrogen bond, as the energy composition of the C-O-H bonds of DTO-NCNP and ^tBuDTO-NCNP conjugates is higher than that of NCNPs (see figures S2 and S4 in supporting information). Analogously, the S-H bond of DTO-NCNP and ^tBuDTO-NCNP conjugates is the main energy component in the high-resolution S spectra.



The native NCNPs show PL (photoluminescence) emission at ca. 405 nm (measured at 330 nm excitation) (see figure S5 in supporting information). But the excitation peaks of DTO-NCNP and ^tBuDTO-NCNP conjugates appear at 413 nm and 424 nm, respectively. This effect is attributed to the relaxation of excitation confinement in NCNP conjugates, owing to the alignment of interfacial orbital energies [32, 33]. The luminescence is suggested to arise from a π - π * transition due to emissive traps or free zigzag sites and/or edge states [34]. Because of the electron transfer on these conjugates' surfaces, CS₂ could be released through the photochemical cleavage reaction of DTO and ^tBuDTO. Figures 2(a) and (b) show that the PL changes of DTO-NCNP and ^tBuDTO-NCNP conjugates depend on irradiation time in the sodium borate buffer solution. However, the intensity of PL decreases with increasing irradiation time in both cases. The insets show the color of the solution of conjugates becomes light with prolonging the irradiation time. This can be contributed to the photo-decomposition of DTO-NCNP and ^tBuDTO-NCNP conjugates under UV light irradiation [35].

For comparison, the optical performances of DTO-CNPs and ^tBuDTO-CNPs (without N doping) are also investigated (see figure S6 in supporting information). However, the PL intensity of DTO-NCNPs and ^tBuDTO-NCNPs are 1.65- and 1.54- fold higher than that of DTO-CNPs and ^tBuDTO-CNPs, respectively. This reveals that the N doping plays an important role in improvement of fluorescence intensity. Doping carbon nanomaterials with heteroatoms can effectively tune their intrinsic properties, including electronic characteristics, surface, and local chemical features. The N atom, having a comparable atomic size and five valence electrons for bonding with carbon atoms, has been widely used for chemical doping of carbon nanomaterials [36, 37]. In this case, we can attribute the improved optical performance observed for NCNPs in the present study to the electron-accepting ability of nitrogen atoms [38]. Doping of carbon with substituent N heteroatoms also could effectively modulate the band gap of CNPs [39].

In order to evaluate the CS₂ production quantitatively, the dithiocarbamate, resultant of CS₂ with amines, is characterized in this report [40]. It has distinctive optical spectra with a strong absorption band in the ultraviolet range. This procedure clearly confirms photochemical CS₂ formation. In this communication, n-octylamine is used to react with CS₂. After irradiation with UV light, the volatile product CS₂ is swept from the conjugates to react with n-octylamine. The product, n-(n-octyl) dithiocarbamate, displays a strong absorption band with λ_{max} at 290 nm (see figure S7 in supporting information). Figure 2(c) shows the CS₂ production through the



Figure 2. The intensity of P 160 D10-NCNP (A) and BuD10-NCNP (b) collidgates, dependent of the matation time from 0-100 s with 20 s intervals in pH = 9.0 solution upon 360 nm excitation (insets are the color of DTO-NCNP and 'BuDTO-NCNP conjugate solutions at the photochemical reaction time at 0 s, 300 s, and 600 s under UV light irradiation), the curve fitting of typical spectra changes upon the reaction of octylamine with photochemically generated CS₂ (C), PL spectra of DTO-NCNP and 'BuDTO-NCNP s(inset) conjugates under Ar, N₂, O₂, and air atmosphere, irradiated under UV light for 300 s before measurement (D).

photolysis in the air. The absorption peak at 290 nm can be observed immediately when the solutions are irradiated by UV light. Furthermore, the absorption intensity at 290 nm increases with prolonging the irradiation time. This procedure clearly confirmed the formation of labile CS₂ as a photoproduct, although the amount of free CS₂ detected exhibits some deviation. However, no absorption at 290 nm can be found when the DTO-NCNP or ^tBuDTO-NCNP conjugate solution is placed in the dark. This indicates that no CS₂ formation is apparent without photolysis.

For evaluation of CS_2 production with the assistance of co-reactants, different gases (Ar, N₂, or O₂) were introduced to the DTO-NCNP and ^tBuDTO-NCNP conjugate solutions under UV light irradiation. Interestingly, under the atmosphere of Ar, N₂, O₂, no obvious differences are observed in the fluorescence intensity or the release of CS_2 compared with only the presence of air. As shown in figure 2(d), the PL emission curves under a different atmosphere almost completely overlap. The formation of CS_2 with no requirement for O₂ as a co-reactant suggest that photolysis of surface-conjugated DTO reversibly leads to transient species that are not trapped by the external oxidant, which is quite different from Ford's results [41].

The PL quenching process can be studied by adding an external quencher either to quench an excited solvent molecule or to quench an excited solute molecule, as the case may be [42]. The NCNPs are similarly strong electron acceptors as well, allowing highly efficient luminescence quenching by known electron donors [43]. The PL quenching by an aromatic electron donor, N, N-dimethyl aniline (DMA), is investigated firstly. As shown in figures 3(a) and (b), the PL quenching spectra of DTO-NCNP and tBuDTO-NCNP conjugates in the presence of DMA are strongly concentration dependent. The higher the concentration of DMA, the lower the PL intensity that can be found in both cases. This reveals that electrons from DMA are transferred to the surface of NCNPs for fluorescence quenching. Thus, the stronger fluorescence quenching in the conjugation systems can be observed due to the presence of more electron donors in them.

