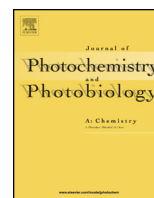




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π - π binding ability of different carbon nano-materials with aromatic phthalocyanine molecules: Comparison between graphene, graphene oxide and carbon nanotubes

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ABSTRACT

The π - π stacking ability of graphene sheets (GS), graphene oxide (GO), and single walled carbon nanotubes (SWCNT) with phthalocyanine (Pc) molecules was studied by the UV-vis absorption, steady state and time-resolved fluorescence spectra. Absorption spectra revealed that strong π - π binding with the Pc ground state (S_0) occurred for GS and GO but not for SWCNT, the binding ability is $GS \gg GO \gg SWCNT$. However, when a Pc molecule is photoexcited, fluorescence study shows that the π - π interaction capability is changed to $GS \gg SWCNT \gg GO$. Although SWCNT exhibits low ability to bind Pc S_0 state, it strongly interacts with Pc S_1 state. The data analysis shows that the dynamic quenching for the nanoscaled carbon quenchers still obeys linear Stern-Volmer relationship, but the static quenching is not linear. An exponential expression is needed to fit the data for GS and SWCNT, which indicates that an effective quenching sphere model is valid for the nanoscaled fluorescence quenchers.

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1. Introduction

Carbon nano-materials (graphene, graphene oxide, fullerenes and carbon nanotubes) are currently under intensive exploitation, due to their excellent electronic, optical, and thermal properties [1–6]. One important aspect is the noncovalent binding of aromatic organic molecules with these materials through π - π interaction [7–11], which is of interest to many applications. For examples, it can be employed to open the band gap of graphene [12], tune the electronic structure and transport properties [7,13–15], adsorb and remove dye pollutants efficiently in wastewater treatment [16], to exfoliate graphite into graphene monolayers [7,8,17]. Understanding the interaction behavior between aromatic dye molecules and carbon nano-materials is therefore very valuable for practical applications. Scheme 1

Most related reports focus on the effect of different small aromatic molecules on the interaction behavior. For example, the

interaction with phthalocyanine (Pc) [18,19], pyrenebutyrate [10], porphyrin [9,20,21], eosin [22], methylene blue [23], F27 [24], pyrene [20], fluorescein [11,19] and rhodamine B [19,23,25,26] has been reported recently by other researchers [9–11,20–25] and us [18,19,26]. However, there have been few reports related to the comparison of different carbon nano-materials in their π - π interaction behavior [27].

In this report, we compare the binding ability of graphene, graphene oxide, and single walled carbon nanotubes. Phthalocyanine is selected as the aromatic molecule for binding, due to its large π -system and is known to be able to form strong noncovalent π - π complex with carbon nano-materials [18,19,26,28].

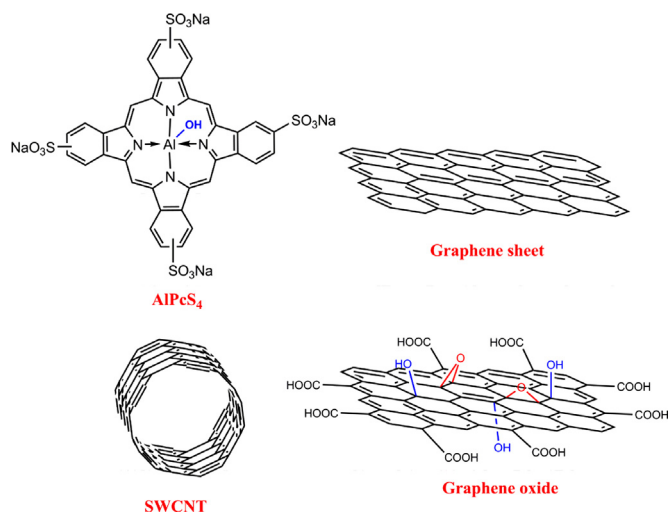
2. Materials and methods

2.1. Materials

The sulfonated aluminum phthalocyanine (AlPcS₄) was home made and characterized previously [29]. Single walled carbon nanotubes (SWCNT) dispersion in 1% (w/v) ionic surfactant (proprietary mixture) was purchased from NanoIntegris, USA. This SWCNT has a diameter range from 1.2 to 1.7 nm, and length range from 300 nm to 5 μ m, the Raman G/D ratios range from 12 to 41, indicating very low levels of amorphous carbon and/or

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Scheme 1. Chemical structure of the Pc and carbon nano-material.

damaged nanotubes. The graphene oxide (GO) and chemically derived graphene (CDG) are the same product as the previously used which were also home made and characterized before [18]. The size of the CDG and GO sheets is typically several hundred nanometers on average. The well-dispersed GO and CDG in aqueous phase is quite stable and no precipitation was observed in 6 months.

Double distilled deionized water was further purified by Millipore Milli-Q system. All other materials were analytical grade and commercially available.

For all the absorption fluorescence quenching measurements, AlPcS₄ dye concentration was kept constant while the concentration of nano-carbon materials was changed. 0.1 mM AlPcS₄ dye and 0.1 mg/mL nano-carbon materials were used as the stock solutions, which were then diluted to get the desired concentrations. A separate solution containing the same concentration of nano-carbon materials but without AlPcS₄ was prepared for background subtraction. The pH value was adjusted and sonicated to maintain a pH 7.6 ± 0.2. The resulted dispersion was swirled and allowed standing for 30 min to get equilibrium before measurements.

