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Noncovalent Functionalization, Exfoliation, and Solubilization of Graphene in Water by Employing a Fluorescent Coronene Carboxylate

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Graphene, with an atomically thin two-dimensional lattice of sp^2 carbon atoms, has emerged in recent years as a novel class of nanomaterial, with remarkable electronic and mechanical properties.[1,2] Molecular engineering of graphene by solubilization, chemical functionalization, and assembly, for example, plays a crucial role in exploring the applications of the resulting compounds in nanoelectronic devices and composite materials.[3] Noncovalent functionalization, which has successfully been carried out in the case of carbon nanotubes,[4] is also of interest for the solubilization of graphene because it enables the attachment of molecules through π–π stacking and hydrophobic interactions while still preserving the intrinsic properties of graphene.[5] Recently, interaction of electron-donor and -acceptor molecules with graphenes has been exploited to control the electronic properties of graphene through molecular charge-transfer interactions.[5a,6] Interestingly, it has been found that electron-withdrawing molecules interact more strongly with graphene.[6] However, multifunctional materials, formed by the noncovalent attachment showing combined properties of graphene and the functionalizing molecules, have not been adequately explored for solubilization, exfoliation, and such purposes.[5,7] We have explored noncovalent functionalization of graphene by making use of charge-transfer interactions with aromatic acceptor molecules, yielding a novel class of water-soluble materials with tunable optoelectronic properties. We also present changes in the absorption and emission properties of graphene composites with aromatic acceptor molecules through strong charge-transfer interactions. Most importantly, we have observed exfoliation of few-layer graphene samples through charge-transfer interactions with organic molecules leading to the generation of large quantities of noncovalently functionalized single-layer graphenes in aqueous medium.[5d,8]

In the present study, we have chosen an anionic coronene derivative, the tetrapotassium salt of coronene tetracarboxylic acid (CS, Figure 1 a) for the noncovalent functionalization of graphene. Coronene is the simplest six-fold symmetrical aromatic molecule after benzene. It is a blue fluorescent material and its derivatives, in the form of esters and

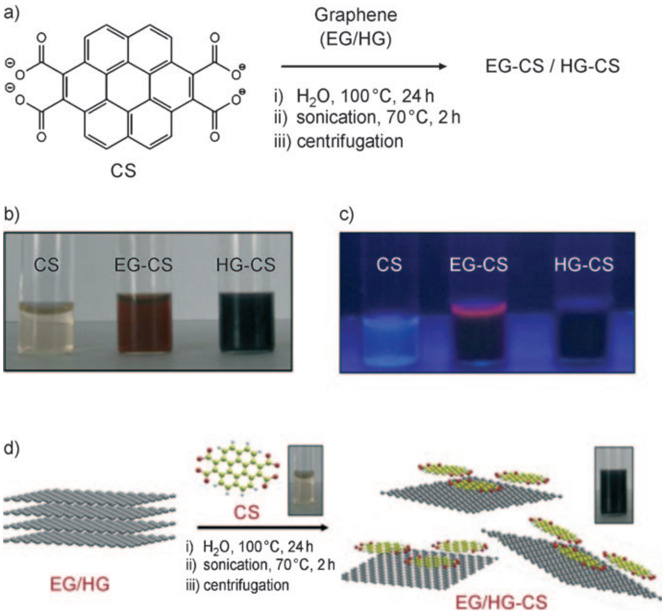

Figure 1. a) Synthetic scheme for the preparation of graphene–coronene composites. b) Photographs of the aqueous solutions of CS, EG–CS and HG–CS and c) corresponding images under UV/Vis illumination. d) Schematic illustration of the exfoliation of few-layer graphene with CS to yield monolayer graphene–CS composites.

