Stability of Graphene Oxide encapsulated Gold Nanorods for optical sensing purposes

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Stability of Graphene Oxide encapsulated Gold Nanorods for optical sensing purposes

Kasun Prabuddha Wasantha Dissanayake*[1], Rahul Kumar, Hien Nguyen, Weiping Wu, Tong Sun and Kenneth T.V. Grattan
School of Mathematics, Computer Science & Engineering, City, University of London, Northampton Square, London EC1V 0HB, UK

*E-mail: kasun.dissanayake@city.ac.uk

Abstract. This paper presents the synthesis and characterization of a graphene oxide encapsulated gold nanorod (GNR) complex, where its stability was investigated over time by recording the absorption spectra obtained using a UV/Visible spectrometer over the wavelength region of 200 nm to 1000 nm. Poly Ethylene Glycol (PEG) stablized GNRs were found to be more stable in the presence of graphene oxide dispersions compared to Cetyl Timethyl Ammonium Bromide (CTAB) stabilized GNRs. These GNR complexes, prepared with an active graphene oxide coating on the surface, are presented as a well-suited platform for the development of localized plasmon resonance-based fibre optic biosensors due to the surface functional groups of graphene oxide that can form bio-composites with other biological nanomaterials.

1. Introduction

Gold nanorods (GNRs) have attracted significant attention for use in various fields of science due to their unique optical properties and their ability to surface functionalize with various types of biomolecules [1]. In particular, their longitudinal resonance peak is sensitive to the external refractive index and this characteristic has been exploited to develop localized plasmon resonance (LSPR)-based optical fibre sensors [2]. Cetyl Trimethyl Ammonium Bromide (CTAB) has been used in the seed-mediated method of synthesis of GNRs. However, this proves to be a problem when it comes to biomedical applications as CTAB is cytotoxic [3]. Therefore, researchers have explored the ways of removing CTAB from the final GNR complex. Replacing CTAB coating on GNRs with Poly Ethylene Glycol (PEG) is one of the effective approaches due to the biocompatibility of PEG [4].

Graphene oxide (GO) has emerged as a very interesting material across a wide range of research fields due to its two-dimensional structure, good biocompatibility, high sensitivity to various molecules and its ability to form bio-composites with many other bio-molecules and bio-structures [5].

Therefore, the study of GO encapsulated GNRs is very interesting and important due to their potential applications in many fields, such as biosensors, drug delivery and photothermal therapy [6]. In this research, a new method of synthesising GO encapsulated GNRs is presented and the stability of GO encapsulated GNR complexes is discussed. As this research progresses, these GO encapsulated GNRs are coated on optical fibres to develop LSPR-based fibre optic biosensors.

[1] To whom any correspondence should be addressed.

2. Experimental methods

2.1. Synthesis of GNR

GNRs were synthesized by using the seed mediated method reported by Jie Cao et al. [2]. In brief, the seed solution was prepared by mixing 5 mL of 0.2 M CTAB solution with 5 mL of 0.5 mM $HAuCl_4.3H_2O$ solution, with vigorous stirring, followed by the addition of 600 µL of 0.01 M ice-cold $NaBH_4$ to the stirred solution. After two further minutes, the seed solution was left undisturbed for 3 hours.

The growth solution was prepared by adding 330 µL of 0.02M $AgNO_3$ solution, 30 mL of 0.2 M CTAB solution and 30 mL of 0.001M $HAuCl_4.3H_2O$ in the same sequence. To the mixed solution, 420 µL of 0.0788M ascorbic acid solution was added, with stirring. In the final step to synthesize the GNRs, 100 µL of seed solution was added into the growth solution and the resulting solution was left undisturbed for 12 hours. All the above steps were performed in a water bath maintained at a constant temperature of 28 °C.

The excess of CTAB present in the GNR solution was removed by using two rounds of centrifugation at 8000 rpm for 20 min for each round. After each round, the supernatant was carefully decanted and the GNRs deposited at the bottom of the centrifuge tube were re-suspended and dispersed in an equal volume of DI water.

To prepare the PEG functionalized sample, 3 mL of the above GNR was added to 300 µL of 2mM K_2CO_3. Then, 30 µL of 1mM PEG solution was added and the mixture was left overnight undisturbed. The solution was centrifuged twice at 8000 rpm for 20 minutes for each round. After each round, the supernatant was decanted and GNRs were re-dispersed in equal quantity of DI water.

