

Online ISSN

3007-3197

Print ISSN

3007-3189

<http://amresearchreview.com/index.php/Journal/about>

Synthesis And Physicochemical Characterization Of Graphene Oxide–Gold Nanoparticle (Go–Aunp) And Reduced Graphene Oxide–Gold Nanoparticle (Rgo–Aunp) Composites With Preserved Plasmonic Integrity For Potential Radiosensitization Applications

Faizan Azmat (Corresponding Author)

Department of Physics, Govt. Graduate College Jaranwala, Punjab, Pakistan

sheikhfaizanofficial@outlook.com

Muhammad Umair Arshad

Department of Physics, Riphah International University, Faisalabad Campus

Aftab Ahmad

Department of Physics, Riphah International University, Faisalabad Campus

ABSTRACT

Graphene-based nanomaterials and gold nanoparticles (AuNPs) are nanomaterials whose optical and electronic properties have increasingly drawn interest in the biomedical field. In this research, AuNPs were prepared using two chemical synthesis processes, i.e., the Turkevich sodium tri-citrate reduction technique and the ascorbic acid reduction method, and combined with graphene oxide (GO) and reduced graphene oxide (RGO) to generate four nanocomposites. X-ray diffraction (XRD) and scanning electron microscopy (SEM) were used to perform structural characterization. UV-Visible spectroscopy and Raman spectroscopy were used to determine optical properties, and TGA and differential scanning calorimetry (DSC) were performed on GO. In all four composite formulations, the localized surface plasmon resonance (LSPR) peak was retained at approximately 525–537 nm, consistent with well-dispersed, non-aggregated AuNPs in the 20–40 nm size range. The preservation of the LSPR peak position across all formulations, independent of reducing agent identity (sodium tri-citrate vs. ascorbic acid) and graphene matrix type (GO vs. RGO), confirms successful non-aggregated AuNP decoration of the graphene sheets. RGO–AuNP composites exhibited substantially higher absorbance across the visible spectrum relative to GO–AuNP composites, attributable to the restored sp^2 conjugation of the RGO lattice. XRD confirmed the successful synthesis of GO and RGO. SEM revealed characteristic sheet morphologies consistent with Hummers-derived GO and ascorbic acid-reduced RGO. Raman spectroscopy of RGO–AuNP composites confirmed D- and G-band features consistent with defect-rich graphene lattices. TGA confirmed GO thermal stability up to 215 °C, well above physiological temperature. These results establish GO–AuNP and RGO–AuNP composites as structurally and optically well-

characterised platforms for potential radiosensitization applications, with the AuNP plasmonic response preserved upon graphene functionalisation.

Keywords— Gold nanoparticles; graphene oxide; reduced graphene oxide; localized surface plasmon resonance; radiosensitization

1. Introduction

Cancer is among the greatest public health concerns to date, and more than 19.9 million new cases were diagnosed in 2022 alone [1]. Radiotherapy, used either as external beam radiation or in combination with surgery and chemotherapy, accounts for approximately 50% of all cancer treatments and plays a central role in the curative management of solid tumours [2]. The radiotherapy therapeutic principle is based on the fact that the ionising energy deposits into the tumour tissue, producing both indirect and direct damage to DNA, leading to the eventual cell death. Traditional radiotherapy uses X-rays of 12-120 keV and up to 1.2 GeV gamma rays to cause irreparable breaks in DNA strands and apoptotic pathways in dividing cancer cells [3].

Though widely used, the basic drawback of conventional radiotherapy is that it lacks spatial selectivity in nature. With the high-energy beams of photons, dose is deposited in the surrounding healthy tissue with similar efficiency to that of the tumour volume itself, especially in the instance of deeply situated tumours. It is this indiscriminateness that causes radiotherapy to have to be administered in week-long schedules because the toleration of normal tissues limits the amount of radiotherapy that can be safely administered in a single session [4]. Developing strategies that maximise radiation dose in tumour cells while sparing normal tissue is therefore an important area of ongoing research.

One such avenue is radiosensitization through nanoparticles. The principle is to target the high-atomic-number (high-Z) nanoparticles to tumour cells, where their high photoelectric interaction with incident light leads to a local radiation dose enhancement by producing photoelectrons, Auger electrons, and reactive oxygen species (ROS) [5]. Gold nanoparticles (AuNPs) are the most commonly studied form of radiosensitizers of all the candidates due to their high atomic number ($Z = 79$), high X-ray photon attenuation relative to soft tissue, chemical inertness, established biocompatibility, and developed surface chemistry, which allows conjugation to tumour-targeting ligands [6]. Preclinical studies of Hainfeld et al. demonstrated that 1.9 nm AuNPs in combination with X-irradiation of 250 kVp, improving one-year survival in tumour-bearing mice from 20% to 86% [7].

