

Electronic Supplementary Information (ESI)

A Graphene-based Composite Material Noncovalently Functionalized with Chemiluminescence Reagent: Synthesis and Intrinsic Chemiluminescence Activity

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Experimental Section

Chemicals and solutions: Graphene oxide (GO) was purchased from XFNANO Materials Tech Co., Ltd. (Nanjing, China). N-(aminobutyl)-N-(ethylisoluminol) (ABEI), luminol and isoluminol were obtained from Sigma-Aldrich (USA). All other reagents were of analytical grade. Ultrapure water was prepared by a Milli-Q system (Millipore, France) and used throughout.

Preparation of ABEI-CCG: To prepare ABEI-CCG, 5 mL (2 mg mL⁻¹) of aqueous ABEI alkaline solution (2 mg mL⁻¹ KOH) were added to 5 mL (0.2 mg mL⁻¹) of exfoliated GO suspension. After ultrasonication for 30 minutes, the mixture was vigorously stirred at 80 °C for 24 h. A homogeneous black dispersion was obtained. The dialysis procedure was used to remove free ABEI and coexisting free molecules from ABEI-CCG dispersion, so that true information about the surface of the graphene composites could be obtained by instrumental characterization. A 3500 molecular weight cutoff dialysis membrane was used, and ultrapure water was refreshed about six times under stirring until no absorption was observed in the UV-visible spectrum of the dialyzed-out solution. A typical dialysis operation needed about 2 days, and finally the dialyzed ABEI-CCG dispersion was obtained.

Characterization: UV-vis spectra were collected using a UV-Vis spectrophotometer (Agilent 8453, USA). AFM images were acquired in tapping mode in air using a DI Innova-Veeco instrument (USA). The samples used for AFM studies were prepared by depositing the corresponding dispersions on new cleaved mica

surfaces. XRD was carried out in a model D/max-rA diffractometer (Rigaku, Japan). XPS was carried on an ESCALABMK II electron spectrograph (VG Scientific, UK) with Al KR radiation as the X-ray source. The FTIR experiments were carried out on a Bruker Vector-22 FTIR spectrometer (Bruker Instruments, Billerica, MA) in a KBr pellet, scanning from 4000 to 400 cm^{-1} at room temperature. Raman spectra were acquired on a LabRamHR confocal Raman microspectrometer (Horiba Jobin Yvon, Edison, NJ, USA). The CL was detected by a microplate luminometer (Centro LB 960, Berthold, Germany). In a typical experiment, 100 μL of ABEI-CCG dispersion was pipetted into each well of microtiter plate, and then 50 μL of 0.1 mol L^{-1} H_2O_2 solution containing 0.1mol L^{-1} NaOH (pH=13) was injected into each well successively. The light emission was measured by the microplate luminometer.

