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Syzygium cumini-mediated synthesis of rGO/Ag-Au nanostructures: Efficient catalysts for rapid degradation of organic dyes

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ABSTRACT

Background: The increasing human health risk caused by contamination of water by both natural and synthetic dye pollutants has become a crucial issue and poses an immense urge to find a sustainable approach for the removal of dye contaminants from wastewater. Photocatalysis performed in the presence of nanomaterials holds huge promise as an efficient and environmentally safe oxidation technology for organic dye removal from waste water.

Methods: Our preparation methodology utilizes the extract derived from the endocarp of Syzygium cumini (SC) effects for concurrent reduction of GO and metal ions to form rGO/Ag-Au. The prepared rGO/Ag-Au nanostructures effectively breakdown organic dye pollutants like methylene blue (MB) and methyl orange (MO) dyes.

Significant findings: A robust interaction between the rGO matrix and the Ag-Au nanoparticles was established by structural characterization, while morphological investigation displayed the nanoscale Ag-Au particles uniformly coated over the rGO sheet surface. The catalytic efficiency of the rGO/Ag-Au nanocomposite toward methylene blue (MB) and methyl orange (MO) chromophores decomposition was assessed with the aid of sodium borohydride ($NaBH_4$). The decoration of well-spaced Ag-Au nanoparticles over the rGO sheet created firm catalytic active sites in the rGO/Ag-Au composite. With the improved catalytic active surface, the MB/MO dye was completely removed in a very short time of 2.5 to 5 min. The rGO/Ag-Au composite exhibited exceptional catalytic prowess in the disintegration of both dyes, leading to complete degradation. The remarkable efficacy in the dye degradation process can be attributed to the predominance of both electrostatic as well as π-π interactions between the nanocomposite and the dyes. As a result, the current study has developed an easy-to-use and green method for creating rGO/Ag-Au composites, offering a workable way to dispose of hazardous organic dyes in an affordable and efficient way.

1. Introduction

Since its discovery in 2004, the exceptional properties of graphene have attracted significant scientific interest. Graphene is a 2D carbonaceous substance that comprises a layered carbon atoms that are structured in a honeycomb lattice pattern. Graphene exhibits exceptional characteristics that make it well-suited for the construction of electronic apparatus, batteries, and sensors [1–3]. Its exceptional characteristics, including superior electronic properties, high surface area, and numerous edge defects, make it an ideal material for these applications, as demonstrated by previous studies. Graphene oxide (GO), a derivative material of graphene, demonstrates similar

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characteristics to graphene, alongside several supplementary benefits, including hydrophilicity, ample hydroxyl functional groups, and adaptable electronic activities [4]. The removal of some oxygen moieties from GO and its conversion to reduced GO (rGO) allows the restoration of the conjugated graphitic network with an sp^2 structure [5].

Reduced Graphene Oxide (rGO) holds copious functional groups with considerable surface area, making it a superior substrate for an extensive array of nanoparticles such as Ag, Au, ZnO, TiO_2, and Fe_3O_4. Thus, the exceptional electrocatalytic and photocatalytic attributes of metal composites based on rGO can be generated [6–9]. Recently, the Ag and Au nanostructures are widely explored for use in wastewater treatment due to their superior biological, physical, and chemical properties. In addition to the previously listed features, these nanostructures possess unique plasmon, thermal, and optical properties that facilitate their effective catalytic ability [6]. Additionally, their extensive applicability is further supported by their affordability, chemical stability, broad absorption spectrum, stability under ambient conditions, and non-linear optical behaviours. Furthermore, numerous approaches for diminishing GO and combining metal/metal oxide nanoparticles onto rGO sheets were studied, with the pursuit of producing rGO-metal/metal oxide nanocomposites. Patil et al. (2016) employed a hydrothermal technique to synthesize composites of rGO and hexagonal boron nitride, while Azarang et al. (2015) produced rGO sheets adorned with ZnO nanoparticles through the sol-gel method [10, 11]. Gao et al. employed a facile phase-transfer method to develop GO—Cds composite in a water/toluene interface [12], and Lin et al. reported an electrochemical template technique to fabricate GO—CdSe composite [13]. As previously mentioned, GO is frequently subjected to chemical reduction using diverse reducing agents such as ethylene glycol, hydrazine hydrate, hydroquinone, and $NaBH_4$ [14,15]. Reduction of GO is also achieved by treating GO thermally [16]. These procedures make the synthesis process complicated, costly and environmentally unfriendly.