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imides, are known to be liquid crystalline with high fluorescence emission in solution as well as in the solid state.[9] Although coronene is electron rich, its imide and carboxylate derivatives are known to be electron deficient.[9,10] We selected CS as the acceptor molecule to promote charge-transfer interactions with graphene because it is highly soluble in water and shows blue emission (Figure 1 b and c). CS has a very large planar aromatic surface that permits strong interaction with the surface of graphene sheets through synergistic noncovalent charge-transfer and π–π-stacking interactions. Furthermore, the negative charge of CS prevents both inter and intra π–π stacking of graphenes, leading to the stabilization of the functionalized graphene sheets. This design strategy has enabled us to obtain highly stable aqueous dispersions of monolayer graphene sheets that could be easily transferred onto surfaces.

Graphene samples were prepared by two different methods, namely, the thermal exfoliation of graphite oxide (EG) and the arc evaporation of graphite in a hydrogen atmosphere (HG) by following the literature procedures described in Refs. [11] and [12]. The graphene samples were characterized by using Raman spectroscopy and different microscopy techniques as previously reported.[11a] The number of layers in the EG and HG samples were found to be 5±1 and 3±1, respectively.[11a] Aqueous solutions of graphene were prepared by the addition of CS to a dispersion of EG or HG in distilled water and heating the mixture at 100 °C for 24 h. The resulting mixture was subsequently sonicated at 70 °C for 2 h to ensure maximum solubilization. Ultrasonication is expected to overcome the van der Waals interactions between the graphene planes in the multilayer graphene and help the anionic CS to solubilize, thereby stabilizing the exfoliated (see below) sheets. The mixture was then centrifuged to remove the insoluble multilayer graphene, which might not have fully exfoliated, to give red and black clear solutions for EG (EG–CS) and HG (HG–CS) samples, respectively (Figure 1 b). The aqueous solutions are transparent and highly stable for months, indicating efficient solubilization of the graphenes.[13] The presence of graphene in the aqueous phase was confirmed by various electron microscopic techniques as well as atomic force microscopy (AFM, see below).[13] The dark-black color of the HG–CS suggests that CS is more efficient in solubilizing HG than EG. By measuring the weight of the centrifuged residue, the concentration of the HG sample solubilized in water was estimated to be 0.15 mg mL^{-1}. Figure 1 d schematically illustrates the formation of aqueous solutions of chemically exfoliated graphene sheets. Characterization of the coronene–graphene composites in solution was carried out by absorption and fluorescence spectroscopy. The supernatant solution composed of single- and few-layer graphene sheets was used for the characterization. Drop-casting of the aqueous graphene solution onto glass/quartz slides enabled the investigation of the deposited sheets by Raman and optical spectroscopy, as well as electron microscopy and AFM.