2.2. Instruments and photophysical measurements

UV–vis absorption measurements were carried out with a StellarNet BLACK Comet C-SR diode array miniature spectrophotometer connected to deuterium and halogen lamp by Optical fiber in 10 mm quartz cuvettes. Fluorescence spectra and lifetimes were monitored using Edinburgh Instruments FLS 920, with 1 nm slits in 10 mm quartz cuvettes. All measurements were carried out at room temperature of 25 °C. All fluorescence spectra were corrected for the sensitivity of the photo-multiplier tube. The fluorescence quantum yield (Φ_f) was calculated by $\Phi_f = \Phi_f^0 \cdot \frac{F_s}{F_0} \cdot \frac{A_0}{A_s} \cdot \frac{n_s^2}{n_0^2}$, in which F is the integrated fluorescence intensity (photon counting), A is the absorbance at excitation wavelength, n is the refraction index of the solvent, the subscript 0 stands for a reference compound and s represents samples. ZnPc in DMF was used as the reference ($\Phi_f^0 = 0.30$) [30]. All solutions were air saturated. Fluorescence lifetime of S₁ state was measured by time-correlated single photon counting method with excitation at 672 nm by a CdS portable diode laser (69 ps pulse width) and emission was monitored typically at 685 nm. Fluorescence lifetimes were obtained by the as supplied software F900, in which the experimental data are fit by using convolution of $I(t) = A_1 \exp(-t/\tau_f) + B_1$ with the measured instrument response function.

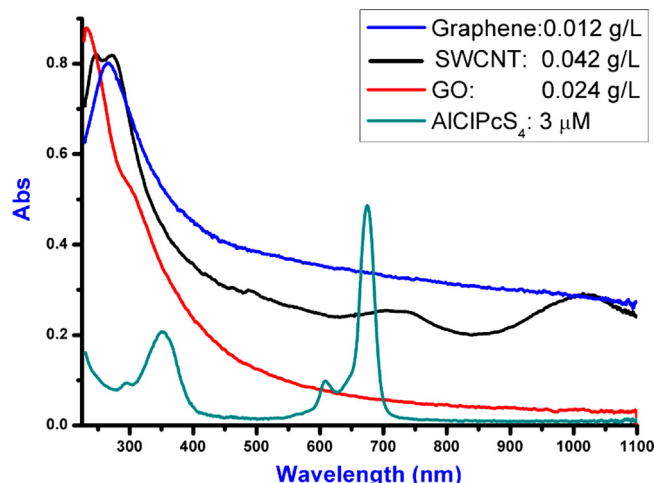


Fig. 1. The UV–vis absorption spectra of AlPcS₄, CDG, GO and SWCNT in water.

3. Results and discussion

Dislike the perfect graphene sheets on a solid substrate which are planar π -systems, CDG sheets in aqueous dispersion are often nonplanar and partially curved, folded or even aggregated [31]. So is the case for GO which also contains hydroxyl, carboxylic, carbonyl on its basal plane, these groups further decrease GO planarity. Carbon nanotubes are nonplanar, but also contain large π -systems. These factors make the π - π interaction complicated for the carbon materials with an aromatic molecule AlPcS₄. It is therefore necessary to measure and compare the differences between them.

3.1. UV–vis absorption spectra of Pc, CDG, GO and SWCNT

Fig. 1 compares the UV–vis absorption spectra for the four materials. A Pc molecule is a planar aromatic π system, in which the delocalized π electrons show very strong π - π^* absorptions in the red region (Q band, 675 nm for AlPcS₄ in aq. solution). AlPcS₄ is used in this study as it is highly water soluble and shows no band at 630 nm due to the dimerization or higher order aggregation.

GO has absorption maximum at 230 nm and a shoulder at 300 nm, its chemically reduced product CDG showed a peak at 265 nm with broad and structureless absorptions in the whole UV–vis-NIR region. The SWCNT sample contains both semiconducting and conducting tubes. Both types of the tubes have absorption at about 255 nm and 1050 nm, while the conducting SWCNT shows the characteristic 700 nm band. These spectra are all consistent with that reported [32]. The relative absorptivity (CDG:GO:SWCNT) is roughly 4:2:1, which mainly reflect the degree of planarity of each carbon nano-material.

3.2. π - π interaction based on UV–vis absorption spectra of Pc upon titration by CDG, GO, and SWCNT respectively

Q band absorptions of Pc are sensitive to the π - π interaction. It was shown previously that the strong π - π attraction leads to the formation of ground state Pc-CDG or Pc-SWCNT complexes [18,19], and the complex has a new red-shifted peak and weaker absorptivity in comparison to that of Pc Q band.

Fig. 2 shows UV–vis absorption change of AlPcS₄ upon the addition of CDG, GO and SWCNT. In all cases a new band appeared in the red region upon the addition of either CDG, GO, or SWCNT. The Q band decrease of free AlPcS₄ is accompanied by the increase of the new band at around 710 nm, and an isosbestic point at ca. 682 nm is clearly observable for CDG and GO. This result indicates the

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