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Synthesis of graphene oxide nanosheets from pencil lead and in-situ synthesis of gold nanoparticles on graphene oxide nanosheets

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Abstract:

In this paper we report the synthesis of graphene oxide (GO) from pencil lead using modified Hummer's method and in-situ synthesis of gold nanoparticles (AuNPs) by bioreduction of $HAuCl_4$ by polyphenolic biomolecules present in young leaves of tea(Camellia Sinensis) extract in the presence of GO. The UV-Visible absorption spectrum of GO dispersion in water exhibits two bands at 228nm and a shoulder at ~300nm corresponding to π-π transitions of aromatic c-c bonds and n-π* transitions of C═O bonds. In photoluminescence (PL) study, GO dispersion in water shows emission band at 555nm, when excited at 325nm. When AuNPs were embedded in GO nanosheets the bands at 228nm and ~300nm of GO disappears and two new UV-Visible bands at 272nm for phenol and 539 nm for transverse surface plasmon resonance (SPR) of AuNPs appears. When AuNPs were embedded on GO nanosheets the PL emission band at 555nm disappears, two new PL emission bands appears at 431 and 658nm. The physical and morphological characterizations were performed by FTIR, XRD and HRTEM. Morphological study revealed that the GO nanosheets were well dispersed in water and AuNPs were embeddedon the GO nanosheets.*

***Keywords**: Graphene oxide, Gold nanoparticles, Camellia Sinensis, Surface plasmon resonance*

Introduction

Graphene is a two-dimentional single layer of carbon atom and one atom layer thick, honeycomb lattice of carbon sheet with interesting physical properties[1]. GO has been con- sidered as the building block of all graphitic structures (carbon nanotube, fullerene, graphite)[1,2,3,4]. All the form of graphitic structure exhibit interesting electrical properties. Currently, graphene, carbon nanotubes and metal nanoparticals has gained much attention and emerged to be an active research area in the field of biosensors, medicine, food quality control, catalytic activity can be greatly enhanced[5]. To improve the electrochemical performance, the direct in-situ deposition of AuNPs on large surface area of GO nanosheets is quite promising[2]. Furthermore, AuNPs embedded on GO nanosheets support can effectively prevent the aggregation of GO nanosheets caused by van der Waal interactions. As a result, the available surface area for energy storage, catalytic activity can be greately enhanced[2]. In this work we report the synthesis of GO from pencil lead using modified Hummer's method [4,6,7] and in-situ synthesis of AuNPs by bioreductions of $HAuCl_4$ by polyphenolic biomolecules present in young leaves of tea(Camellia Sinensis) extract in the presence of GO.

Experimental

Materials And Methods

Graphite pencil was collected from local market. Sulfuric acid (H_2SO_4, 98%), potassium permanganate ($KMnO_4$, 99%), hydrogen peroxide (H_2O_2, 30%) and Sodium nitrate ($NaNO_3$) were purchased from Merk. Gold(III) Chloride hydrate ($HAuCl_4$ xH_2O) 99.99% metal basis was obtained from Aldrich and used as such.

UV-Visible and photoluminescence spectroscopy measurements were carried out on UV-1800 Shimadzu UV spectrophotometer and Hitachi F-2500 fluorescence spectrophotometer respectively. The FTIR spectra were recorded using Affinity-I Shimadzu spectrophotometer. The TGA was carried out on TGA/ DSC 1 STAR system METTLER TOLEDO.

Preparation Of Tea Extract

Fresh young leaves and leaf buds of tea was collected from local tea garden of Assam, India. 20 gms. of fresh young leaves and leaf buds were washed several times with deionized water and then leaf was cut and grinded with a morter and a pastel. The finely grinded tea paste was transferred into a 100ml round bottom flask and then stirred with 50ml of deionized water at room temperature for 3 hours and then allowed to stay for 1 hour. The reddish brown color tea extract was decanted gently and filtered to remove the solid undissolved residues of tea leaves. This reddish brown color filtrate was used as reducing and stabilizing or capping agents for $HAuCl_4$[8].

Synthesis Of GO From Pencil Lead

GO was exfoliated from graphite pencil lead via modified Hummer's method[4,6]. In a typical synthesis, finely powdered graphite pencil lead (0.5gms) was added to 20 ml 98% H_2SO_4 (at 0^oC) and stirred with a magnetic stirrer for 2 hours. 0.5 gms. $NaNO_3$, 3 gms. $KMnO_4$ were added slowly to the mixture during the stirring process. Then the mixture was allowed to stir for 3 days at 35^oC on a water bath. To the well mixed slurry 140 ml deionized water , 3 ml H_2O_2 (30 %) were added and the mixture was heated at 90^oC for 1 hours with continuous stirring. The resulting suspended solution was precipitated for 12 hours and the supernatant was collected and centrifused at 10000 RPM for 10 minutes. The resulting GO solution was washed with 10% HCl and deionised water successively for 3-4 times using a centrifuged for 10000 RPM for 10 minutes. The brown color of GO was allowed to dry at room temperature and stored at room temperature. In this chemical oxidation process introduces oxygen containing functional groups such as carbonyl, hydroxyl, and peroxyl in between carbon layers of graphite. Upon insertion these functional groups between the inter carbon layers, sp^2 lattice is partially degraded into a sp^2-sp^3 sheet that possesses a less π-π stacking stability. As a result weakens the van der waals bonds between the carbon layers which cause the graphene layer to peel off layers from graphite [4,6].