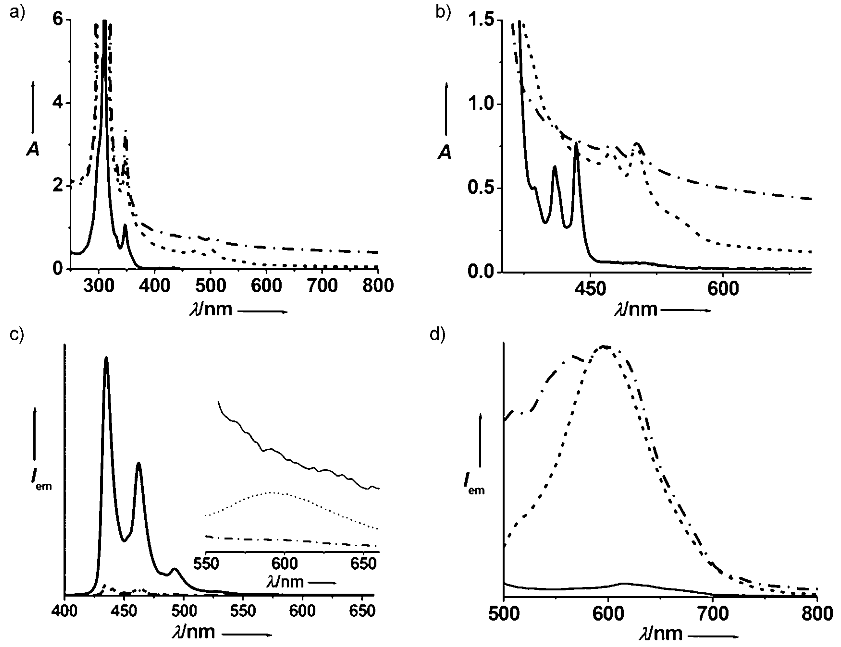

Figure 2. Absorption and emission characteristics of the aqueous solutions of CS, EG–CS, and HG–CS. a) Absorption spectra, b) corresponding normalized absorption of the redshifted band, c) emission spectra on excitation at 350 nm (inset shows the portion of the redshifted emission around 600 nm), and d) emission spectra on the selective excitation of solutions at 475 nm (—— = CS, ••••• = EG–CS, –•–• = HG–CS).

The easy and efficient stabilization of graphene in aqueous solution by coronene molecules implies that there are strong π–π interactions between the molecules and graphene. Such π–π interactions should result in changes in the optical properties of the chromophore and, therefore, we carried out detailed optical spectroscopic studies. Figure 2 a and b show the absorption spectra of CS, EG–CS and HG–CS in water.[14] The spectrum of CS exhibits strong absorption at 310 nm and weak bands between 400 and 450 nm, consistent with the spectra of coronene-tetraester derivatives.[9,13] Interestingly, solutions of EG–CS and HG–CS showed absorption bands that were significantly redshifted, appearing at 470 and 505 nm. This observation indicates that the adsorption of CS onto the graphene surface perturbs its electron states. The changes in the absorption spectra of the composite samples are in agreement with the color changes shown in Figure 1 b. Although both EG and HG composites exhibit similar bands due to CS, the new band is more intense in the former absorption (Figure 2 b), suggesting a stronger electronic interaction of CS with EG than HG. On the other hand, enhanced scattering and the dark color of the HG–CS solution suggest more efficient solubilization of graphene compared with the EG–CS.

Decisive evidence for the coronene–graphene interactions and the nature of the excited-state processes is provided by fluorescence measurements, which show significant quenching of coronene emission in hybrid samples (Figure 2 a and b).[15] CS shows intense blue fluorescence with emission maxima at 435 and 462 nm, but the emission intensity of the EG–CS and HG–CS solutions is reduced by a factor of 27 and 20, respectively. However, the quenching of fluorescence in coronene–graphene composites is accompanied by the appearance of a weak redshifted emission around 600 nm, responsible for the slight red fluorescence of the composite samples as shown in Figure 1 c. To investigate the origin of this redshifted emission band we have selectively excited the ground-state coronene–graphene complexes at 475 nm. The resulting spectrum shows an emission band with maximum around 600 nm (Figure 2 b). The redshifted emission is, therefore, attributed to the ground-state coronene–graphene complexes. Although the absorption spectra showed the presence of a significant amount of unbound or loosely bound chromophores in the composite samples (strong absorbance in the range 300–350 nm), the corresponding emission from the free/loosely bound chromophores in the region 430–480 nm was significantly quenched on excitation at 350 nm. This suggests that apart from the formation of ground-state complexes, photoinduced electron or/and energy transfer may also be possible pathways of fluorescence quenching from the loosely bound chromophores. Recently, various organic fluorescent dyes such as pyrene[5a] and perylenebisimide[5b–d] have been used to functionalize graphene, and quenching of fluorescence is generally observed. Note that although chromophores interacting with carbon nanotubes and graphenes usually loose their fluorescence, the graphene–CS composites formed by the noncovalent functionalization of graphene with aromatic acceptor molecules remain fluorescent.