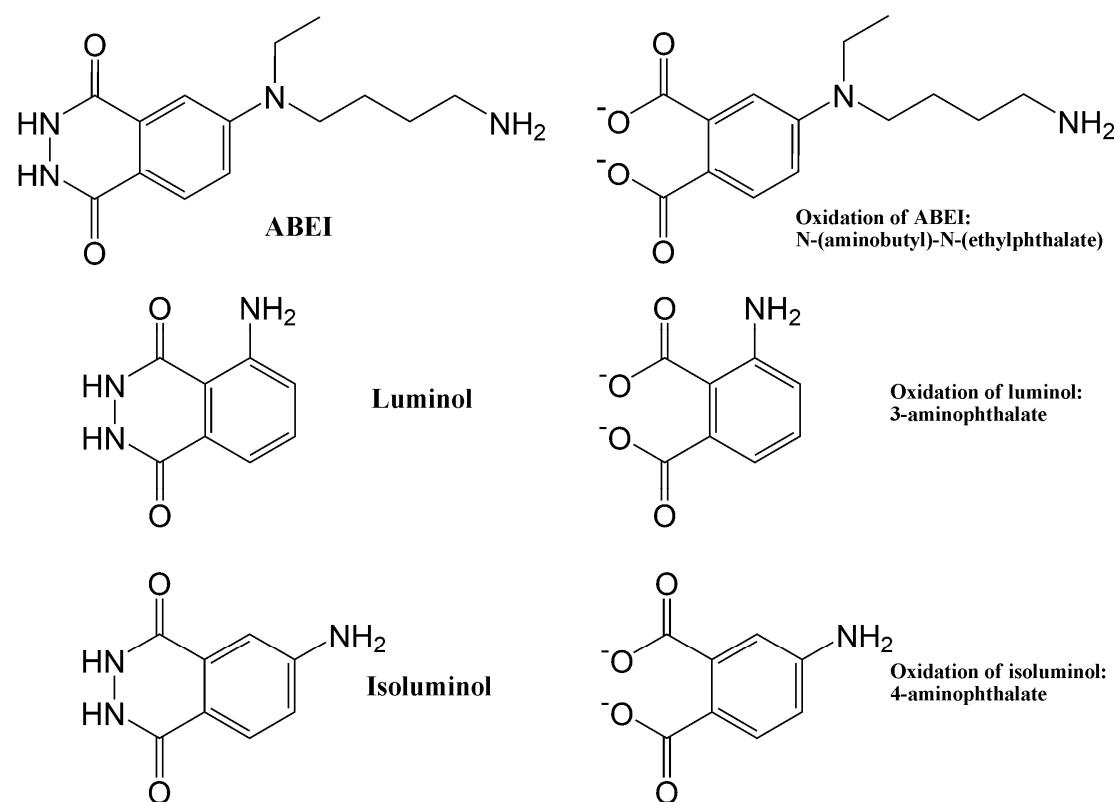


Figure S1. Molecular formulae of ABEI, luminol, isoluminol and their oxidation products.

X-ray Photoelectron Spectroscopic (XPS) Spectra of GO, u-CCG, and ABEI-CCG

XPS was performed to confirm the reduction of GO and to characterize the surface state of ABEI-CCG. Figure S2 shows that the oxygen content in exfoliated GO decreased remarkably after the reduction, i.e., 24.7% in ABEI-CCG versus 36.9% in GO. Moreover, the oxygen content in u-CCG is 28.7%, which indicates a higher reduction degree in the ABEI-reduced graphene nanosheets. Meanwhile, compared with GO, the survey of ABEI-CCG showed the presence of N1s originating from ABEI, indicating that the noncovalent functionalization of graphene by ABEI successfully occurred. The XPS study clearly reveals that ABEI-CCG has a better deoxidation efficiency than u-CCG, and as-prepared ABEI-CCG hybrid nanosheets were protected by ABEI molecules.

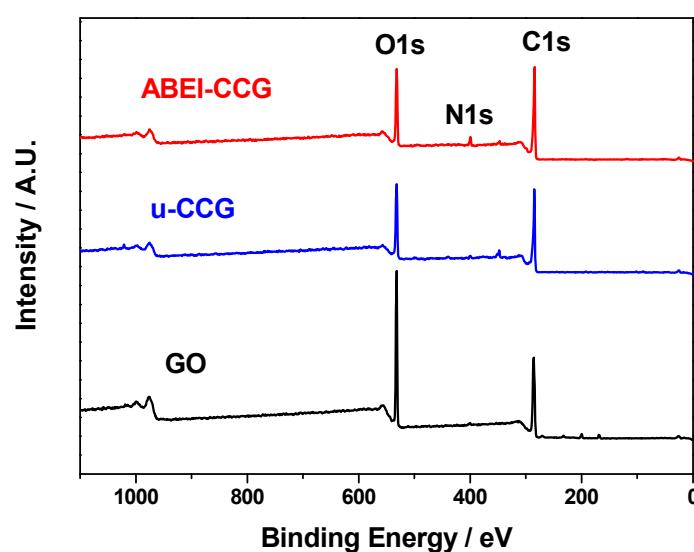


Figure S2. Survey XPS spectra of GO, u-CCG, ABEI-CCG.

Raman spectra of GO, u-CCG and ABEI-CCG

Raman spectroscopy is an efficient tool to characterize graphene-based materials. Herein it is used to monitor the structural changes occurring during the synthesis of ABEI-CCG from GO. The Raman spectrum of GO shows two peaks, centered at 1600 and 1349 cm^{-1} , which can be attributed to G and D bands, respectively. Similarly, the ABEI-CCG and u-CCG also contains both G and D bands with a higher D/G intensity ratio as compared with that of GO, and the D/G intensity ratio of ABEI-CCG is higher than that of u-CCG. The Raman spectral results agree well with those reported by Stankovich and Xu,^{1,2} indicating that the GO has been well deoxygenated in ABEI-CCG, and the efficiency of deoxygenation of ABEI-CCG is higher than that of u-CCG.