In-Situ Synthesis Of Aunps On GO

1 ml GO suspension (0.05 gm./5 ml) deionized water), 0.05 ml aqueous $HAuCl_4$ solution were sonicated for 20 minutes. To the well-sonicated mixture of GO and $HAuCl_4$, 0.7 ml tea extract was added and the mixture was shaked well, and then allowed to stand for 30 minutes. Slow reduction of Au^{3+} to Au^o takes place as shown by stable light purple or brilliant red color of the mixture [8].

Results and discussions

UV-Visible spectra of GO and GO/AuNps

The UV-Visible spectra of aqueous GO exhibits two absorption bands that can be used as a means of identification: a maximum absorption band at 228nm corresponding to π-π* transitions of aromatic C=C bonds, and a shoulder at~300nm, which can be attributed to n-π* transitions of C=O bonds. When AuNPs were embedded into GO nanosheets, the 228 and ~300nm bands of

GO disappear and two new UV-Visible bands appear at 272nm (for polyphenols present in the tea extract) and 539nm (TSPR of AuNPs[8]). This spectral evidence shows that the AuNPs were embedded into GO nanosheets.

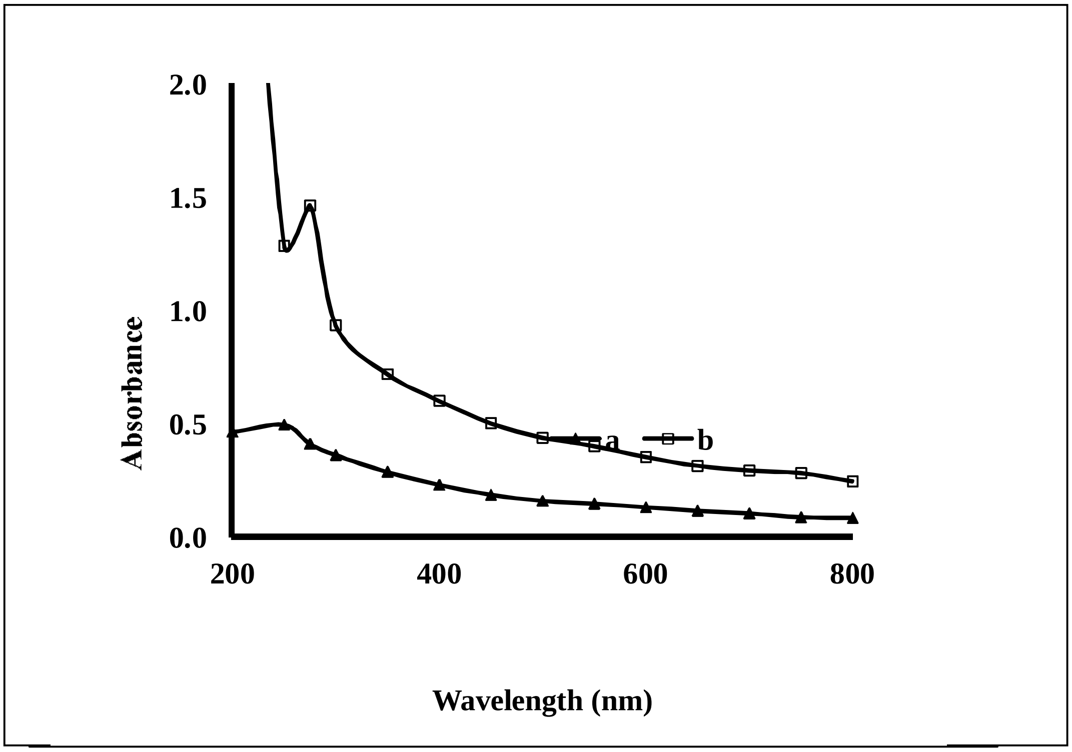


Figure 1: UV-Visible spectra of (a) GO , (b) GO/AuNPs

PL Spectra Of GO And GO/Aunps

In PL study, GO dispersion in water shows a emission band at 555nm, when excited at 325nm. This PL character of GO originates from the recombination of electron-hole (e-h) pairs, localized within small sp^2 carbon clusters embedded within an sp^3

matrix. When AuNPs embedded into GO nanosheets the PL emission band at 555nm disappears, two new PL emission bands appear at 431 and 658 nm for embedded AuNPs on GO nanosheets. These emission bands are due to the local field enhancement via coupling to the TSPR and LSPR[8].