Graphene and its variants, such as graphene oxide (GO) and reduced graphene oxide (RGO), have separately been considered as bionanomedicine materials due to the unique physicochemical characteristics of the two-dimensional materials. Graphene was first isolated in 2004 by Novoselov et al. [15] and its oxidised form, GO, has subsequently been well-investigated as a nanocarrier, photosensitizer and therapeutic platform due to its high surface area, rich surface functional groups (epoxy, hydroxyl, carboxyl), solubility in water and tunable optical properties as a result of its sp^2 hybridised two-dimensional carbon lattice [16,17]. The biomedical use of GO is

Online ISSN

3007-3197

Print ISSN

3007-3189

<http://amresearchreview.com/index.php/Journal/about>

especially appealing due to the fact that oxygen-based functional groups of the surface make conjugation sites to drugs, targeting ligands, and metal nanoparticles without the need to subject the surface to severe conditions of surface modification [18,19].

One of the optical properties of graphene that is of particular relevance to surface plasmonics is its ability to support surface plasmons at much lower photon energies than more traditional metallic systems, due to its large carrier density and linear band dispersion at the Dirac point [20]. In composites of AuNPs with GO or RGO, the graphene substrate modifies the local dielectric environment of the nanoparticles and may enable charge transfer at the metal–graphene interface. The extent and direction of any resulting LSPR shift have been reported to depend sensitively on synthesis conditions, AuNP size, and the degree of electronic coupling between the metal and graphene matrix [21–23]. Preservation of the LSPR peak upon composite formation, without aggregation-induced broadening or redshift, is itself an important indicator of successful non-covalent AuNP decoration and is a prerequisite for any application requiring a well-defined plasmonic response.

In this work, we report the synthesis and physicochemical characterisation of four GO/RGO–AuNP composite preparations prepared with two reducing agents. UV-Visible spectroscopy demonstrates that the LSPR peak of AuNPs is preserved at approximately 525–537 nm across all composite formulations, indicating successful non-aggregated decoration of graphene sheets without plasmonic disruption. Their structural, optical, and thermal characteristics are reported and discussed with reference to their potential as a platform for radiosensitization applications.

2. Background

2.1 Gold Nanoparticles as Radiosensitizers

The idea of local radiation dose amplification using high-Z nanoparticles in a tumour tissue dates back to the beginning of the 2000s. The pioneering *in vivo* experiment of Hainfeld et al. [7] established the principle of AuNP-based radiosensitization, and the field expanded rapidly thereafter. Further studies have established that AuNPs sensitize cancer cells to both kilovoltage and megavoltage radiation across a variety of *in vitro* and *in vivo* model systems and have been able to increasingly explain the underlying physical, chemical, and biological processes [6,9].

Radiosensitization by AuNPs is thought to take place mostly through the physical effect of the high mass-energy absorption coefficient of the particles compared to soft tissue at keV photon energies. When exposed to ionising photons, AuNPs can also create a cascade of photoelectrons and Auger electrons, of low energies, which will create energy in the immediate surroundings of the nanoparticle, increasing the ionisation density locally [5,8]. The secondary electrons produced at the chemical level react with water molecules in the environment to produce the ROS, especially hydroxyl radicals, which are highly toxic to DNA [11]. On the biological level, AuNPs have been reported to alter the cell cycle, apoptosis, and DNA repair pathways, which lead to increased cell kill than can be predicted by such a physical dose enhancement alone [6,9].

AuNPs have a radiosensitization efficiency that is dependent on a variety of parameters such as particle size, surface chemistry, concentration, and energy of incident radiation [6,8]. Smaller particles are generally more capable of having higher photoelectric cross-

sections/unit mass and higher surface-to-volume ratios in ROS generation, whereas larger particles might have an advantage of tumour retention [12]. Polyethylene glycol (PEG)-functionalisation of surfaces, peptide and antibody-based functionalisation, has been extensively used to enhance circulation time, decrease non-specific uptake, and enable tumour target delivery [10,13]. Although there is substantial preclinical data, the clinical translation of AuNP radiosensitizers remains an active area of development, with ongoing challenges related to biodistribution, dosimetry, and regulatory clearance [6,14].

2.2 Graphene Oxide and Reduced Graphene Oxide: Synthesis and Properties

Graphene oxide is a derivative of graphite, which is synthesized by use of a chemical oxidizing process known as the Modified Hummers' Method [35]. The graphite is reacted with strong oxidising agents (potassium permanganate in a mixture of sulphuric and phosphoric acids) to add oxygen-containing functional groups between and on the basal plane of the graphitic layers to produce an increase in the interlayer spacing of approximately 0.34 nm in graphite to 0.710 nm in GO [27,36]. XRD confirms the successful conversion by the disappearance of the graphite (002) peak at 2θ of 26° and emergence of the typically present GO (001) peak at 2θ of 10° - 12° [28,37].

The D and G bands of the carbon lattice give complementary structural information as given by Raman spectroscopy. The G band at about 1580 cm^{-1} is caused by the in-plane vibration of the sp^2 -bonded carbon atoms, whereas the D band at about 1350 cm^{-1} indicates the existence of the defects and disorder in the lattice [32].

A high D/G intensity ratio in comparison to pristine graphite is a typical indication of successful GO manufacturing since the incorporation of oxygen functional groups breaks the long sp^2 system [28,51]. SEM images of GO usually show a typical crumpled wrinkled sheet structure that forms due to the lattice deformation caused by the oxidation reaction [27,28].