In recent times, scientists have emphasized the development of nanocomposites based on rGO with exceptional catalytic characteristics for efficient elimination of dye pollutants from water reservoirs. Yao et al. recommended an uncomplicated technique for producing $MnFe_2O_4$-rGO nanocomposites and assessed their catalytic efficacy in peroxymonosulfate-mediated dye oxidation [17]. Additionally, Wu et al. have explored the impact of visible light on the $ZnFeO_4$/rGO photocatalytic performance during methylene blue degradation [18]. Furthermore, Yang et al. have discovered the catalytic potential of Fe_3O_4@rGO@TiO_2 composites for organic pigment degradation [19]. However, these studies have limitations, such as incomplete removal of oxygenated species, the presence of nitrogen and toxic elements, and the generation of toxic gas.

On the other side, the ultimate objective of organic pollutant degradation from aquatic sources is to reuse them as water scarcity has become a most challenging problem for humanity. The utilization of toxic reducing agents and chemical synthetic protocols in the fabrication of nanocomposites that rely on reduced graphene oxide (rGO) generates perilous byproducts and leads to the pollution of precursor chemicals. This contributes to environmental toxicity and undermines the crucial goal of research into dye degradation. Hence, a non-toxic, clean, cost-effective and eco-friendly technique involving photosynthesis autotrophs is on the pursuit for the formation of nanoparticles and nanocomposites. Although, a number of efforts have been reported using the extracts of plant, fruits and seeds for the bio-synthesis of nanoparticles, the reports have been limited for rGO based nanocomposites. *Syzygium cumini* (*Sc*) is one of the evergreen tropical trees that belongs to Myrtaceae family and the various parts of the tree including the endocarp of seed are used in various alternative healing systems (Ayurveda, Sidda and Unani) to treat ailments, specially *diabetes mellitus* and for curing digestive problems [20]. Setia et al. (2022) have described that the endocarp of *Sc* (Sapindus mukorossi) seeds can effectively reduce both GO and metal ions owing to the existence of phytochemical constituents like gallic acid, ellagic acid, phenolics, flavonoids, carotenoids, and vitamin C [21]. Hence, the present investigation employed the endocarp extract of Syzygium cumini seeds as a reductive agent to concomitantly reduce GO and Ag, Au ions, ultimately leading to the production of rGO/Ag-Au nanocomposites. The utilization of a green synthesis technique resulted in the generation of an exceedingly efficient catalyst material, which was successfully employed for the disintegration of MB and MO. The MB and MO are synthetic dyes widely used in the textile, pharmaceutical, leather, and paper industries. However, the discharge of these dyes into water resources creates severe health issues, including eye irritation, respiratory tract infections, carcinogenic disorders, and skin disease. Hence, the removal of MB and MO is highly essential before discharge into water. As a novelty of this present investigation, the naturally occurring endocarp extract of Syzygium cumini seeds was used to prepare the rGO/Ag-Au nanocomposites without the use of any harmful or expensive external additives. The performed in-situ approach simultaneously reduced the GO and Ag/Au ions, facilitated the composite formation, decreasing the total reaction time and material preparation costs. According to previously published results, catalyst made using the in-situ method exhibit higher catalytic performances compared to those prepared using the ex-situ method. In comparison to previously published catalysts, the prepared rGO/Ag-Au in this study demonstrated a superior catalytic performance on MB and MO dye removal, providing credence to the above presumption. Hence, a systematic examination of rGO/Ag-Au synthesis and their photocatalytic activity provides a new avenue for cutting-edge waste management process.

