Hybrid Films of Reduced Graphene Oxide with Metal Oxide Nanostructures for Applications as Renewable SERS Substrates

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Abstract

Graphene and reduced graphene oxide (rGO) is widely used as a platform to assemble various metal or metal oxide nanostructures to generate functional materials with unique properties. rGO is known for its high surface area, atomic thickness and excellent 2D conductivity. High surface area and remnant functional groups of rGO promote adsorption of various molecules and anchoring of nanoparticles while carbon network promotes electron delocalization and shuttling that aids in fluorescence quenching and photocatalysis.[1,2] Metal or metal oxide nanostructures with the desired properties such as photoexcitation, photoconductivity, charge transfer, surface plasmon resonance or magnetism may be chosen to be adsorbed on rGO. Hence, a synergy of the properties due to rGO and assembled nanostructures operate in these hybrid systems imparting unique properties to such functional materials.

Syntheses of rGO-metal/metal oxide nanoparticle hybrids are generally achieved by chemical methods as they provide a simple and cheap route to obtain large quantities of the materials. We have been utilizing the liquid/liquid interface to generate ultra-thin films of rGO with noble metal nanoparticles following in situ chemical reduction.[3] The liquid/liquid interface provides a constrained environment for the self-assembly of solid materials and is thermodynamically favoured by a reduction in the interfacial energy. [4]

In this work, we have synthesized free standing, thin films of reduced graphene oxide (rGO) with ZnO, CuO and SnO_2 nanostructures at a liquid/liquid interface (water/toluene) employing a simple interfacial reaction of the precursors and self-assembly. The method can be adopted as a general route to prepare rGO based metal oxide films. The structure, optical properties and morphology are studied by X-ray diffraction, UV-visible absorption spectra, photoluminescence and high resolution electron microscopy. rGO-ZnO, rGO-CuO and rGO-SnO_2 films exhibit unique morphologies such as hexagonal cylinders, elongated splinters, and balls, respectively, wrapped by rGO layers. rGO-metal oxide nanostructures show surface enhanced Raman scattering (SERS) effect of rhodamine 6G dye caused by a synergic effect of charge transfer between the dye, metal oxide and rGO, fluorescence quenching by rGO and dye molecular resonance. The enhancement factor follows the sequence rGO-CuO > rGO-ZnO > rGO-SnO_2. SERS enhancement is further improved by introducing a very small concentration of Ag^+ ions in the reaction system to obtain Ag nanoparticle doped rGO-ZnO films, exploiting the electromagnetic effect of metal surface plasmons. rGO-Ag-ZnO hybrid films show higher detection sensitivity up to 10 µM dye with an enhancement factor of 10^4. The higher photodegradation rates provided by rGO based metal oxide hybrids and metal nanoparticle doped hybrids enable regeneration of the used SERS substrate. The reusability of the hybrid films is exemplified by degradation of rhodamine 6G by UV irradiation and SERS recording of a different dye, methylene blue adsorbed on the renewed substrate (Figure 1).

References

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Figures

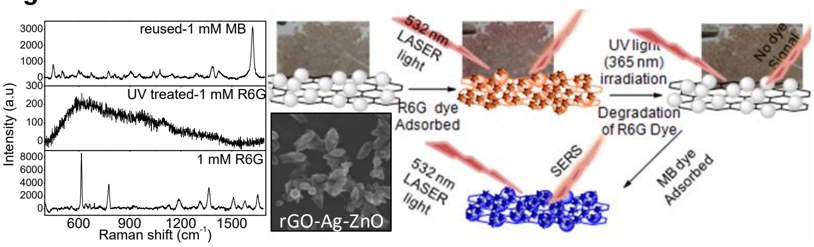

Figure 1: Multifunctional nature of rGO-metal oxide films doped with metal nanoparticles formed at a liquid/liquid interface is exploited for the SERS of dyes and recyclability of the films; facilitated by a combined effect of chemical and electromagnetic enhancements and photodegradation.