Because the transfer of the stabilized coronene–graphene composites in solution to the solid state is a prerequisite for possible use in an electronic device, we investigated the optical properties of the composites on solid substrates. We prepared thin films of EG–CS and HG–CS by drop-casting the corresponding aqueous solutions on glass substrates. The films showed optical changes similar to those in solution. However, the absorption bands around 310 nm, corresponding to the free molecule, are significantly suppressed compared with those in solution as shown in Figure 3 a. Furthermore, emission bands at 435 and 462 nm, corresponding to the loosely bound molecules, are quenched in the film confirming efficient charge-transfer processes in the solid state. Films of EG–CS and HG–CS show emission maxima at 566 nm and 539 nm, respectively, when excited at 350 nm as shown in Figure 3 b. This redshifted emission band of the EG samples compared with the HG samples is considered to be due to stronger interaction. The difference in the intermolecular interactions in the film samples results in the coverage of the emission over a wide range of wavelengths (450–650 nm) from blue (free coronene molecule) to red emission.[13]

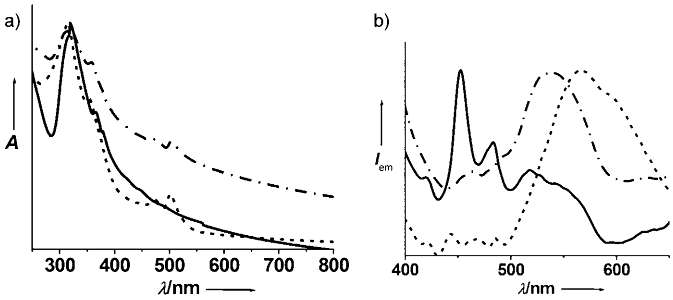

Figure 3. Normalized a) absorption and b) emission spectra (λ_{exc} = 350 nm) of CS (——), EG–CS (•••••), and HG–CS (–•–•) on quartz plate.

As proof for the occurrence of charge-transfer interactions in graphene–CS composites in the solution and solid states, we have carried out Raman measurements (Figure 4). The G band in the Raman spectrum is known to be shifted to lower frequencies (softening) by electron-donor molecules and to higher frequencies (stiffening) by electron-acceptor molecules. By comparing the G bands of graphene and graphene–CS films, it is evident that the G band of EG–CS (1592 cm^{-1}) and HG–CS (1586 cm^{-1}) composites stiffens by 17 and 13 cm^{-1}, respectively, relative to pure EG (1579 cm^{-1}) and HG (1569 cm^{-1}). For EG, the position and intensity of the defect-related D band is not changed, but the intensity of the 2D band markedly decreases. For HG, the D, G, and 2D bands are all shifted to higher frequencies, although the shift of the D band is smaller (from 1322 to 1327 cm^{-1}) and that of the 2D band is substantial (2642 to 2658 cm^{-1}). Furthermore, the sharp 2D peak of HG–CS suggests the presence of single- or double-layer graphenes. The significant Raman shifts of the G and 2D bands in the graphene–coronene composites confirm the occurrence of charge-transfer interactions between CS and graphene as indicated by optical spectroscopy. Similar Raman spectral changes have been reported for electron-acceptor molecules

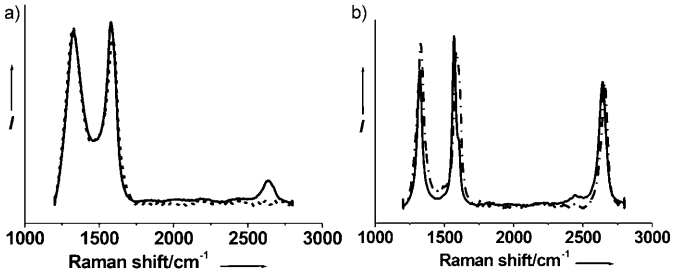

Figure 4. Raman shift of a) EG (—— = EG, ••••• = EG–CS) and b) HG (—— = HG, –•–• = HG–CS) upon interaction with CS on glass substrates.

such as TCNE (TCNE = tetracyanoethylene) and nitrobenzene, and hence the acceptor nature of the coronene salt in charge-transfer interactions with graphene is proven.[6,11a,b]

