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Graphene nano-mesh-Ag-ZnO hybrid paper for sensitive SERS sensing and self-cleaning of organic pollutants

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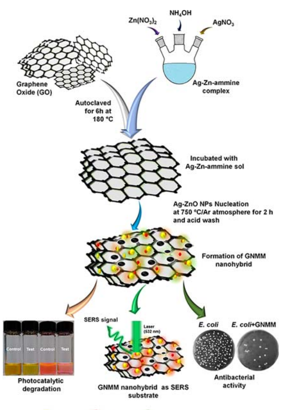
GRAPHICAL ABSTRACT



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ABSTRACT

Rationally designed self-assemble, functional 3D architecture of graphene nano-meshes with unique plasmonic resonance metal nanoparticles can be excellent nanohybrid Raman scattering (SERS) substrate in spotting the low levels of environmental organic pollutants. In this study, graphene nano-mesh-Ag-ZnO metal (GNMM) nanohybrid was prepared by self-assembled hydrothermal reduction of graphene oxide (GO) followed by thermal annealing of site-localized metal-salts as a highly sensitive surface-enhanced Raman scattering (SERS) substrate. The crumpled graphene nano-meshes decorated with Ag-ZnO nanoparticles created SERS hot spots (holes) that manifested high SERS sensitivity to model organic pollutants such as methyl orange (MO), rhodamine 6G (Rh-6G) and paraquat (PQ) with detection limit as low as 10^{-11}, 10^{-13} and 10^{-14} M, respectively. A maximum enhancement factor (EF) of 1.97×10^{11} was obtained with PQ molecules on synthesized GNMM substrate. The enhancement in signal can be supported through charge transfer mechanism that induced strong enhancement of the local electric field on free available graphene nano-mesh edges abundant with hotspots. This novel nanohybrid SERS substrate realized self-cleaning by photocatalytic degradation of model organic Rh-6G molecules adsorbed on the nanohybrid paper and shows reusability during the detection process. Meanwhile, GNMM nanohybrid also possesses highly effective antimicrobial activities for *Escherichia coli*. The detection of organic pollutants by GNMM nanohybrid SERS substrate has several advantages such as low cost, easy and simple

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preparation method, sensitive detection and reusability that can be potentially applied for detection of variety of environmental pollutants and antimicrobial agent applications.

1. Introduction

In recent years, water-soluble toxic organic compounds such as dyes from the textile industries and herbicides used in agriculture are major source of environmental pollution [1,2]. The presence of these pollutants in the environment is highly toxic and hazardous for ecosystem. For instance, rhodamine 6G (Rh-6G) is generally used as basic dye for staining wool, cotton and papers to generate highly fluorescent shades while azo dyes such as methyl orange (MO) are abundantly used in textiles and leather industries [3]. These organic molecules finally find their way into the environment and hence, cause toxicity problems [4,5]. Recently, innumerable analytical methods have been employed to detect organic compounds such as high performance liquid chromatography [6] and enzyme-linked immunosorbent [7]. Although, these analytical methods are widely accepted but none of these techniques are simple, low cost, rapid and sensitive towards determination of organic molecules. As compared to conventional detection methods, SERS have been discovered as non-destructive, ultrasensitive, cost effective, portable and multiplexing analytical technique in chemical and biological sensing applications [8]. SERS uses nanostructure surface phenomena to enhance weak inelastic-scattering of light to detect the analyte fingerprints [9]. The SERS signal is directly related to SERS substrate characteristics such as shape, size and distribution of the metal nanostructures which facilitates better molecular adsorption and sensitive detection of analytes by electromagnetic mechanism (EM) and chemical mechanism (CM) [10]. The EM originates from substantial increase in the local electromagnetic field and amplifies pristine Raman signal by $\sim 10^8$ times or more [11]. Whereas, CM is triggered by the charge transfer between target molecules that leads to SERS substrate exhibiting an increment of several order of enhancement factor [12]. To fabricate SERS substrates with higher molecular specificity and sensitivity, several noble metals like Ag and Au have been widely used as they provide large enhancement via surface plasmon resonance (SPR) [10]. Recent reports documented that EM enhancement in SERS signal is contributed by metal nanoparticles (NPs) and cumulative enhancement factor that depends on the SERS substrate morphology with tunable plasmonic properties around NPs (hot spots) [10]. However, integration of foreign materials with metal NPs favored sensitive detection of target analytes [10]. Moreover, it is extremely challenging to carry out controllable fabrication of hotspots, therefore, it becomes necessary to invoke additional chemical enhancement to improve the effectiveness of SERS substrates. Further, an efficient photo-catalyst with antimicrobial properties is a critical issue for an environmental remediation due to major organic pollutants originated from the different industries [13]. Now days, it becomes one of the most challenging tasks to detect and exterminate the organic dye pollutants from the water as well as other environmental contaminated samples. Also, the safety concerns continuous emphasis on the resistant microbes have stressed out for the improvement of traditional antimicrobial agents or pursuit for other favorable substitutes [14]. The low cost and easy method to synthesize nanohybrid materials with self-cleaning has great potential in the fields of sustainable energy and environment. The synthesis of SERS nanohybrid materials with multi functionality has several advantageous such as low cost, easy sample preparation and can be applied not only for rapid sensing/detection with recyclability purposes but also their antibacterial and antifouling properties could be exploited for environmental applications.