2.2. Synthesis of GO

An improved Hummer's method [7] was applied to synthesize the GO used in this work. In this approach, graphite flakes (500 mg) and $NaNO_3$ (500 mg) first were mixed with concentrated H_2SO_4 (22.5 mL) in an ice bath for 4 hours. Following that, 3 g of $KMnO_4$ was added very slowly to the mixture, before adding 46 mL of DI water and stirring for another 1 hour in the same ice bath. The mixture then was stirred again for 2 hours at 35 °C and afterwards kept in a reflux system at 98 °C for 10-15 minutes, following which the temperature was changed to 30 °C to obtain a brown coloured solution. The mixture was again stirred for 2 hours at room temperature. Afterwards, 13.3 mL of 30% H_2O_2 was added very slowly (due to high rate of reaction) and the mixture turned to a very bright yellow colour. Following that, 100 mL of DI water was added to the prepared solution and it was stirred for another 1 hour at room temperature. The mixture was then kept for 24 hours, without stirring, until the particles were seen to settle at the bottom of the vessel. Then, water was filtered out using a paper filter and the resulting mixture was washed repeatedly by sonication and centrifugation with 10% HCl and DI water several times until a gel-like substance was formed. The resultant gel-like substance was vacuum-dried for 8 hours to create the GO dry powder.

2.3. Synthesis of GO PEG-GNR complex

1 mL of PEG-stabilized GNR solution was dropped into 3 mL 0.5 mg/mL GO solution (to synthesis 1:3 GO PEG-GNR complex) with a continuous stirring. After stirring for 1 hour, the solution was centrifuged at 8000 rpm and the precipitates were collected and re-dispersed with 10 mL of DI water to create the GO encapsulated PEG-GNR colloidal solution.

3. Results and Analysis

Figure 1(a) illustrates the UV/Vis absorption spectra of GO, PEG-GNR and two different GO PEG-GNR complexes (1:1 and 1:3 ratios of GO and PEG-GNR solutions). All these absorption measurements were recorded using a LAMBDA 35 UV/Vis spectrometer (Perkin Elmer Inc.) monitoring over the wavelength range from 200 nm to 1000 nm, in steps of 1 nm. As is evident from figure 1(b), which presents a zoomed version of figure 1(a) to illustrate the GNR absorption peaks, the

GNRs exhibit two plasmon bands. The absorption peak at around 520 nm corresponds to the transverse resonance (oscillation of free electrons along the width of the GNRs) and the other absorption peak at around 660 nm peak corresponds to the longitudinal resonance (oscillation of free electrons along length of the GNRs), which is tunable over the range from the visible to the near-infrared. This longitudinal resonance band is also tunable with the aspect ratio of the GNRs and is more sensitive to the surrounding refractive index change. This unique optical characteristic of GNRs is useful to develop very efficient GNR based LSPR sensors in a wide range of fields.

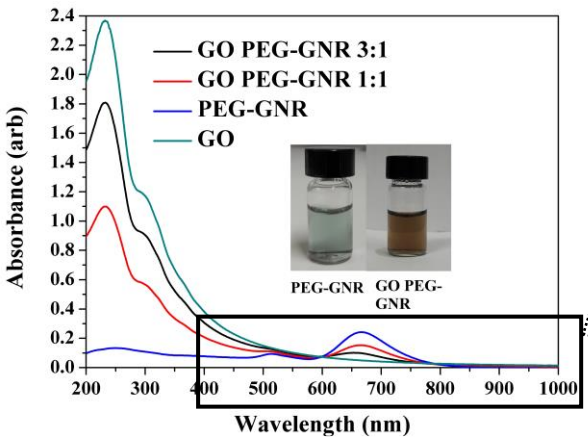

Figure 1(a) UV/Vis absorption spectra of GO, PEG-GNR and GO PEG-GNR

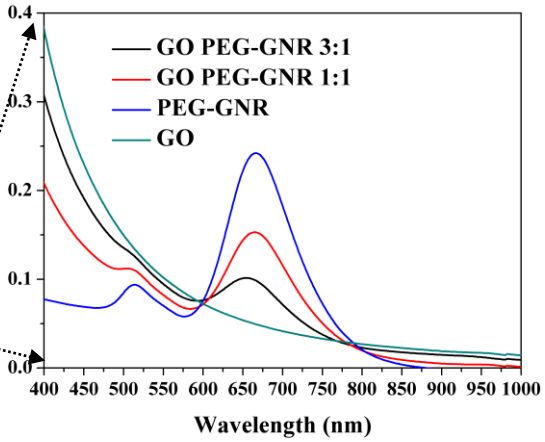

Figure 1(b) GNR absorption peak at around 660 nm for different GNR complexes

When it comes to GO, as it is evident from the green curve in figure 1(a), the most prominent absorption peak can be observed at around 230 nm, which corresponds to the π-π* transitions of the aromatic C=C bond and a shoulder at about 300 nm (ascribed to π-π* transition of C=O bonds). From the intensity of the 230 nm peak, the amount of single layered GO sheets present in the aqueous dispersion can be directly calculated. The more intense peak at 230 nm indicated that the GO dispersion contained single layer and few layer GO flakes, but not multi- and thick-layer GO flakes.

