Producing Photoluminescent Species from Sp2 Carbons

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The treatment of sp2 carbon materials, including micrographite, nanographite, HOPG, onion-like-carbon, and single-walled carbon nanotubes, in a 3:1 sulfuric to nitric acid mixture produced photoluminescent reaction solutions. These colloidal, aqueous solutions appeared photoluminescently stable under a UV lamp and ranged in color from red to blue. The photoluminescent wavelength shifted to shorter wavelength with increasing reaction time or increasing reaction temperature. Raman spectroscopy showed evidence of defect structures in graphitic residue, and transmission electron microscopy showed unusual structures present in the supernatant including graphitic balls.

Keywords Graphite, oxidation, exfoliation, photoluminescence

Introduction

Bright, photoluminescent nanoparticles have long been sought for biological labeling. While photoluminescence from quantum dots and metallic nanoparticles span the visible wavelength range, they are not ideal for diagnostic applications because of their potential cytotoxicity. Other photoluminescent nanoparticles, such as nanodiamonds and carbon dots, are being used as alternatives for biological imaging modalities. The production of carbon dots, graphene, and other graphitic-type nanoparticles are largely based upon traditional chemical approaches by Hummers, Brodie, and Staudenmeier (1,2). With a similar methodology, we report that a sulfuric/nitric acid mixture produces colloid stable, photoluminescent supernatant solutions in a range of colors from the oxidation products of sp2 carbons. It was reported in 1930 that a range of colors and fluorescence resulted from the solid oxidation product of graphite (3), and since this time most studies have concentrated on this solid residue (4–6). However, the notable graphite oxidation study by Lu et al. reported a range of photoluminescent colors arising from the product supernatant solution, using ionic liquids in an electrochemical oxidation method from highly oriented pyrolytic graphite (HOPG) (7). We report that photoluminescent nanocarbon-based solutions can be prepared from various sp2 carbon particles, including micrographite (MG), nanographite (NG), HOPG, single-walled carbon nanotubes (SWCNTs), and onion-like-carbon (OLC). Intercalation and exfoliation of graphitic carbon is most likely responsible for the production of nanoparticle-based supernatant structures that photoluminescence, while likely

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candidate species include graphite oxide (3), graphene oxide (8), graphene quantum dots (9), and nanoribbon structures (7).

**Experimental**

MG, NG, HOPG, OLC, and SWCNTs were refluxed in a 3:1 volumetric ratio of 95–98% sulfuric acid and 68% nitric acid. The acid mixture and solid residue were separated by centrifugation. The supernatants were placed in glass vials and illuminated by a hand-held UV lamp with an emission wavelength of 365 nm. Photoluminescent samples were photographed using a Cannon Lumix DMC-ZS1 camera. Fluorescence spectra were taken with a SPEX Fluorog 322 T-format spectrofluorometer located at the UNC Macromolecular Interactions Facility, UNC-Chapel Hill (Chapel Hill, N.C., USA). High resolution transmission electron microscopy was performed on a FEI Titan aberration-corrected microscope operated at 80 kV (EMAT, University of Antwerp, Antwerp, Belgium). For Raman spectroscopy, the residue was washed with water until the supernatant reached a value of pH 5. The residue was dried overnight under vacuum at 50°C. Raman spectra were taken using a Horiba Jobin Yvon LabRam ARAMIS confocal microscope at the Shared Materials Instrumentation Facility at Duke University (Durham, N.C., USA).

**Results and Discussion**

The acid mixture (3:1 sulfuric acid to nitric acid) to oxidize graphitic carbon materials is useful for: 1) purifying nanodiamonds from sp2 carbon (10), 2) functionalizing carbon nanotubes with carboxylic functionalities (11), and 3) shortening carbon nanotubes (12). This acid mixture has also been used for making graphite intercalation compounds (4–6). The mechanism of degradation of graphitic carbon is well understood and involves a concerted progression of intercalation, dilation, and exfoliation.