The most widely used material for SERS application is use of noble metals due to their excellent plasmonic properties [15,16]. Additionally, metal NPs based approach is surface modification of Au or Ag NPs to achieve sensitive SERS substrate, where functional molecules allow sensitive detection [17,18]. However, surface modification of metal based substrate required complex process for preparation of the functional molecules and expensive chemicals (reagents). Further, metal NPs need to be prepared with desired dilution with homogenous dispersion in order to achieve sensitive Raman signal and it is time taking process which involved tedious steps such as centrifugation. Therefore, there is a high demand to develop novel hybrid SERS substrates with easy, simple, rapid and cost effective method for the detection of organic pollutants. Graphene has been widely reported as SERS substrate due to its unique 2-D honeycomb structure accompanied with its physical/chemical properties [19,20]. Graphene can be easily combined with metallic substrates that results into fabrication of sensitive SERS substrates having EM from metal and CM from graphene [21]. Additionally, fluorescence quenching property of graphene reduces SERS background and improves Raman signal to noise ratio [21]. Furthermore, graphene has sp^2 carbon interconnected network and its large surface area to volume ratio advantageous for SERS due to enhanced adsorption of dye molecules through π–π stacking on its surface [20,22]. These properties of graphene could be combined easily with metal NPs for SERS detection with better enhancement factor as compared with individual components and other conventional materials [10]. Also, graphene based materials has been reported as promising nanomaterial for the designing of potential biocidal agents [23]. Recently, a new derivative of graphene materials as graphene nano-meshes (GNMs) have gained extensive attention because of unique properties such as open energy band gaps, enlarged specific surface areas, and photocatalytic activity [24]. Also, the occurrence of quasi-periodic nano-holes on GNMs provides the edges and active sites for rapid electron transport as compared to planar structure in bare graphene sheets [24]. Therefore, these excellent characteristics of GNMs in combination with bi-metallic nanoparticles could offer novel nanohybrid that can be used for rapid sensing/detection of organic molecules with recyclability and as a photocatalyst as well as antibacterial agent.

In this study, we designed the graphene nano-mesh decorated with bi-metallic (Ag-ZnO) NPs (GNMM) nanohybrid by thermal reduction approach. Here, ZnO was chosen additionally with Ag because of its the intrinsic absorption and emission bands, which are near to the surface plasma peak of Ag at resonant coupling. It is also possible to induce an electron transfer from Ag to ZnO because the Fermi energy of Ag is higher than that of ZnO conduction band [25]. The accumulated electrons near the Ag/ZnO interface can be induced the electromagnetic field and magnified the local field significantly. Both Ag/ZnO hybrid nanostructures are expected to exhibit both surface plasmon resonance and local electromagnetic field enhancement than individual ZnO or Ag. Further, among the different metal oxides, ZnO has been seeking attention as an excellent photocatalyst because of its suitable band gap (~3.37 eV) and large free exciton binding energy (60 meV) [26]. Also, ZnO has nontoxicity, physico-chemical stability, capability to form in various morphologies, low-cost production, flexible synthesis method as compared with other metal oxides (such as TiO_2) with excellent photocatlytic activity which are favorable for recyclable SERS substrate sensing applications [26]. As-synthesized GNMM nanohybrid formed SERS hot spots that could effectively modulated EM and CM and enabled sensitive detection of environmental model organic pollutants. The nanohybrid also showed self-cleaning through photocatalytic degradation of organic molecules adsorbed on the SERS nanohybrid substrate along with improved antibacterial properties.