To corroborate the results obtained from optical and Raman spectroscopy, microscopic studies were carried out. AFM, transmission electron microscopy (TEM), and field-emission scanning electron microscopy (FE-SEM) of samples generated from aqueous solutions showed the characteristic structure of graphenes. Furthermore, we have conducted statistical AFM height analysis (Figure 5) to compliment our suggestion of exfoliation of graphene by CS. A typical cross-section picture of a HG–CS sample indicates a height distribution between 0.5 and 1.0 nm, suggesting the exfoliation of few-layer graphenes to mostly single-layer graphene (Figure 5 a).[13] In addition to the large quantities of single-layer graphene on the surface, double-layer graphenes with thicknesses between 1 and 2 nm were also observed in a few places that have coronene molecules between the layers or on the outer surface. On the other hand, AFM analysis of the residual graphene after centrifugation showed broad height distribution between 2–6 nm, suggesting the presence of multilayered graphene (Figure 5 b). Prolonged reaction of the residual samples with an excess of CS lead to complete solubilization and resulted in stabilized single-layer graphene solutions.[13] This result suggests that the coronene molecules help to exfoliate few-layer graphene and selectively solubilize single- and double-layer graphenes. Electrostatic repulsion forces appear to prevent the graphene sheets from aggregation (Figure 1 d).

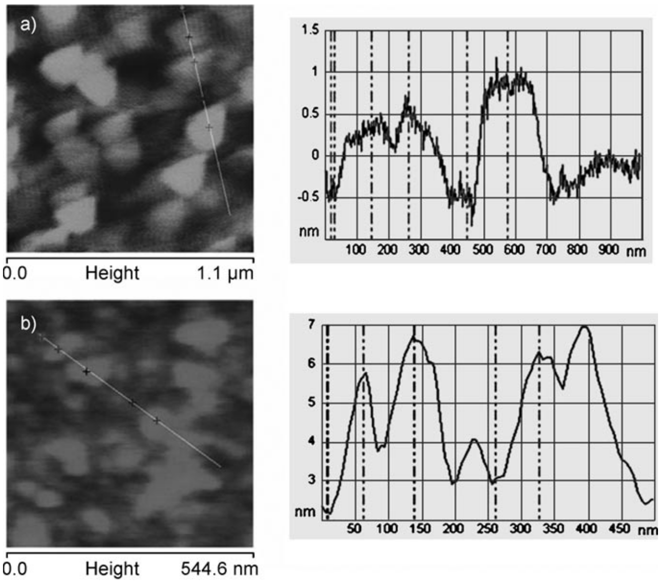

Figure 5. Contact-mode AFM images of a) drop-casted HG–CS aqueous solution and b) of residual HG obtained by centrifugation. Corresponding cross-sectional height analyses are shown on the right.

In conclusion, we have demonstrated a simple and efficient methodology to make stable aqueous solutions of single- and few-layer graphenes by exploiting noncovalent interactions with a coronene carboxylate acceptor molecule. Optical and Raman spectroscopy unambiguously shows the strong molecular charge-transfer interactions with the graphene. Furthermore, microscopic studies reveal exfoliation and stabilization of single- and few-layer graphene in large quantities. The fluorescent sheets of the composite with strongly bound electron-deficient fluorescent coronene molecules could be of use in nanoelectronics. Furthermore, this approach can be extended for the separation of metallic and semi-conducting carbon nanotubes by selective charge-transfer interactions[6c] and subsequent solubilization, and experiments in this direction are in progress.

Experimental Section

EG and HG samples were prepared and characterized according to the literature procedures.[10,11] The synthetic scheme for the preparation of CS and other experimental details are given in the Supporting Information.

Acknowledgements

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Keywords: charge transfer · coronene · exfoliation · graphene · noncovalent interactions

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[13] See the Supporting Information.

[14] Although the optical density corresponding to free CS molecules (300–400 nm) are above the acceptable limit, we are interested only in the additional band formed owing to the graphene–coronene complexes (450–550 nm).

[15] For the fluorescence experiments, thin quartz cuvettes were used (1 mm path length) and the fluorescence was collected in a front-face geometry to prevent self-absorption.

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