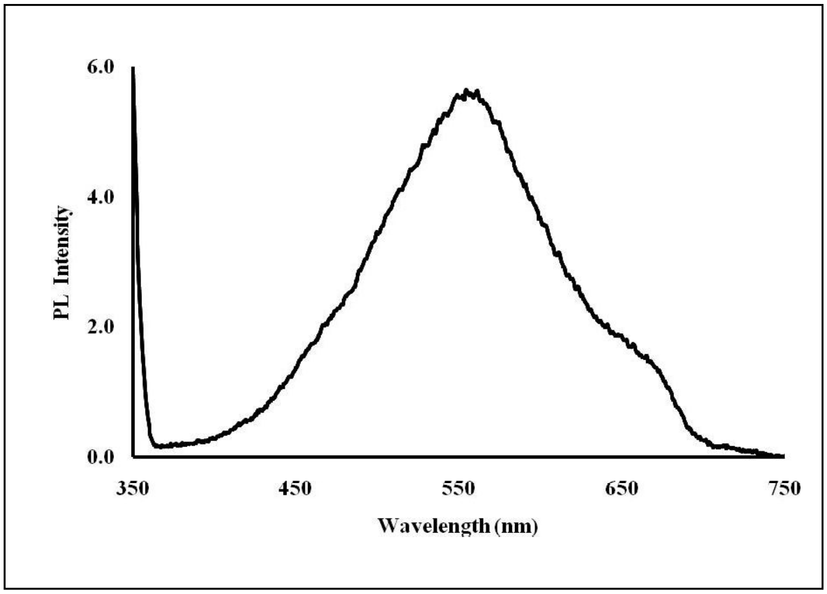


Figure 2(a) : PL spectra of GO

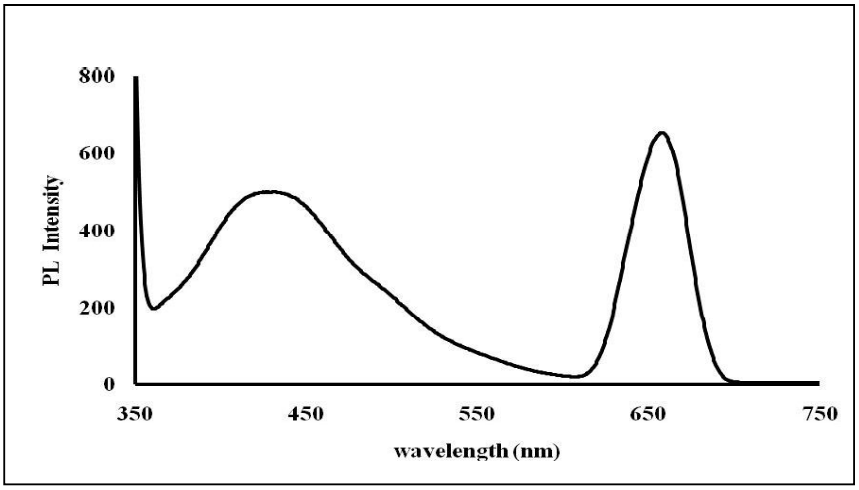


Figure 2(b): PL spectra of GO/AuNPs

FTIR Spectra Of GO

The obtained GO was characterized by FTIR using ZnSe windows. For this purpose a thin film of GO was prepared by drop casting from aqueous GO dispersions. This film was formed by evaporation of the solvent at room temperature. FT-IR of GO exhibits the presence of C-OH stretching vibration (3444 cm^{-1}); C=O (carbonyl/carboxy 1736 cm^{-1}); C=C aromatic (1635 cm^{-1}); C-O-C epoxides (1290 and 883 cm^{-1}); alcoxy C-O (1053 cm^{-1}); C-O stretching vibrations (1188 cm^{-1}).

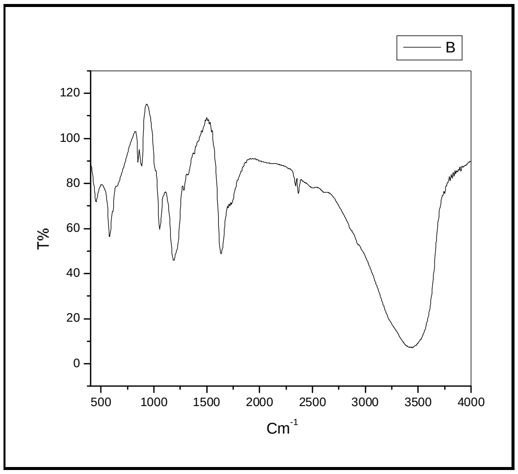


Figure 3: FT-IR of graphene oxide

Thermogravimetric Analysis

Figure 4 shows that the thermogravimetric plot of our GO. The first 21.71% mass loss (at 108°C) is due to water molecules adsorbed into the GO, the second 17.36% mass loss takes place for elimination of remaining labile oxygen functional groups, the third 8.74% (at 527.29°C) mass loss due to carbon combustion and further decomposition takes place up to 700°C.