2. Experimental methods

2.1. Materials

The fruits of Syzygium cumini were procured from a marketplace in the southern Indian city of Madurai. The graphite powder, silver nitrate (AgNO3, purity $\geq$ 99.9 %), and chloroauric acid (HAuCl4, purity $\geq$ 99.999 %) were obtained for the experiment. Methylene blue ($C_{16}H_{18}N_3SCl$, AG, $\geq$ 82 %), Methyl orange ($C_{14}H_{14}N_3NaO_3S$, The ACS reagent (85 %) and sodium borohydride ($NaBH_4$, powder, 98 %) utilized in the research were procured from Sigma-Aldrich and were deemed sufficiently pure for use without any additional purification procedures.

2.2. Extraction of Sc kernel endocarp

The seeds from fresh fruits of *Sc* were removed, washed well with deionized water until the pink colour on the endocarp of seed disappeared. The washed seeds were dried well under air atmosphere and the endocarps of the seeds were collected. To generate the 10 % extract, a sufficient amount of endocarps was subjected to boiling in deionized water and subsequently sterilized for 15 min. The solution was subsequently filtered and kept at 4 °C overnight before utilization.

2.3. Preparation of rGO

The modified Hummer's method derived GO was used for rGO preparation. 10 wt% extract of endocarp was introduced into a GO dispersal (0.5 mg/ml) and subjected to vigorous agitation with a magnetic stirrer for duration of 48 h. Then the mixture was heated to 100 °C for 24 hour and the obtained material is centrifuged, washed with deionized ethanol/water, and dried at 80 °C for 6 h.

2.4. Preparation of rGO/Ag and rGO/Ag-Au composites

2 mM solution of $AgNO_3$ and 1:1 mole ratio of $AgNO_3$—$HAuCl_4$ was separately introduced into a GO dispersion (0.5 mg/ml) and vigorously stirred using magnetic stirrer. Following this, 10 wt% endocarp extract was added into the above solutions and the obtained mixtures were

subjected to a fermentation process for six hours at a temperature of 100 °C. The resulting mixtures were cooled down and centrifuged to get rGO/Ag and rGO/Ag-Au nanocomposites. The separated nanoparticles were washed with D.I H_2O/ethanol before being dried for six hours at a temperature of 80 °C.

2.5. Dye degradation experiment

The effectiveness of nanoparticles in degrading MB and MO was assessed using UV–Vis spectroscopy through a Jasco V-730 spectrometer. A total of 4 mg of rGO, rGO/Ag, and rGO/Ag-Au catalysts were added to a solution containing 3.13×10^{-5} M MB/MO dye and 2.64×10^{-2} M $NaBH_4$ and subjected to sunlight irritation. The solution was subjected to constant stirring for various periods. By employing a sedimentation technique, the catalyst was extracted from the solution, and subsequently employed UV–Vis spectrophotometry to ascertain the residual pigment content in the filtrate.

3. Results and discussion

3.1. Morphological properties

To examine the morphology of rGO, rGO/Ag, and rGO/Ag-Au nanocomposites, SEM and TEM were performed and obtained results are demonstrated in Figs. 1 and 2. The images in Figs. 1a and 2a illustrate that the surface and edges of the rGO consist of a thin, transparent, paper-like layer with wrinkles and folds. Furthermore, Figs. 1b and 2b reveal that Ag nanoparticles with an average size of 21 nm are uniformly dispersed over rGO sheets. Similarly, as illustrated in Figs. 1c and 2c, the Ag-Au bimetallic nanoparticles exhibited a comparable spherical morphology to that of the rGO/Ag particles, with an average size of 18 nm. However, the Ag-Au nanoparticles were observed to have agglomerated slightly to create particle islands, as evidenced by the TEM.