The efficiency of oxidizing graphitic carbon for the acid mixture is dependent upon the ratio of sulfuric acid to nitric acid, as shown in the following reaction,

$$24nC + 3H_2SO_4 + HNO_3 = C^{+}_{24n}HSO_4^- \cdot 2H_2SO_4 + H_2O + NO_2$$

where n is the stage index or the degree of expansion of the graphitic planes (4). For the ratio of 3:1 sulfuric to nitric acid, the expansion of the graphitic planes is at its largest, Stage 1, and thus is most easily oxidized (13). Interestingly, it is possible to visualize the stage index of the graphitic carbon by observing the color of the graphitic material in the presence of the intercalation compounds at room temperature (13). When the acid mixture is added to sp2 carbon materials at room temperature, such as HOPG, MG, NG, and carbon fibers, the color of the graphitic carbon changed from grey to blue, as seen in Figure 1A for HOPG. It is also possible to visualize the dilation of graphitic planes of HOPG in the 3:1 mixture as compared to the non-expanded HOPG block of the same size in the presence of nitric acid alone. The mechanism of graphite oxidation is caused by intercalation of these acids (see Figure 1B). Intercalation causes dilation of the graphitic planes, which then leads to exfoliation at the graphitic carbon edges as well as the formation of microcracks and dislocations of the graphitic planes. Eventually, the graphitic carbon breaks down into nanoparticles. At room temperature, intercalation can occur, but the exfoliation process is slow. Thus, these reactions were performed under refluxing conditions.
Figure 1. Photographs of HOPG in a solution of 3:1 sulfuric to nitric acid solution and in nitric acid alone at room temperature (A) and the proposed mechanism of oxidation to produce photoluminescent supernatants (B) (color figure available online).

When the graphitic carbon and acid mixture are treated under refluxing conditions, the graphitic carbon becomes oxidized to produce a brown-colored supernatant solution; this solution is composed of oxidized nanoparticles and is photoluminescent. The emission wavelength is broad spanning from the UV to red wavelengths. As can be seen under UV illumination, the photoluminescent emission color is dependent upon the reaction temperature. Lower temperatures result in emission spectra of longer wavelengths, while higher temperature leads to shorter emission wavelengths as observed by UV illumination. As an example, the reaction supernatants of micrographite that were treated at three different temperatures are shown in Figure 2. These brown supernatants show that the lowest temperature produces a dark red photoluminescence emission, while the highest temperature produces a suspension that has a light orange emission under UV light. These suspensions were diluted in water and have the same blue wavelength shift as the reaction temperature increased. Surprisingly, as was typical of these product solutions, the highest reaction temperature changed color from yellow to green upon dilution in water. In addition, it was found that short oxidation reaction times produced photoluminescent colors at long wavelengths, while longer oxidation times produced photoluminescent colors that were blue-shifted. An example of this time dependent trend in photoluminescence color is seen for the reaction of OLC. The OLC material, prepared by annealing detonation nanodiamond at 1450 K, produced a graphitic sp² shells around a nanodiamond core. The OLC was oxidized with the acid mixture to produce an orange photoluminescent reaction solution after 20 minutes at 98°C (see Figure 3A). The mixture treated for a longer time (45 minutes) produced a green photoluminescent reaction solution (see Figure 3B). The green photoluminescent solution was not as prominent after overnight sedimentation, but recovered when redispersed by sonication. These sediment particles are most likely nanodiamonds from the OLC core. In another example, SWCNTs treated in the acid mixture for 30 minutes produced yellow photoluminescence, while after 60 minutes there was no visible photoluminescence color. It also appeared that the photoluminescence was stable under low intensity UV lamp illumination.

