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Synthesis and characterization of gold graphene composite with dyes as model substrates for decolorization: A surfactant free laser ablation approach

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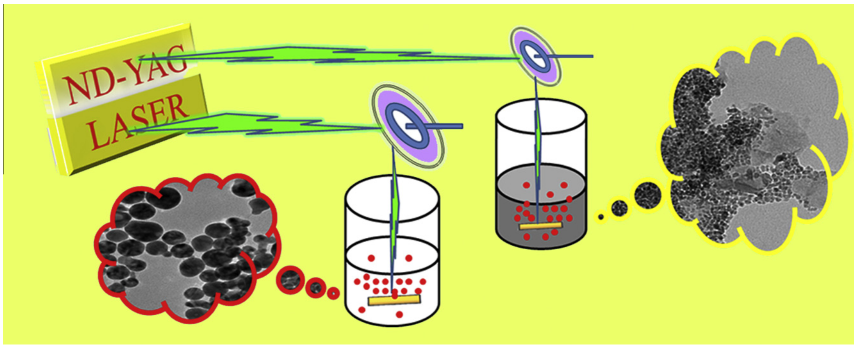
HIGHLIGHTS

- Surfactant free synthesis of gold–graphene by laser ablation.
- 170 folds faster reduction for Rhodamine B than uncatalyzed reaction.
- 17,000 folds faster reduction for Methylene blue than uncatalyzed reaction.
- Doubled rate for the reduction of Rhodamine B than commercial gold nanoparticles.
- Synergism between gold nanoparticles and graphene for enhanced catalytic activity.

GRAPHICAL ABSTRACT



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ABSTRACT

A facile surfactant free laser ablation mediated synthesis (LAMS) of gold–graphene composite is reported here. The material was characterized using transmission electron microscopy, field emission scanning electron microscopy, energy dispersive X-ray spectroscopy, powdered X-ray diffraction, Raman spectroscopy, Zeta potential measurements and UV–Visible spectroscopic techniques. The as-synthesized gold–graphene composite was effectively utilized as catalyst for decolorization of 4 important textile and laser dyes. The integration of gold nanoparticles (AuNPs) with high surface area graphene has enhanced the catalytic activity of AuNPs. This enhanced activity is attributed to the synergistic interplay of pristine gold's electronic relay and π–π stacking of graphene with the dyes. This is evident when the Rhodamine B (RB) reduction rate of the composite is nearly twice faster than that of commercial citrate capped AuNPs of similar size. In case of Methylene blue (MB) the rate of reduction is 17,000 times faster than uncatalyzed reaction. This synthetic method opens door to laser ablation based fabrication of metal catalysts on graphene for improved performance without the aid of linkers and surfactants.

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Introduction

Graphene is a one atom thick single layer of graphite with hexagonal rings containing sp^2 hybridized carbon atoms [1]. Single layer graphene (SLG) has a high theoretical specific surface area ($2600\ m^2/g$), high electrical conductivity (9.6×10^5 S/cm), high thermal conductivity ($\sim$5000 W/m K), and a much captivating transport phenomena such as quantum hall effect [2,3]. A plethora of applications are associated with the unique properties of graphene [4,5]. Graphene is a leading alternative to other forms of carbon as a good catalytic support material due to its high surface area associated with superior conducting properties [6,7]. This has resulted in its application in field emission, sensors, super-capacitors, batteries, membrane materials, and in catalysis [8,9]. Practical applications of single layered graphene have become limited due to the cumbersome procedures involved in its growth, handling and large scale production [10,11]. As a result of this the focus has been shifted towards few layered graphene (FLG). Currently synthesis of FLG suffers from scalability, multilayer formation or usage of toxic chemicals. In this regard, exfoliation of graphite oxide under a reductive hydrogen gas ambience offers a compromised approach to obtain large quantities of FLG sheets also known as hydrogen exfoliated graphene (HEG) (BET surface area $\sim$430 m^2/g) with good electrical conductivity [12]. Subsequent treatment of this material by acids has shown to produce functionalized few layer graphene (f-HEG) that can be dispersed in aqueous solvents and has sufficient defect sites for anchoring suitable functional moieties such as metal/metal oxide nanoparticles [13]. Metal nanoparticles (MNPs) on the other hand catalyze chemical reactions by an efficient relay of electrons to the substrate. The integration of graphene's high surface area with MNPs catalyzing power furnishes unique composite nanomaterials with enhanced catalytic performance. These nano-catalysts not only decrease the reaction time but also pave way for synthesizing next generation hybrid graphene based catalysts. However, the problem in synthesizing these MNPs modified graphene catalysts has been the utilization of surfactants for stabilization that reduces the catalytic performance [14,15]. Many researchers have synthesized gold graphene composites using bottom up approaches utilizing surfactants [16,17]. Thus laser ablation of gold strip in this study causes the ablation of pristine surfactant free AuNPs and also deoxygenation of f-HEG into laser converted graphene (LCG). This results in the deposition of AuNPs over LCG to form Au-LCG. We report here a novel in situ and surfactant free technique for the synthesis Au-LCG using laser ablation mediated synthesis (LAMS).

