



IC-FNM 2016

Adsorption of Dyes on nanocolloidal gold surfaces: The key towards understanding the mechanism of SERS.

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Abstract

The adsorptive parameters of biologically significant Methylene Blue (MB) and Malachite Green (MG) dye molecules adsorbed on gold nanocolloidal particles of varied sizes have been reported with the aid of fluorescence spectroscopy study. Fluorescence spectroscopic studies have been further applied to estimate the concentration of probe molecules actually adsorbed on gold nanocolloidal particles surface. The effects of graphene oxide (GO) on the adsorptive parameters of MG molecule are also been estimated.

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Selection and/or Peer-review under responsibility of International Conference on Functional Nano-Materials, 2016.

Keywords: Fluorescence Spectroscopy; Absorption Spectroscopy; Adsorptive parameters; Gold nanocolloids.

1. Introduction

Surface Enhanced Raman Scattering (SERS) is characterized by large enhancement of Raman signals from molecules at trace concentrations down to single molecule detection limit [1]. It is a highly efficient spectroscopic technique to understand the adsorptive behaviours of probe molecules with the nanostructured surfaces [2]. The exact mechanism behind the phenomenon is still unknown, albeit, it is generally believed that a long range electromagnetic (EM) and a short range charge transfer (CT) mechanisms are simultaneously operative [3, 4]. Since, the accidental discovery of SERS, gold and silver nanocolloids are established as proven SERS active substrates for recording the vibrational signatures of wide range of organic molecules at ultrasensitive concentrations. The

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enhancement factor (EF) of Raman bands of probe molecules are estimated by comparing the intensities of SER bands at trace concentrations with that from the corresponding normal Raman spectrum (NRS) of the bulk. However, the estimations of such EFs are only apparent as the concentrations of the probe molecules in the system and the concentration of the molecules actually adsorbed on the nanostructured surfaces are not explicitly considered. Estimations of proper enhancement factors are not only essential for correct representations of signal amplifications, but also they steer towards understanding the basic physics behind the phenomenon.

Considering the above concerns in mind, here we report the adsorptive behaviours of dyes [ca. Methylene Blue (MB) and Malachite Green (MG)] with gold nanocolloidal particles of varied sizes with the aid of fluorescence spectroscopic technique. The variations of the adsorptive parameters with the size of the nano colloids are also reported herewith.

Nomenclature

MB	Methylene Blue
MG	Malachite Green
AuNC	Gold Nanocolloid
GO	Graphene Oxide

2. Experimental Procedure

The MB and MG molecules of spectroscopic grade were purchased from Sisco Research Laboratory, India and were used without further purification. Four different sets of gold nanocolloids AuNC(I), AuNC(II), AuNC(III), and AuNC(IV) of mean particle diameters ~ 16, 32, 55, and 73 nm respectively were prepared by citrate reduction method [5, 6]. Briefly, in a typical preparation, an aliquot of 50 mL aqueous solution of HAuCl₄ (0.25 M) was heated up to boiling and 1000, 625, 400 and 300 μ L trisodium citrate (1%) were added into it under vigorous stirring resulting in the synthesis of four sets of gold nanocolloids AuNC(I), AuNC(II), AuNC(III), and AuNC(IV) respectively. Graphene oxide (GO) was prepared by exfoliation of graphite flakes by Hummers method [7]. Briefly, 1 g of graphite and 0.5 g of NaNO₃ were mixed with 23 mL of concentrated H₂SO₄ (98 %) with gentle stirring in an ice water bath for 2 h. Then 3 g of KMnO₄ was added and the mixture was allowed to stir for 12 h. After stirring, the mixture was slowly transferred into a flask containing 20 mL H₂O₂ (35%) solution. The resulting solution was washed several times with HCl and water and GO was obtained. All the required solutions were prepared with deionized water from Milli-Q-plus system of Millipore Corporation, USA. The fluorescence spectra of the samples were recorded using a JASCO Spectrofluorimeter (Model: 8200). All the spectra reported in the figures are original raw data directly transferred from the instrument and processed using Microcal Origin version 7.0.

