CARBON 82 (2015) 24–30

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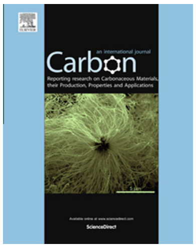

Photoluminescence quenching of graphene oxide by metal ions in aqueous media

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ARTICLE INFO

Article history:
Received 9 July 2014
Accepted 9 October 2014
Available online 16 October 2014

ABSTRACT

The photoluminescence (PL) quenching of water-soluble graphene oxide (GO) solution was systematically investigated in the presence of transition metal ions. Their PL spectra were analyzed by the Stern–Volmer equation, and the trend of the quenching efficiency was $Fe^{2+} > Co^{2+} > Ni^{2+} > Cd^{2+} > Hg^{2+}$. The results of the steady-state and time-resolved PL spectra of the GO solution suggested that the PL quenching was related to the new non-radiative optical transitions from the bridging states due to the hybridization of the sp^3 orbitals of GO and the 3d orbitals of metal ions, proven by density functional theory calculations. The overall results indicated that the bridging states from the hybridization of GO sp^3 and *unfilled* 3d orbitals (Fe^{2+}) in comparison with *filled* 3d orbitals (Hg^{2+}) were highly localized, and their energy levels were more suitable for being non-radiative transition states.

1. Introduction

Recently, two-dimensional (2D) solid nanostructures with unique photoluminescence (PL) properties including graphene, graphene oxide (GO), and metal chalcogenides have been extensively explored [1–4]. Studies of the origins of PL have generated great interest to further develop potential applications based on these 2D nanostructures. In particular, GO containing a variety of oxygen functional groups [4,5] exhibits interesting steady-state PL characteristics. For example, low-energy fluorescence in the red to near-infrared (NIR) region from 600 to 1100 nm for suspensions and solid thin films of as-synthesized GO has been demonstrated [6,7]. In addition, broad luminescence between 400 and 800 nm from oxygen plasma-treated single-layer graphene sheets has been reported [8]. Blue fluorescence with relatively narrow bandwidth when excited with ultraviolet (UV) irradiation has been observed from chemically reduced GO (rGO) or graphene quantum dots [9–11]. Recently, a unique tunable PL of GO was demonstrated as a result of changing the heterogeneous electronic structure of GO with variable sp^2 and sp^3 hybridizations through reduction [5].

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http://dx.doi.org/10.1016/j.carbon.2014.10.017

In comparison to layered inorganic metal chalcopyrite semiconductors (MoS_2, $MoSe_2$, etc.), GO has higher solubility in water, stronger mechanical strength, and easier chemical modification. Several chemical-sensing devices for the detection of aromatic hydrocarbon molecules have been demonstrated based on the blue shift of GO PL while the chemical molecules are absorbed or bonded on the GO surface [6–9]. These specific characteristics of GO have provided great advantages in the development of new types of sensing platforms that, in particular, can detect target molecules in the water solution directly [10,12].

In addition to modification of GO by N-doping [13,14], adsorbing molecules and metal ions can also result in interesting PL of GO or rGO. For example, the PL characteristics of Mn^{2+}-bonded rGO were reported and enhanced PL emission was obtained by enhancing the long-wavelength (450–550 nm) emission [15], as a result of the resonant energy transfer between the Mn^{2+} and sp^2 clusters of the rGO. By contrast, the PL quenching of GO was also reported while GO was modified by the Ag nanoparticles for detecting different biological species such as DNA, peptide, and protein [16]. In addition, GO as a highly effective quencher was also reported with the PL of metal ions, polymers, dyes, and quantum dots [17–21]. However, the quenching mechanism is still unclear. In this study, we would like to demonstrate the PL quenching behaviors of GO solutions when different transition metal ions are added. The PL quenching efficiency of the GO solution with Fe^{2+}, Co^{2+}, Ni^{2+}, Cd^{2+}, and Hg^{2+} ions added at different concentrations was compared and fitted by a dynamic Stern–Volmer model. Steady-state and time-resolved PL spectroscopy was performed to investigate the optical transition properties of GO solution with added metal ions. Furthermore, the first-principles calculations based on the density functional theory (DFT) were used to explain the possible PL quenching mechanism of GO modified with different metal ions. The overall results demonstrated that the GO with strong PL quenching characteristics could be potentially utilized as a sensor for the detection of transition metal ions.