Since varying degrees of oxidation of nanocarbon products are found within a reaction mixture, it is possible to separate the nanoparticles as a function of size. The separation of nanoparticles by size produced a similar color change from longer to shorter photoluminescent wavelengths as seen for larger to smaller particle filtrate sizes, respectively. For example, the yellow supernatant solution (see Figure 4A) produced from
Figure 2. Photographs of the wavelength shift for increasing reaction temperature of the micrographite reaction supernatants treated with the acid mixture for 120 minutes. The reaction solutions were diluted in water. Photos were taken with white light (top) and with UV illumination (bottom) (color figure available online).

Figure 3. A photograph of the reaction solutions after the acid mixture treatment of OLC after 20 minutes (A) and 45 minutes (B), as seen under a UV lamp (color figure available online).
Figure 4. Photoluminescence emission spectra taken of the reaction product of nanographite (A) before and after filtering the solution through a 1,000 MW cut-off filter (B). The inset shows that the starting solution is yellow and that the filtered solution is blue when excited with UV light (color figure available online).

The oxidation of nanographite was filtered using a size exclusion filter of 1,000 molecular weight. This filtrate containing smaller carbon particles showed a strong blue photoluminescence (see Figure 4B), which agrees with the photoluminescence emission spectra also shown in this figure.

A comparison of the reaction product residues of HOPG, micrographite, and nanographite to their untreated form was completed by Raman spectroscopy (see Figure 5). The as-received HOPG sample contains a prominent narrow peak at 1580 cm\(^{-1}\) (G band) (Figure 5A), corresponding to graphitic in-plane vibrations with E\(_{2g}\) symmetry. MG and NG samples contain two prominent peaks (Figure 5B, C), located at about 1360 cm\(^{-1}\) (D band) and 1580 cm\(^{-1}\), as well as an additional weak shoulder at about 1610 cm\(^{-1}\) (D’ band). D and D’ bands originate from lattice defects and disorder. As can be seen from Figure 5, the acid treatment of all three samples caused an increase in intensity of the D band and especially the D’ band, which is consistent with the large amount of defects generated during acid treatment.

Transmission electron microscopy of yellow and green photoluminescent solutions produced from graphite oxidation showed that carbon-based particles in the supernatant are composed of spherical onions, graphitic balls, and ribbons (see Figure 6). The yellow photoluminescent solution (see Figure 6A) consisted on average of larger sized particles as compared to the green photoluminescent solution (see Figure 6B). Thus, the yellow supernatant is on average made up of larger particles compared to the green suspension. This observation follows the correlation that longer reaction times produce photoluminescence shifts to shorter wavelengths, which are likely caused by smaller carbon-based particles. Although the carbon particle environment changes over the reaction time with the loss of gaseous products, the dilution of the supernatant in the 3:1 sulfuric to nitric acid solution did not appreciably change the photoluminescence color. However, it was observed that the photoluminescence color is dependent upon the pH of the solution. Therefore, further studies are required to determine the mechanism of photoluminescence in these reaction suspensions.
Figure 5. Raman spectra for the starting materials HOPG, micrographite, and nanographite and the residue collected before and after acid treatment (color figure available online).
Figure 6. Transmission electron micrographs of supernatant solutions taken from the oxidation of graphite. Particle size measurements showed that the average particle size in the yellow solution with onions and graphitic ball structures was larger (~10–60 nm (A)) than the green photoluminescent solution (~5–40 nm (B)) containing onions, carbon spheres, and ribbons (color figure available online).

Conclusion
In this work, we found that the commonly used 3:1 sulfuric to nitric acid mixture produced photoluminescent supernatant solutions from the oxidation of a variety of sp² carbon materials. As the reaction temperature or reaction time increased, the photoluminescence of the supernatant solution changed from longer to shorter wavelengths. It was also found that the reaction with graphite yielded a yellow supernatant solution that could be filtered to extract a blue photoluminescent solution. Raman spectroscopy showed evidence of defect structures in the remaining carbon reaction products, and transmission electron microscopy showed unusual structures from the reaction supernatant solutions of graphite, including graphitic balls.

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