In accordance with Hsu and Chen's earlier findings, the HR-TEM image of rGO-Ag/Au shown in Fig. 3a displays a D-layer spacing of 0.23 nm [22]. The observed D-spacing value is related with the (111) plane of the fcc Ag (2014). Moreover, the inset of HR-TEM images depicts a SAED pattern that articulates the polycrystalline nature of the rGO/Ag-Au nanoparticles synthesized through a green synthesis method, as reported by Bar et al. [23]. The EDAX spectrum of rGO/Ag, as depicted in Fig. 3b, reveals strong peaks for the elements Ag and C. The elemental peaks of C, Ag, and Au observed in Fig. 3c indicate that rGO/Ag-Au is composed of a combination of these three elements.

3.2. XRD analysis

The XRD pattern of graphene oxide (GO) in Fig. 4a displays a prominent peak at 10.27°, corresponding to the complete oxidation of graphite to GO on the (001) reflection plane, consistent with previous findings reported by Vinothkannan and colleagues in 2015 [24]. According to Tavakoli et al. (2015), the loss of 10.27° peak and the rising of new peak at 24.5° with (002) plane can be relevant to the formation of

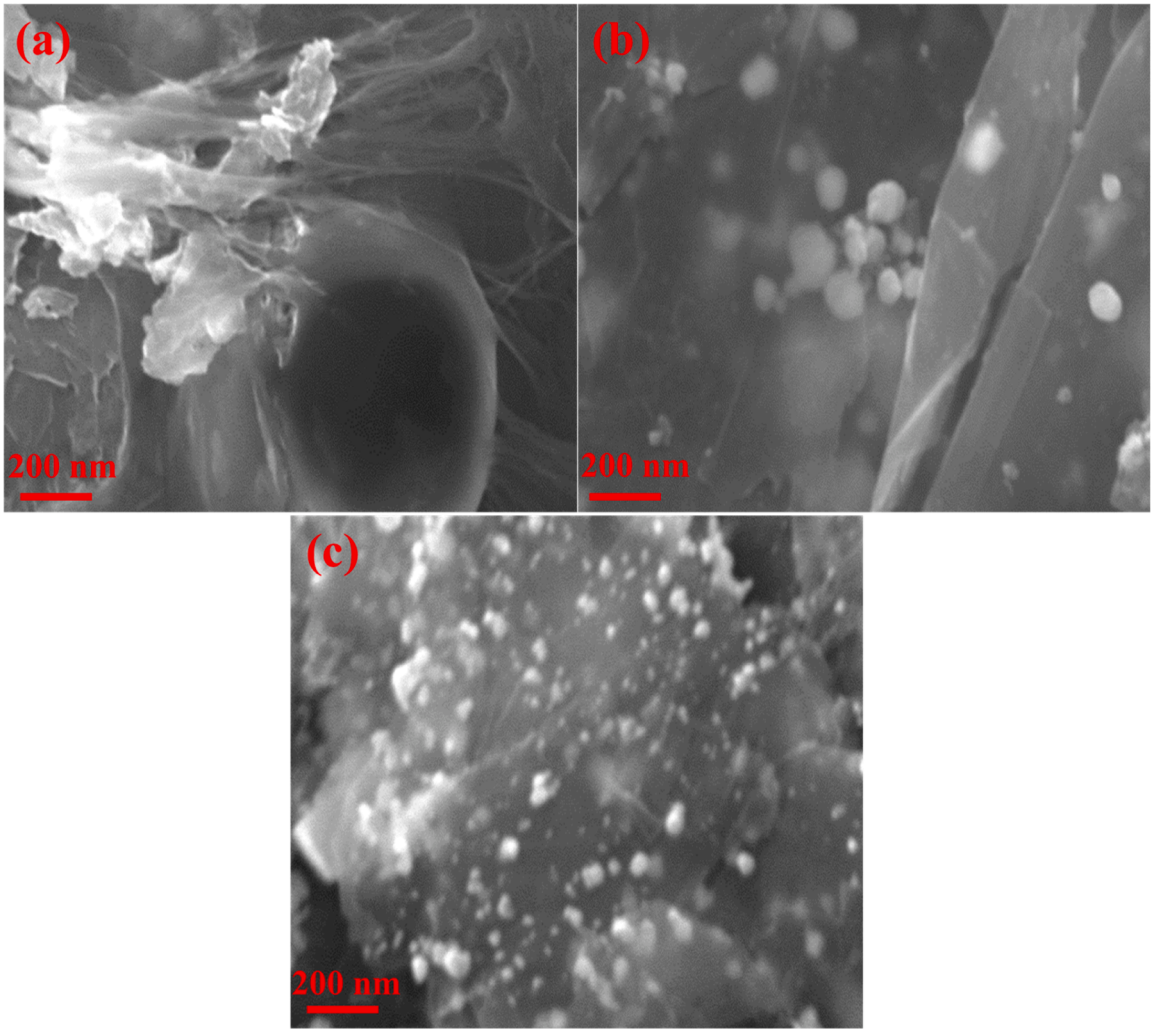

Fig. 1. SEM features of (a) rGO, (b) rGO-Ag, and (c) rGO/Ag-Au nanocomposites.