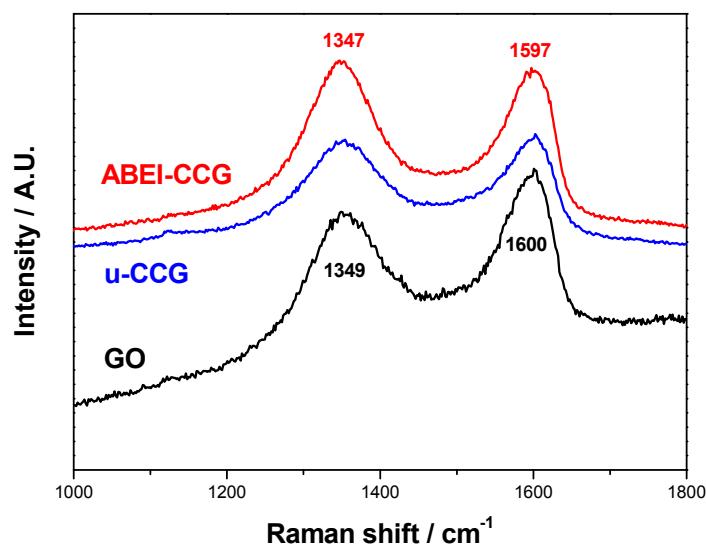


Figure S3. Raman spectra of GO, u-CCG, and ABEI-CCG.

XRD Patterns of GO and ABEI-CCG

The crystal structure of ABEI-CCG was examined by XRD. The feature diffraction peak of exfoliated GO at 10.6° (001) is observed with interlayer space (d -spacing) of 0.76 nm.³ For the resulting ABEI-CCG, the disappearance of the peak at 10.6° after the reduction process indicates the great reduction of GO and the exfoliation of the layered ABEI-CCG.⁴

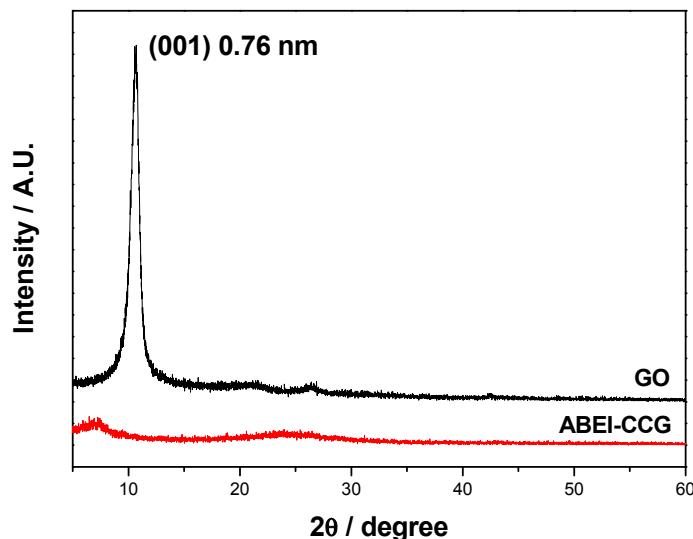


Figure S4. XRD patterns of GO and ABEI-CCG.

FT-IR Spectrum of GO and ABEI-CCG

The FT-IR spectra of GO (Figure S5) shows a strong absorption band at 1730 cm^{-1} due to the C=O stretching. The spectrum of GO also exhibits the presence of O-H ($\nu_{\text{O-H}}$ at 3412 and 1410 cm^{-1}), C=C ($\nu_{\text{C=C}}$ at 1625 cm^{-1}), and C-O ($\nu_{\text{C-O}}$ at 1073 cm^{-1}).⁵ As shown in Figure S5, after the GO is chemically reduced, the characteristic

absorption bands of oxide groups ($\nu_{\text{O-H}}$, $\nu_{\text{C=O}}$, and $\nu_{\text{C-O}}$) decreased dramatically, suggesting the considerable deoxygenation by the chemical reduction process. The stretching band of the amide C–N peak appears at 1254 cm^{-1} .⁶ And the peak at 833 cm^{-1} can be assigned to C–N vibrations.⁷ These results clearly indicate that the existence of ABEI molecules on the new graphene composites.