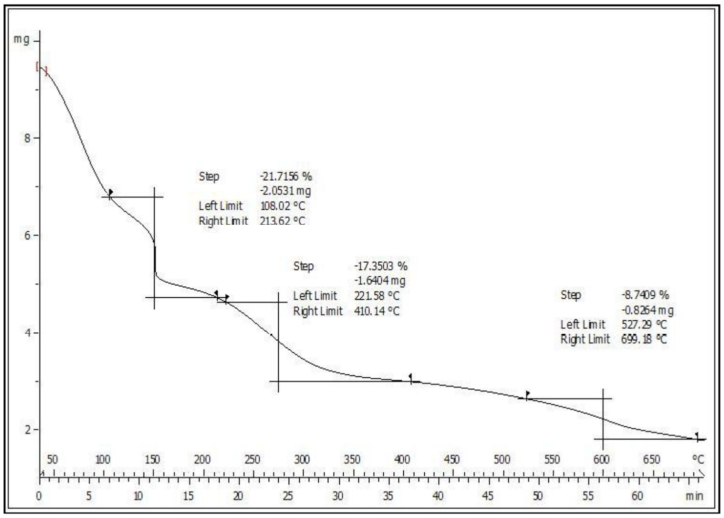


Figure 4: TGA Plot for graphene oxide

XRD Studies

XRD measurement of the GO dispersion drop-coated on to glass substrates were done on a Philips X' PERT PRO instrument operating at a voltage 40 KV and a current of 30 mA with CuKα radiation. In the XRD pattern of GO, the strong and sharp peak at $2\theta = 10.23^o$ corresponds to an interlayer distance of 0.80nm. This is in agreement with the previous studies of XRD pattern of GO **[4]**.

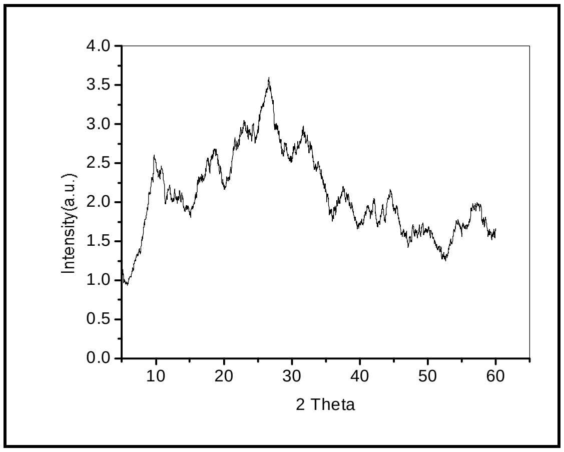
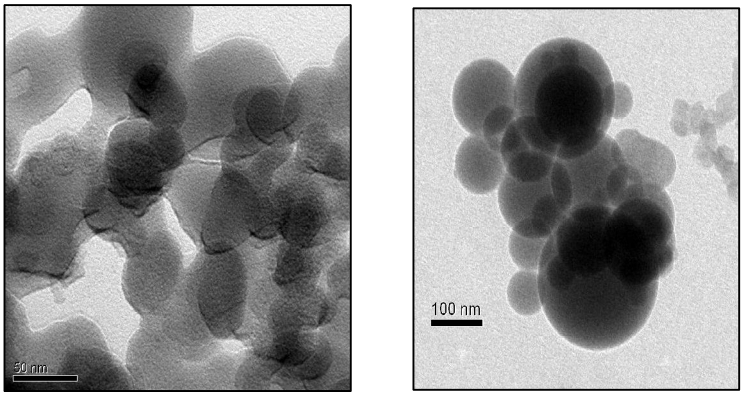


Figure 5: XRD of graphene oxide

HR- TEM Analysis

HR-TEM images were obtained by using TEM, JEM-2100, Jeol. The typical HR-TEM images obtained for GO nanosheets under different magnifications are shown in the Figure 6.



(a) (b)

Figure 6: HR-TEM images of GO under different magnifications
(a) 50nm, (b) 100 n

Conclusion

We had successfully synthesized GO nanosheets from pencil lead using Hummer's method. Also in-situ synthesized AuNPs into GO nanosheets using young leaves and leaf buds of tea extracts as bioreducing, stabilizing or capping agent. AuNPs synthesized by this method was well embedded into the GO nanosheets.

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