2. Experimental

2.1. *The synthesis of GO solution*

GO solution was prepared by the Hummers method with some modifications [22,23]. Raw graphite (2.5 g) was mixed with 1.5 g of $NaNO_3$ (purity 99%) and 67.5 mL of H_2SO_4 (purity 96%). The mixture was stirred while being cooled in an ice water bath. $KMnO_4$ (9 g, purity 99%) was gradually added within an hour. The mixture was cooled in an ice bath for 2 h and then allowed to stand for 5 days at approximately 20 °C with gentle stirring. In order to wash out the excess reactant, 1 L of 5 wt% H_2SO_4 aqueous solution was added to the resultant mixture and stirred for 2 h. Afterward, 30 g of H_2O_2 (30 wt% aqueous solution) was added to reduce the excess $KMnO_4$. Manganese ions from the oxidant were facilitated by repeat wash with an aqueous solution of 3 wt% H_2SO_4/0.5 wt% H_2O_2 for the removal of ions. Deionized (DI) water was added to the final product and then vortexed well to make a uniform suspension for storage.

2.2. *Characterizations*

High-resolution transmission electron microscopy (HR-TEM) images were obtained using a Philips Technai G2 (FEI-TEM) microscope operating at 200 kV. The atomic force microscope (AFM) images were obtained using scanning probe microscopy (Innova, Veeco Inc., Germany) in tapping mode with a Si tip (resonance frequency: 75 kHz; spring constant: 4 N m^{1}) at a scanning rate of 0.5 Hz. Fourier transform infrared spectroscopy (FTIR) and the UV–visible (vis) absorption spectra of samples were obtained using ThermoNicolet NEXUS470 and JascoV-570 UV/vis/NIR spectrometers, respectively. XPS spectra were obtained using a VG Scientific ESCALAB 250 system. A 405-nm continuous-wave (CW) laser was used as an excitation source for PL measurements. In time-resolved photoluminescence (TRPL) measurement, the excitation source was a 372-nm pulsed diode laser (LDH-P-C-372B, PicoQuant, Germany) operating at 20 MHz. All metal salts were dissolved in 0.5 M sulfuric acid. The fluorescence of the samples after light dispersing by the triple-grating monochromator was directed into the single-photon avalanche diode (SPAD), which was connected to a time-correlated single photon counting (TCSPC) module (PicoHarp 300, PicoQuant) to obtain the PL decay curves. Isothermal titration calorimetry (ITC) experiments were obtained using a VP-ITC Micro Calorimeter.

2.3. *DFT simulation*

The Gaussian 03 package was applied for DFT calculation. The electronic structures were established based on GO nanoclusters containing 54 carbon atoms bonded with two transition metal ions, Hg^{2+} and Fe^{2+}. All oxygen atoms were placed at the bridge sites to form an epoxy structure. The edges of the GO nanocluster were passivated by hydrogen atoms, ensuring that all carbon atoms were sp^3 hybridized. Metal ions were placed at the hollow sites of GO nanoclusters. PBE1PBE functional and LanL2DZ basis sets were used in the geometry optimizations. Suitable settings of spins and charges were introduced. The models were fully optimized and the absorption sites of metal cations in the GO sheet were already tested. The tested sites are the hollow site, the bridge site, and the atop site, which are the most considered sites in dealing with the surface absorption. Although energy differences are very small between cases, the model with the hollow-site metal cation is energetically favorable among all. The possible reason is that the number of neighboring oxygen atoms (i.e., electron-rich functional groups in GO) of the metal cation is three for the hollow site, two for the bridge site, and 1 for the atop site. The lower system energy of the hollow-site model may result from the higher number of neighboring oxygen atoms.

3. Results and discussion

3.1. *The characterization of GO solution*

GO solution was prepared by the Hummers method with some modifications. The resulting GO was dissolved in DI water with brown color. The structural characterization of