Tetrathiafulvalene (TTF) and tetracyanoethylene (TCNE) are known for their charge transfer interaction with aromatics, including NCNPs. In the case of DTO-NCNP and ^tBuDTO-NCNP conjugates, electron-







donating TTF shows significant quenching of luminescence (figures 3(c) and (d)), similar to DMA. Unlike TTF, electron-accepting TCNE interacts differently with DTO-NCNP and ^tBuDTO-NCNP conjugates. As shown in figures 3(e) and (f), the FL intensity of DTO-NCNP and ^tBuDTO-NCNP conjugates increases with the addition of 0.1 and 1.0 mM TCNE but decreases on further increasing the TCNE concentration to 10 mM.

The electron acceptor TCNE initially occupies some of the surface-emissive sites. The specific interaction of TCNE with DTO-NCNP and ^tBuDTO-NCNP conjugates is to be expected, since the NCNPs can act as electron donors, while TCNE is an electron acceptor. To further understand this behavior, the broad PL emission spectra of DTO-NCNP and ^tBuDTO-NCNPs conjugate have been deconvoluted into multiple Gaussian functions (figures 3(g) and (h)), which indicate the presence of multiple emissive sites [44]. Under UV light irradiation, the electrons are excited from NCNPs for the cleavage reaction and transferred to ligands. The new electrons are released simultaneously during the photodecomposition of DTO or ^tBuDTO. These released electrons are transferred back to NCNPs, which leads to quenching of fluorescence. For confirmation of the above assumption, TCNE has been added for detection of CS₂ release. Less CS₂ can be detected after the addition of TCNE into the conjugates' systems under UV light irradiation (see figure 8 in supporting information). This further reveals that the excited electrons from NCNPs are captured by TCNE.

To further confirm the energy/electron transfer process between NCNPs and DTO or ^tBuDTO, a timeresolved fluorescence study is performed, because decay time measurements are more sensitive than PL quenching efficiencies, where errors come from the fluctuations in the lamp intensity [45]. We have used pulsed excitation (measured at 375 nm) to measure the decay times of these conjugates at their maximum PL peak. Figure 4(a) shows the time-resolved fluorescence decay curves of native NCNPs and their conjugates. The decay profiles are well fitted with triexponentials. The average decay time is 2.50, 1.87, and 1.74 ns for native NCNPs and, after conjugation, for DTO and ^tBuDTO ligands. The faster components decrease from 0.39 (55.0%) to 0.21 (68.0%) and 0.17 ns (72.0%) after conjugation; other two components varied from 3.67 (34.0%) to 2.94 ns (24.0%) and 15.27 (6.0%) to 9.43 ns (11.0%). The decay time parameters are given in table S2. The PL quenching and the shortening of decay time definitely indicate the nonradiative quenching process of conjugates due to electronic interaction between NCNPs and ligands. The faster component of the decay time decreases rapidly after conjugation, indicating the presence of an electron transfer process during light irradiation [46].

The observed emission lifetime can be combined with fluorescence quantum yield to determine the radiative and nonradiative rates [47]. The radiative decay rates are 12.67% for DTO-NCNPs and 15.80% for ^tBuDTO-NCNPs, and the nonradiative decay rates are 40.80% for DTO-NCNPs and 41.67% for ^tBuDTO-NCNPs (see table S3 in supporting information). The change of the nonradiative rate of excited state deactivation also can be calculated [48]. The change of the nonradiative relaxation rate of DTO-NCNPs and ^tBuDTO-NCNPs are found to be 1.35×10^8 and 1.75×10^8 , respectively (see table S4 in supporting information). This nonradiative relaxation process mainly occurs either via electron transfer or energy transfer processes. Due to spectral overlap between the emission spectrum of the NCNPs and the absorption spectrum of the DTO or ^tBuDTO, as shown in figure 4(b), the energy transfer process also plans an important role in PL quenching [45]. The energy transfer efficiencies of DTO-NCNP and ^tBuDTO-NCNP conjugates are found to be 25.20% and 30.40%, respectively (see table S3 in supporting information). Therefore, the PL quenching occurs both by energy transfer and the electron transfer process. It is proposed that the photodecomposition mechanism involves electronics released from the NCNPs under UV irradiation and transferred to the DTO/^tBuDTO ligands for cleavage. The holes

obtained from excitation-induced of NCNPs are transferred to DTO/^tBuDTO. The electronics from photodecomposition of DTO or ^tBuDTO are transferred to the holes of NCNPs, accompanied by energy transfer between the CNPs and ligands, and fluorescence quenching takes place accordingly.

3. Conclusions

In summary, the preparation of photo-sensitive conjugates by displacing 1, 1-dithiooxalate and o-tert-butyldithiooxalate on NCNPs through hydrogen bonds has been described. The PL quenching phenomena for the conjugated solution can be observed under light irradiation. The PL quenching of these conjugates is mainly due to energy transfer and electron transfer between NCNPs and DTO or ^tBuDTO ligands, based on analysis of their electronic interaction by titration analysis and time- resolved fluorescence spectroscopy. Photolysis in solutions leads to the photocatalytic decomposition of these surface DTO or ^tBuDTO ligands with CS₂ release. The photochemical release of CS₂ from these hybrid conjugates is found to be suitable for potential applications in drug release and delivery therapeutic systems.

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