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HIGH CONCENTRATION DEPENDENT COLORIMETRIC SENSOR FOR SURFACTANTS

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ABSTRACT

Surfactants are an area of interest in many of the environmental-related industries and pharmaceutical industries. Among the various surfactants, sodium dodecyl sulfate (SDS) has gained much attention for its effective dirt removal potential and is thus utilized in toothpaste, shampoo, and detergents. The supramolecular assembly of brilliant green over graphene oxide functioned as sensor for SDS with high selectivity. Furthermore, this sensor displayed exceptional sensitivity for SDS of having higher concentrations, (> 10^{-2} M SDS). Indeed, several of the commercial products used higher concentrations of SDS in their products and thus this sensor would be useful for the detection of higher concentrations of SDS and it will complement the other sensors developed for SDS.

Keywords: Surfactants, supramolecular assembly, Brilliant Green, Sensor, Graphene Oxide.

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INTRODUCTION

Surfactants are compounds that are amphiphilic in nature and they are capable of functioning for the removal of oil and dirt; thus, the utility of these molecules has been dramatically increased since the discovery of surfactants. The utilization of surfactants is enormous and recently polymeric surfactants for various applications have been explored.[1] Sensors for surfactants have been dramatically increased as the utilization of the surfactants has been increased in many industries including pharmaceutical, chemical, food, biochemical, electroplating, and many other industries. Sensors for all types of surfactants have been frequently developed. Sensors that work for anionic may not work for the cationic and the development of sensors for non-ionic surfactants is very scarce.[2] We have recently developed a graphene oxide bound rhodamine B as a sensor material for the detection of surfactants of anionic, cationic, and for non-ionic, and among them, we have also shown the selectivity for the anionic surfactant.[3] SDS (sodium dodecyl sulfate) is a good example of an anionic surfactant, that has been widely utilized in cleaning and hygiene products. SDS has been detected by several methods including the UV-visible method using methylene blue and ethyl violet,[4-7] which are convenient compared to other methods and other methods such as ion-selective electrode method,[8,9] separation-based techniques such as Gas chromatography,[10,11] HPLC,[12-15] and capillary electrophoresis,[16,17] are very sensitive methods. Several synthetic receptors (sensors)[18,19] have been explored for the detection of anionic surfactants. However, we have developed a very selective sensor for the SDS, with the help of the supramolecular assembly of a dye over graphene oxide for the visible recognition of SDS. Furthermore, rhodamine B tethered graphene oxide has been utilized in fluorescence sensors of cucurbit[7]uril, among the cucurbituril homologs.[2] In continuation, we have tested the assembly of the graphene oxide- brilliant green supramolecular assembly for the detection of surfactants. Unlike the previous studies of graphene oxide-rhodamine B supramolecular assembly, which detected both the ionic and non-ionic surfactants, the graphene oxide-brilliant green (GBG) supramolecular assembly helped to detect the anionic surfactants more selectively. Surprisingly, GBG displayed excellent selectivity as it worked only for the anionic surfactants such as SDS and it could sense

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only the SDS of having the higher concentrations, which is a rare phenomenon among similar sensors. For the on-spot detection of SDS surfactant, GBG would be very handy as it does not require any instrument and is conveniently performed by the naked eye detection. Overall, we have developed a visual sensor for the detection of anionic surfactants, using GBG with the detection of the limit of 5×10^{-3} M. GBG also displayed excellent selectivity towards the anionic surfactants.

EXPERIMENTAL

Material and Methods

Chemicals such as Brilliant Green and SDS, sulphuric acid, and hydrogen peroxide were purchased from Avra Synthesis Private Ltd and graphene oxide was synthesized using graphite, which was purchased from Otto Chemie Pvt Ltd, India. Analytical-grade chemicals were utilized. For the UV-visible measurement, Ocean Optics, USA (Model: USB-2000) was used.

Synthesis of Brilliant Green Anchored Graphene Oxide (GBG)

Synthetic procedure for graphene oxide can be obtained from our previous study,[20] In 100 mL of water, 200 mg of graphene oxide has been dissolved through sonication for a long duration; from which suspended particles have been eliminated by Whatman filter paper. To this solution, 100 mg of brilliant green dye was added and subsequently, 500 µl of diluted hydrazine hydrate was introduced. This solution was left for 3 days in the dark. It formed plenty of precipitates, which were collected by centrifugation, and the unbound dye in the water layer was discarded and continuously washed with water and ether until it showed no more color of the brilliant green. To the final precipitate, water (10 mL) was added and used in sensor studies.

Selectivity and Sensitivity of GBG towards SDS

We prepared the stock solutions of SDS, cetyl trimethyl ammonium bromide (CTAB), and TritonX100 (TX100) in the range of 1×10^{-1} M, 1×10^{-2} M, and 1×10^{-3} M for the analysis. For the testing, 100 µL of GBG and 1mL of the surfactant were added and mixed thoroughly.

Detection Method

We have used the UV-visible spectrophotometer for the detection of surfactant sensitivity using the quartz cuvette at room temperature. For the visual detection of surfactants, we have used no instrumentation.