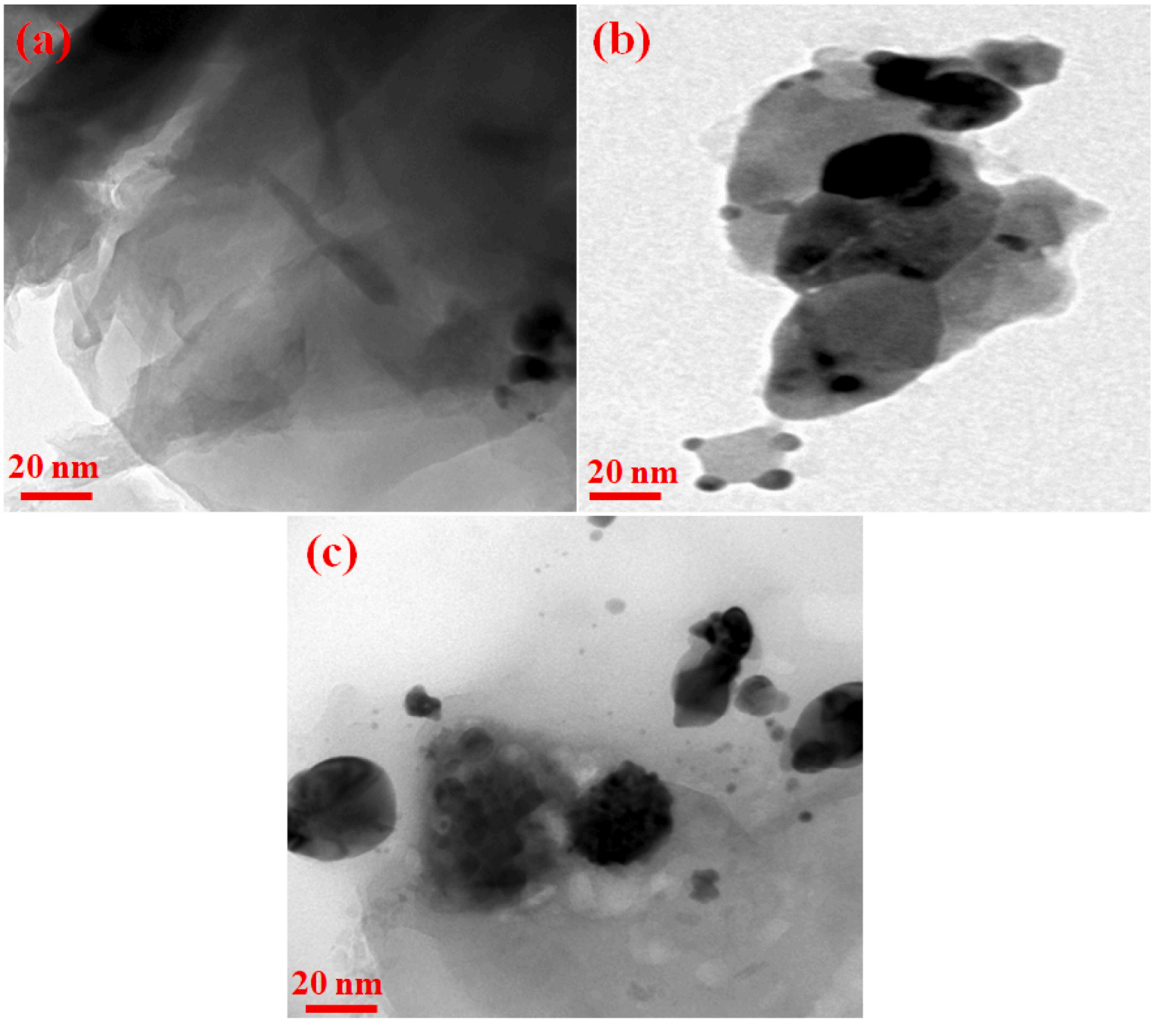

Fig. 2. TEM images of (a) rGO, (b) rGO-Ag, and (c) rGO/Ag-Au nanostructures.

rGO [25] (Fig. 4b). Fig. 4c exhibits the pattern of the rGO/Ag with distinct diffraction peaks at 38.58° (111), 44.74° (200), 64.88° (220), and 78°(311), endorsing the existence of fcc crystalline Ag nanoparticles [26].

In Fig. 4d, the XRD spectra of the rGO/Ag-Au nanocomposites are comparable to those of rGO-Au, indicating no significant difference. The lattice characteristics of the rGO/Ag (4.0806 Å) (JCPDS card no. 4–0783) and rGO/Ag-Au (4.0362 Å) (JCPDS card no. 4–0784) nanocomposites are highly similar [27].

3.3. UV–Vis spectra

The absorbance properties of mono- and bimetallic nanoparticles were analyzed using UV–Vis spectroscopy, as illustrated in Fig. 5. The SPR band at 231 nm and the shoulder peak at 299 nm observed in GO, as shown in Fig. 5a, were caused by the π-π* and *n*-π* transitions of the aromatic C—C and C = O bonds [28,29].

Fig. 5b exhibits the red-shift of the C—C bond after the reduction of GO with SC endocarp extract. In 2014, Gnana Kumar et al. discovered that the absence of a C = O bond at 299 nm confirms the GO reduction and its electronic conjugation restoration [29]. Also, the composite material formation between rGO and Ag was observed from Fig. 5c. This is supported by the existence of a clear SPR band at 265 nm for rGO and an SPR band at 420 nm, indicating the well Ag nanoparticles formation [30]. As in Fig. 