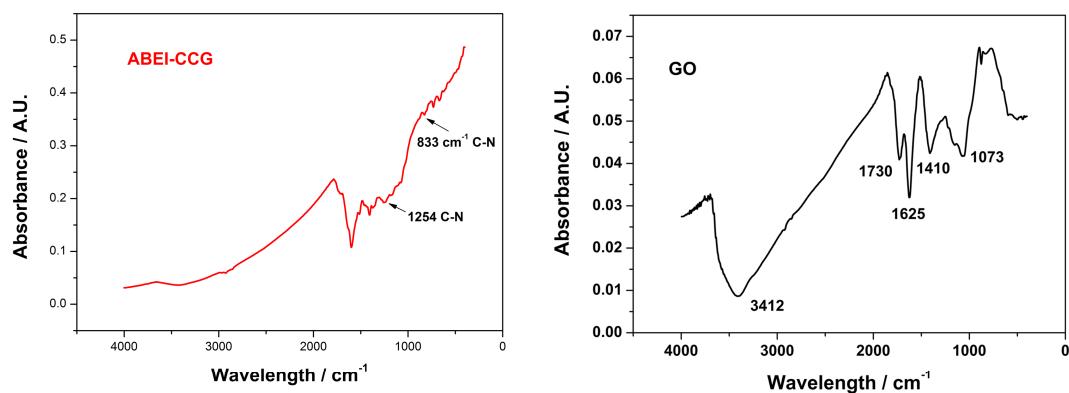


Figure S5. FT-IR spectrum of the GO and ABEI-CCG.

AFM images of GO, u-CCG and ABEI-CCG

As shown in Figure S6, AFM images provide detailed information on the π -interactions between graphene sheets and ABEI molecules at the solid state. The cross-sectional view of the typical AFM image of a single-layer exfoliated GO (Fig. S6a) indicates that the average thickness of GO sheets is about 0.76 nm, being consistent with the interlayer spacing of GO (0.76 nm) measured by XRD (Fig. S4) and the characteristic value reported in the literature.⁸ An average thickness of u-CCG

around 1.0 nm is observed (Fig. S6b), which is in agreement with the result reported by Li and coworkers.⁹ The mean thickness of ABEI-CCG is determined to be about 1.6 nm (Fig. S6c). There is 0.6-nm increment compared with that of u-CCG, owing to the presence of ABEI on the graphene sheet surfaces. If we assume that monolayered ABEI molecules may cover both sides of graphene sheet via π - π interactions, the estimated thickness of ABEI layer on graphene is calculated to be about 0.3 nm. This data is consistent with the thickness of a single ABEI molecule calculated by Chemdraw (0.25 nm). Accordingly, we can expect that these sheets are uniformly graphene monolayers. Furthermore, from points E to F in Figure S6c, the height of the sample shows two stages with similar increment of 1.6 nm, corresponding to one and two layers of ABEI-CCG sheets, respectively. The result confirms successful noncovalent functionalization of graphene with ABEI via π - π interactions.

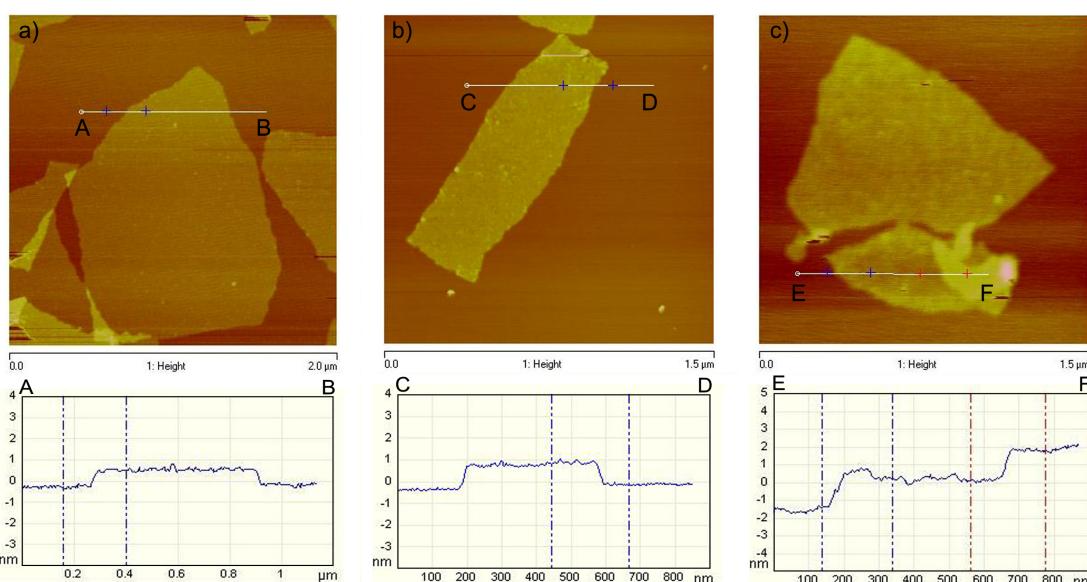


Fig. S6 Tapping mode AFM images and cross-section graphs of a) exfoliated GO, b) u-CCG and c) ABEI-CCG dispersion dip-coated on mica.