3. Results and Discussions

Adsorptive parameters of MB and MG molecules adsorbed on AuNCs

The fundamental issue concerning the concentration of probe MB and MG dye molecules actually adsorbed in the gold nanocolloids has been addressed with the aid of fluorescence spectroscopic technique. Appropriate amounts of MB molecules were mixed with the *as prepared* gold nanocolloids AuNC (II, III, IV) systems so that the final ligand–nanocolloidal mixtures attain the desired concentrations. The mixtures were then incubated for several hours. The supernatants were obtained after repetitive centrifugation and the fluorescence spectra of each of the *as obtained* supernatant solutions were recorded. They are shown in Fig. 1. The fluorescence spectra from the supernatant solutions are thus expected to exhibit emission from the MB molecules which are not adsorbed on the

nanocolloidal surfaces. The concentration $[\Gamma]$ of the probe molecules actually adsorbed on the nano particle surfaces, has been estimated using the following relation [8]:

$$[\Gamma] = [C] - C_{dis} \frac{I_{fl,NA}}{I_{fl,dis}} \quad (1)$$

where $[C_{dis}]$ and $[C]$ are the concentration of free and adsorbed molecules on the nano surface respectively. $I_{fl,NA}$ is the fluorescence intensity maximum of the supernatant solution and $I_{fl,dis}$ is the fluorescence intensity maximum of the ligand molecule in reference solutions.

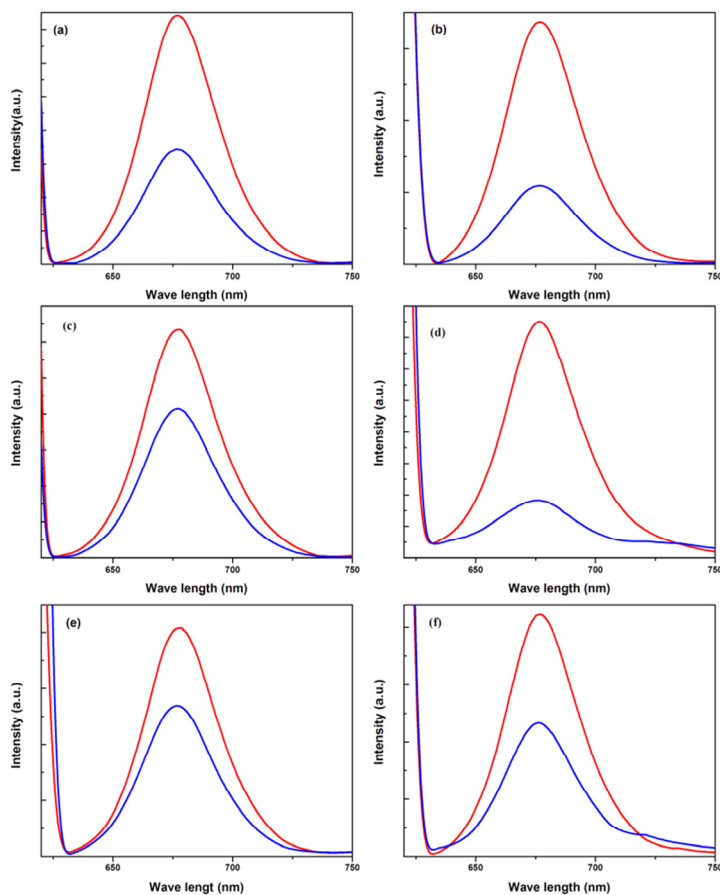


Fig.1: Fluorescence spectra of freshly prepared MB molecule (Red Line) and that of the supernatant solutions (Blue line) for AuNC(II) at: (a) 1.0×10^{-6} M, (b) 7.0×10^{-7} M; AuNC(III) (c) 1.0×10^{-6} M, (d) 7.0×10^{-7} M; AuNC(IV) (e) 1.0×10^{-6} M, (f) 7.0×10^{-7} M concentrations ($\lambda_{ex} = 612.0$ nm).