The catalyst was utilized in the reduction of Rhodamine B (RB), Methylene blue (MB) dye systems that are widely used in the textile industries along with Sulforhodamine 101 hydrate (SR) and Fluorescein (FS) that are used as fluorescent staining dyes. These dye reductions were observed to be kinetically slow in the absence of the catalyst. Our results indicate that Au-LCG catalyzes the reduction along with decolorization of MB at 17,000 times faster than uncatalyzed reaction and 7100 times faster than f-HEG as catalyst. In case of RB reduction the catalyst has been compared with a commercial citrate capped AuNPs of similar size and the catalyst has shown 1.7 times faster than the commercial one. The added advantage of the decolorization process is that, we could follow the kinetics using UV–Vis spectrophotometer at room temperature.

Experimental

Synthesis of f-HEG and Au-LCG

f-HEG was synthesized based on our previous reports [13,18]. MNPs were synthesized using LAMS approach [19]. In brief, an aqueous solution of f-HEG was first prepared by ultrasonically dispersing 1 mg of f-HEG in 25 ml of millipore water. A gold metal strip of dimension (2 cm $\times$ 1 cm) was ultrasonically cleaned in 5 ml piranha solution (caution) and placed in a 25 ml glass beaker containing 3 ml of aqueous solution of f-HEG. A high power nanosecond Nd:YAG (Surelite III) with its fundamental harmonic at 1064 nm was used as the irradiation source. The intense laser pulse was optically steered and focused on to the gold foil using a convex lens (focal length = 10 cm). The laser pulse energy (50 mJ) and repetition rate of 10 Hz were kept constant throughout the ablation period. Similar procedure was followed to obtain pristine AuNPs in plain millipore water as the solvent. The weight of the gold strip was monitored before and after the application of the LAMS procedure (ablation time 40 min) to ensure the release of 0.3 mg of gold into the solution. The LAMS procedure is illustrated in the graphical abstract.

Characterization

The Au-LCG was observed using a transmission electron microscopy (TECNAI F-20, S-TWIN, 200 kV). The samples for TEM measurements were prepared by placing a few drops of sample on carbon coated Cu grids (SPI supplies, 200 mesh). FESEM and EDAX studies were done on indium tin oxide surface using field emission scanning electron microscope (FESEM, Zeiss). The Raman spectra were obtained using a Dilor XY triple grating monochromator micro-Raman spectrometer (with a 100$\times$ objective). The 514.5 nm excitation wavelength of an Ar+ ion laser at low power (<1 mW) was used to excite the samples. Zeta potential studies were done for Au and Au-LCG using a Malvern Zetasizer instrument. The increased loading of gold on graphene substrate with increasing ablation time was measured using a Shimadzu 2450 PC UV–Vis spectrophotometer.

Catalytic dye reduction

Catalytic reductions were carried out on different dye systems: cationic (RB and MB), anionic (FS) and a bipolar dye (SR). A stock solution (10^{-3} M) of the dye in water was diluted to 10^{-5} M at the time of experimentation. A solution of reducing agent, sodium borohydride (0.1 M aq. $NaBH_4$) was freshly prepared for the experiment. The reaction was carried out in a quartz cuvette containing 2.5 ml of 10^{-5} M dye, 0.5 ml of 0.1 M of $NaBH_4$ and 50 μl of the catalyst (Au-LCG). The tabulated procedure can be found in the Supporting information Table S1. Similar reduction was carried out with pristine AuNPs and f-HEG separately. The catalysis was monitored using a Shimadzu 2450 PC UV–Vis spectrophotometer coupled with Julabo F 25 thermostat. A complete decolorization was observed for all of the systems on a time scale of few seconds to minutes. The reaction rates and kinetics of the process were studied to understand this phenomenon. Positive and negative controls for the systems were maintained by studying the dye reductions in the absence of any catalyst (with $NaBH_4$ alone) or in the presence of either f-HEG or AuNPs respectively. To investigate whether the reaction was diffusion controlled, 40 mg of sucrose (viscogen) was added to 10 ml of 10^{-5} M RB dye solution and the same dye reduction procedure was repeated to study the effect on the reaction rates [20,21]. To compare the rates with surfactant capped AuNPs, citrate capped AuNPs of sizes 20 nm, 80 nm, and 200 nm were purchased from BBI solutions. The catalyst was also compared with plant based AuNPs synthesized using the stem extracts of *Breynia rhamnoides* [22].

Results and discussion

Electron microscopy and other characterization

The synthesized samples have been examined by electron microscopy and results are presented in Fig. 1. Fig. 1a shows the