UV-vis spectroscopy of GO, pure ABEI and ABEI-CCG

The GO dispersion displays a maximum absorption at 231 nm (Fig. S7a), which is due to the $\pi-\pi^*$ transition of aromatic C=C bonds, and a shoulder at ca. 290-300 nm corresponding to the n- π^* transition of the C=O bond.¹⁰ The characteristic absorption peaks of ABEI solution appear around at 290 nm and 320 nm (Fig. S7b), respectively.¹¹ After the reduction of GO to ABEI-CCG, the absorption peaks at 231 nm red-shift to about 245 nm (Fig. S7c), corresponding to deoxygenation of GO under the reduction processes.¹⁰ Meanwhile, the dual peak of ABEI is also observed for the ABEI-CCG dispersion, which strongly supports that ABEI molecules are attached to the surface of the as-prepared graphene composites.

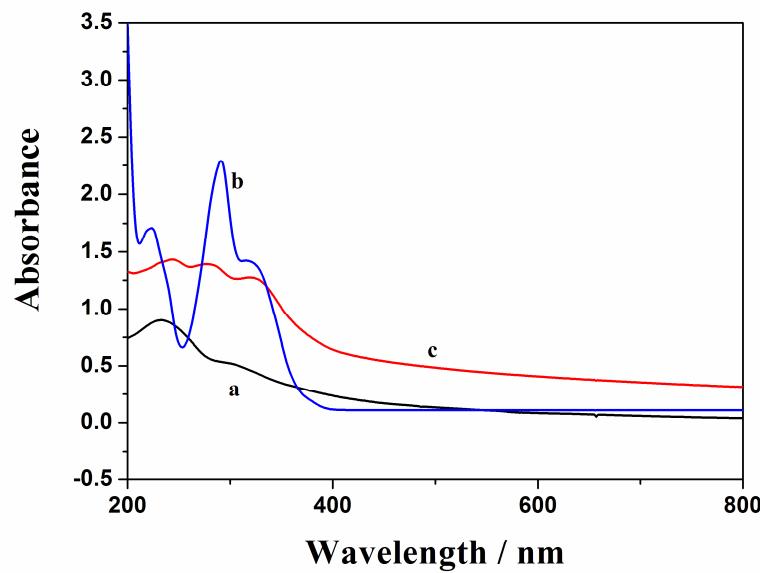


Figure S7. UV-visible absorption spectra of a) exfoliated GO suspension, b) pure ABEI solution and c) ABEI-CCG dispersion.

CL quenching ability of graphene

The CL quenching ability of graphene was evaluated via CL measurements of ABEI in the presence of graphene. As shown in Fig. S8, the CL emission of ABEI in the presence of graphene (a) is scarcely quenched compared with that in the absence of graphene (b). The integral of CL intensity within 3 seconds shows that only 0.6% of the total CL intensity is quenched by the addition of graphene. The ultra-low quenching efficiency indicates that graphene has little quenching ability on ABEI CL system.

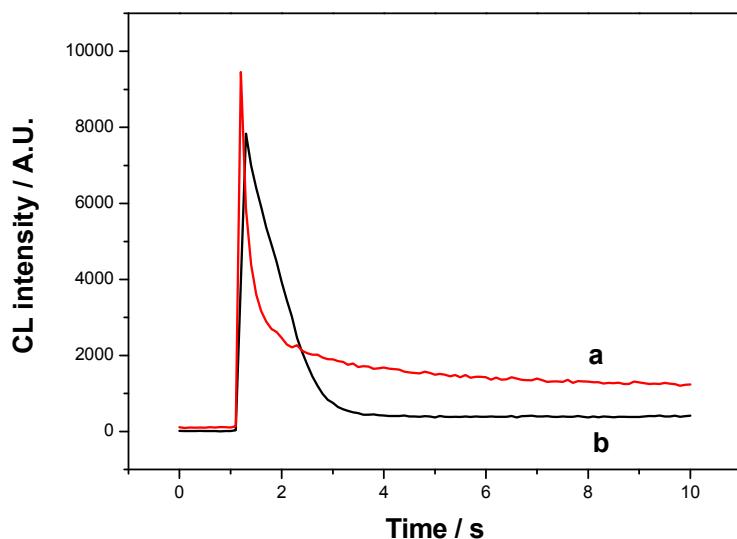


Figure S8. CL kinetic curves of 10^{-5} mol L⁻¹ ABEI solution in the presence (a) and absence (b) of graphene.

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