The UV/Vis absorption spectra of GO encapsulated PEG-GNRs exhibit few variations compared to pure GO and pure PEG-GNR absorption spectra. The intensity of the GO absorption peak at 230 nm and the GNR resonance peak at 660nm were observed to be weaker in GO encapsulated PEG-GNR dispersions. This is due to the decrease of concentrations of pristine GO and GNR in GO encapsulated PEG-GNR dispersions compared to the pure GO or PEG-GNR dispersions. The most important characteristic that can be seen in figure 1(b) is the longitudinal resonance peak of GO encapsulated PEG-GNRs. This peak at around 660nm is observed to undergo a blue shift with increasing PEG-GNR concentration of GO encapsulated PEG-GNR dispersions and this indicates that GO has been successfully coated on PEG-GNRs. Moreover, the prepared GO encapsulated PEG-GNR dispersion was monitored and found to be stable over time.

Before performing the PEG coating on CTAB-GNRs, an experiment was conducted to coat GO on CTAB-GNRs. 1 mL of CTAB-GNR dispersion was mixed with 3 mL of GO solution. As soon as these two solutions were mixed, immediate coalescence of nanoparticles occurred. The picture in the inset of figure 2 shows this agglomeration phenomenon. A UV/Vis spectrum of this mixture was recorded, as shown in figure 2. The absorption peak of GO (which previously was observed at 230nm) and the CTAB-GNR resonance peak observed at 680nm, both seemed to disappear and this further confirmed the coalescence of CTAB stabilized GNRs in the presence of the GO solution.

As a result, based on these experimental results obtained, it was confirmed that PEG stabilized GNR was much more stable in the presence of GO compared to CTAB stabilized GNR, when observed over time. Having a GO layer on GNRs provides the opportunity to develop a wide range of biosensors, with high selectivity. They have potential applications in many fields, including cancer

therapy, as has been discussed by Turcheniuk et al. [8]. Many biomolecules and biomaterials have the ability to form bioconjugate complexes with GO sheets and these new GO-based bio-complexes can be used to make efficient biosensors with enhanced sensitivity. The research is progressing and the next step is creating GO hybrided PEG-GNR on optical fibres, to investigate their properties as a new LSPR-based optical fibre biosensors.

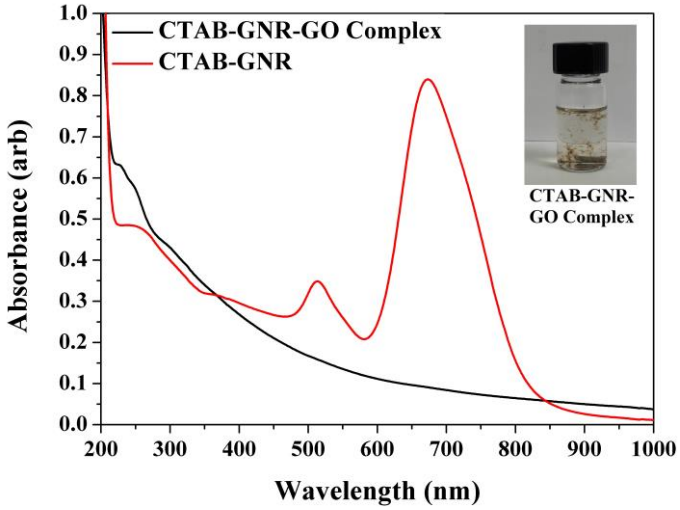

Figure 2 UV/Vis spectrum of CTAB-GNR-GO complex

4. Conclusion

Two different types of GNRs (CTAB and PEG) functionalized by GO were synthesized successfully to make colloidal solutions. Following that, GO and GNR dispersions were mixed with each other to coat GO on the surfaces of GNRs. PEG stabilized GNRs were found to be more stable in the presence of GO, compared to CTAB stabilized GNRs. GO was successfully functionalized on PEG-GNRs and the dispersion was found to be stable over time. The promise of the results obtained can be exploited in the future direction of this research, to coat GO encapsulated GNRs on optical fibres, to develop LSPR-based fibre optical biosensors.

References

[1] Huang X, Neretina S, El-Sayed M A 2009 *Adv. Materials* **21** pp 4880-4910
[2] Cao J *et al Sens. Actuator B-Chem* 2013 **181** pp 611-619
[3] Liao H and Hafner J H *Chem. Mater* 2005 **17.18** pp 4636-4641
[4] Lau I P *et al Nanotoxicology* 2011**6:8** pp 847-856
[5] Soleimani K *et al Ecotoxicol Environ. Saf.* 2018 **147** pp 34-42
[6] Wei Q *et al RSC Adv.* 2015 **5** pp 54971-54977
[7] Paulchamy B *et al* A simple approach to stepwise synthesis of graphene oxide nanomaterial *J Nanomed Nanotechnol* 2015 **6: 253**
[8] Turcheniuk *et al RSC Adv.* 2016 **6** 1600