The concentrations $[\Gamma]$ so obtained are used to plot $[C]/[\Gamma]$ vs $[C]$ graph, as shown in Fig. 2. The plot exhibits a linear fit obeying the Langmuir adsorption equation [9]:

$$\frac{C}{\Gamma} = \frac{1}{K\Gamma_{max}} + \frac{C}{\Gamma_{max}} \quad (2)$$

where K is the adsorption coefficient and $[\Gamma_{max}]$ is the saturated or monolayer concentration of the ligand molecule

on nanocolloidal surface. Determination of K allows the estimation of the adsorption free energy (ΔG_{ads}) using the following relation [10]:

$$K = \exp\left(\frac{-\Delta G_{\text{ads}}}{RT}\right) \quad (3)$$

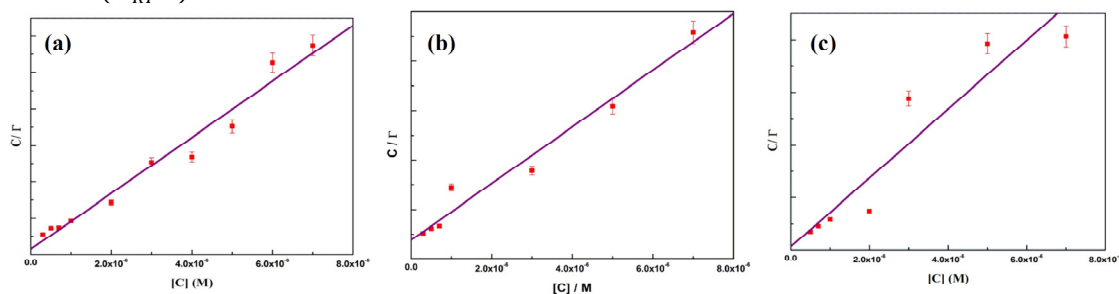


Fig. 2: C/Γ versus $[C]$ plot for (a) AuNC (II), (b) AuNC(III), (c) AuNC(IV) systems.

The adsorptive parameters of MB on AuNC(II/III/IV) systems are shown in Table 1. Table 1 shows the estimated values of Γ_{max} and ΔG_{ads} of MB molecule adsorbed on AuNC(II, III, IV) system. The appreciable values of adsorption free energies (ΔG_{ads}) signify the possibility of charge transfer (CT) interaction of the probe molecules with the nanocolloidal surfaces. The CT contribution to SERS is indeed reported to be appreciable for the MB molecule as reported elsewhere [11].

Table 1: Adsorptive parameters of AuNC-MB system

AuNC-MB System	Γ_{max} in M	ΔG_{ad} in k J/M
AuNC(II)-MB	6.5×10^{-7}	-38.67
AuNC(III)-MB	6.8×10^{-7}	-36.06
AuNC(IV)-MB	3.05×10^{-7}	-40.25

The adsorptive parameters of MG molecules on AuNC(I) and AuNC(II) surfaces have been estimated. It has been found that MG adsorbed on AuNC I and II surfaces at the monolayer coverage concentrations $\sim 9.8 \times 10^{-5}$ M and 3.5×10^{-5} M respectively. Free energies of adsorption (ΔG_{ads}) for MG-AuNC(I) and MG-AuNC(II) systems are estimated to be ~ 22.58 and 24.06 kJ/M respectively, which signify the possibility of CT contribution to SERS. The effects of GO on the adsorptive parameters of MG have also been investigated. The estimation of adsorptive parameters of MG on AuNC(II)-GO systems (dispersion of 2.5 mg GO in Milli-Q water) shows monolayer surface coverage concentration $\sim 5 \times 10^{-5}$ M and free energy of adsorption ~ 22 kJ/M. The effect of adsorptive parameters of MG molecule with the increase in concentration of GO on AuNC(II) is in progress.

4. Conclusion

The adsorptive behaviours of industrially and biologically significant MB and MG dye molecules adsorbed on AuNCs of varied sizes have been investigated with the aid of fluorescence spectroscopic studies. The free energy of adsorption and monolayer surface coverage has been estimated from Langmuir type adsorption curve. The estimated concentration of monolayer surface coverage and free energy of adsorption does not show appreciable change in values with the size of the nanocolloids. The appreciable values of adsorption free energies signify the possibility of CT interaction of the probe molecules with the nanocolloidal surfaces.

Acknowledgements

The authors like to thank DAE-BRNS for the financial support to carry out the research work through the research projects (Project No. 2012/37 P/27/BRNS).

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