RESULTS AND DISCUSSION

Our previous method of detection of surfactants using the graphene oxide-rhodamine B supramolecular assembly[2] intrigued us to investigate the utilization of brilliant green dye for the visual detection method for the surfactants. Among the various dyes that we examined, brilliant green produced an excellent supramolecular assembly with no release of dye with water.[20] Thus, this supramolecular assembly of GBG has been previously examined for the sensing of cucurbit[7]uril.[20] We anticipated that GBG has the potential to release the dyes upon interaction with the surfactants and thus we envisaged to develop a visual detection method for the surfactants using GBG. While working with the graphene oxide-rhodamine B, we found that this supramolecular assembly failed to show any selectivity among the anionic, cationic, or non-ionic surfactants. Thus, we anticipated that the GBG would display a similar behavior as that of graphene oxide-rhodamine B with surfactants with no selectivity. Surprisingly, GBG responded only to anionic surfactants and failed to respond to cationic and non-ionic surfactants.

Selectivity of GBG Towards Anionic Surfactants

Initially, we attempted GBG with ionic (cationic and anionic) and non-ionic surfactants with 10^{-3} M concentrations and obtained no release of dye. Upon trial and error, we noticed that the higher concentrations of surfactants that are above 10^{-2} M interacted with the GBG and released the dye. As shown below, GBG displayed the release of Brilliant Green only with concentrations above 10^{-2} M. Furthermore, no surfactants have responded, except the anionic surfactants such as SDS. In general, 100 µL of GBG and 1 mL of the surfactant were mixed together, and the release of brilliant green can be monitored by the visual detection method. The sensor GBG showed a good response to the SDS (anionic) surfactant, while other surfactants such as CTAB (cationic and Triton X-100 (non-ionic) did not respond

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to the GBG, due to the strong binding affinity of brilliant green towards the graphene oxide. Unexpectedly, it showed less sensitivity towards the anionic surfactants as shown in Fig.-2. that the solutions above the concentrations of 10^{-2} M GBG displayed the release of dye. Thus, GBG can be used for the detection of anionic surfactants of higher concentrations with good selectivity.

Fig.-1: Supramolecular Assembly of Graphene Oxide – Brilliant Green Displayed Good Selectivity Towards the Anionic Surfactants

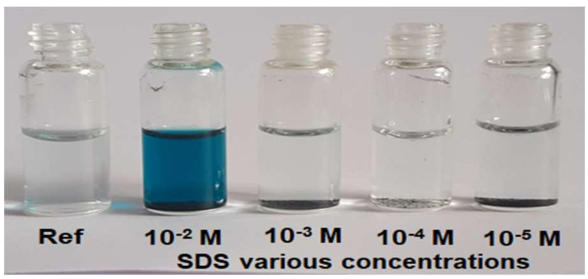

Fig.-2: Supramolecular Assembly of Graphene Oxide – Brilliant Green Displayed Moderate Sensitivity Towards the Anionic Surfactants

Furthermore, the UV-visible spectrophotometer studies also supported the sensitivity of the GBG toward the anionic surfactants as shown in Fig.-3.

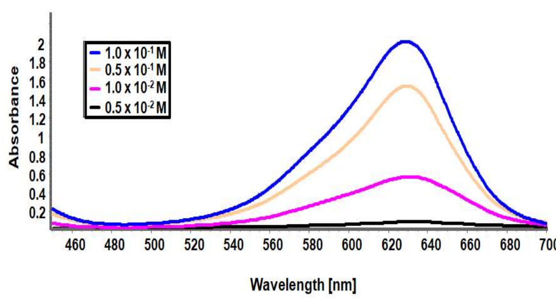

Fig.-3: UV-Visible Spectroscopy Studies of Anionic Surfactants (SDS) Sensitivity Studies Using the Supramolecular Assembly of GBG

The sensor, GBG has displayed good detection potential for anionic surfactant with good selectivity. Surprisingly, it displayed exceptional selectivity towards the anionic surfactants having only higher concentrations. It is a very rare example and it could be helpful for the detection of higher concentrations of surfactants that have been released from industries because higher concentrations of surfactants mostly affect the bacteria present in the soils.

CONCLUSION

In conclusion, a sensor for anionic surfactant (SDS) having higher concentration has been demonstrated with high selectivity using GBG. Furthermore, GBG did not respond to other cationic and non-ionic surfactant materials in water and selectively responded only to the anionic surfactant. Besides, the preparation of GBG does not involve multistep synthesis. The sensor can be prepared by the mixing of graphene oxide and brilliant green in the presence of hydrazine hydrate, followed by the removal of unbound dyes by solvents. There are many advantages to the present sensor that the sensor can be prepared with any desired dyes in combination with graphene oxide and is less time-consuming and the results can be visualized by the naked eye. Besides, SDS has been used to a larger extent in various applications in various industries with higher concentrations, and thus the present method could be useful for the examination of environmental, biochemical, detergents, and cleaning material samples. Therefore, the present method will be supportive of other existing methods of detection of SDS and other anionic surfactants. Development of sensors for anionic and non-ionic surfactants is in progress with high selectivity.

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CONFLICT OF INTERESTS

The authors declare that there is no conflict of interest.

AUTHOR CONTRIBUTIONS

All authors contributed significantly to this manuscript, participated in reviewing, and approved the final draft for publication. The research profile of the authors can be verified from their ORCID IDs given below:

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