5d, the rGO/Ag-Au combination has a unique SPR band at 265 nm, confirming the presence of the rGO layer. Additionally, there is a clear absorption band in the visible spectrum, representing the occurrence of both Au and Ag. As per previous reports, the pure Au nanoparticle exhibits a SPR band at 520 nm. Here, the no peak was observed for Au nanoparticle, suggesting that there are the Ag-Au bimetallic nanocomposites formation instead of individual Ag and Au nanoparticle formation [31].

3.4. Raman studies

The D and G peaks observed at 1342 cm^{-1} and 1608 cm^{-1} are clearly visible in all the materials [32] (Fig. 6). Fig. 6a corresponds to GO, yielding I_D/I_G ratio of 0.92. According to Fig. 6b, the G band observed in rGO showed a slight displacement towards 1604 cm^{-1}, which suggests that the Syzygium cumini endocarp extract contributed to the reduction of GO. Afterwards, the G band in both rGO/Ag and rGO-Ag-Au composites was observed to shift towards lower wavelengths, as depicted in Fig. 6c and d. The I_D/I_G calculated for rGO, rGO/Ag, and rGO/Ag-Au are 0.99, 1.02, and 1.07, respectively. These ratios are slightly higher than that of GO. This elevation in the intensity ratio is hypothesized to be due to the emergence of localized sp^3 defects in the sp^2 framework, which is likely to augment the catalytic activity of the synthesized composites [33,34].

3.5. Dye degradation studies

The efficacy of nanostructures fabricated via environmentally benign