Graphene oxide is reduced into reduced graphene oxide by chemical, thermal, or photochemical means to eliminate some of the oxygen functional groups. Reduction with ascorbic acid has drawn significant interest as a non-toxic, greener alternative to the traditional reductants [29,52]. Reduction using ascorbic acid under moderate temperatures allows restoring some extent of the sp^2 conjugation of the graphene lattice, as the XRD peak changes its position from (001) to (002) near 2θ of 24° to 26° , and the Raman D/G ratio is altered when compared with that of GO [34,52]. The resulting RGO still has the remaining oxygen groups, rendering water solubility and surface functionality without losing part of the electronic characteristics of graphene.

GO and RGO have numerous biomedical uses such as nanocarriers of anticancer drug delivery, photosensitizers of photothermal therapy and photodynamic therapy, tissue engineering scaffolds, biosensing and bioimaging platforms [18,38,39,40]. GO has high drug-loading potential due to the high surface area and functional groups, whereas the accessibility of functional groups to functionalise the surface with targeting ligands allows the delivery of drugs to tumour cells selectively [19,42]. The thermal stability of GO has also been systematically characterised using TGA, where the rapidity of mass loss is observed to increase beyond about 200°C due to pyrolysis decomposition of labile oxygen functional groups [34].

Online ISSN

3007-3197

Print ISSN

3007-3189

<http://amresearchreview.com/index.php/Journal/about>

2.3 Gold Nanoparticle Synthesis: Turkevich and Ascorbic Acid Methods

In 1951, the Turkevich technique was created, and it is one of the most popular pathways in the synthesis of colloidal AuNPs [45]. In this procedure, aqueous gold (III) chloride is reduced by trisodium citrate at high temperature to form quasi-spherical nanoparticles, which are capped by citrate to achieve electrostatic stabilisation. The molar ratio of citrate to gold salt mainly determines the size of the particles, and the larger the concentration of citrate, the smaller the particles tend to be [25,45]. The resultant AuNPs exhibit a characteristic LSPR absorption peak around 520-530 nm for particles in the 15-40 nm size range, which is well-defined by the Mie theory and the body of literature [31,46].

Reduction of gold salts by ascorbic acid is the second example of a single-step, room-temperature synthesis pathway that does not require heating and allows the rapid assembly of nanoparticles [26]. Ascorbic acid (vitamin C) is both the reducing agent and a mild capping agent, and transforms Au^{3+} to Au^0 at room temperature. Ascorbic acid reduction can also provide a larger size distribution and a lower monodispersity of the resultant nanoparticles compared to the Turkevich method, depending on reaction conditions, yet resultant nanoparticles exhibit similar LSPR peak positions [26,47]. Both of these methods are suitable for the preparation of AuNPs that will then be combined with graphene-based matrices [29,30].

2.4 GO–AuNP and RGO–AuNP Composites: Optical Properties and Applications

The decoration of sheets of graphene with AuNPs creates a hybrid system that has the plasmonic properties of gold and the large surface area of graphene, as well as the electronic properties of graphene. The presence of AuNPs inside the graphene matrix causes changes in the local dielectric environment of the nanoparticles, which results in changes and widening of the LSPR peak as compared to the composites without AuNPs [21,22,23]. Transference of charge between the sp^2 carbon lattice of a graphene sheet and the metal nanoparticles has been broadly recognized as one of the significant factors in the observed LSPR shifts, and the direction and magnitude of the shift vary with the degree of electronic coupling [21,44].

GO–AuNP composites were reported in various applications. AuNPs on GO have also been utilized as plasmonic interlayers in photovoltaics to increase light collection in organic solar cells with LSPR-mediated local field enhancement [22]. Recent applications of GO in biosensing have shown that a combination of the surface chemistry of GO and the plasmonic sensitivity of AuNP has made the detection of biomolecules by LSPR shifts label-free and highly sensitive [24,44,54].

The composite structure in catalysis has a high-surface-area support used to stabilise AuNPs against aggregation whilst preserving their catalytic activity [23]. The increase in SERS enhancement by AuNPs supported on graphene has also been extensively used for ultrasensitive detection of molecules [33,54].

The location of the LSPR peak of GO–AuNP composites is of vital interest. The published articles present LSPR variations of different magnitudes based on the synthesis pathway, the concentration of GO/RGO, and the size of AuNPs [21,22,23]. Any change in the LSPR towards the 650–900 nm biological optical window, where tissue absorption by haemoglobin and water is the least, would make GO–AuNP

Online ISSN

3007-3197

Print ISSN

3007-3189

<http://amresearchreview.com/index.php/Journal/about>

composites potential in vivo photon-activated applications such as photothermal therapy and photon-activated radiosensitization [20, 48]. In the present study, the LSPR is retained at 525–537 nm, which remains within the visible range active for AuNP photoelectric excitation.

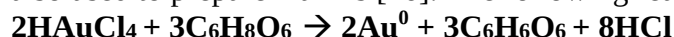
Although there is an accumulated literature on GO–AuNP composites, there is no systematic comparative study of the LSPR response as a function of reducing agent identity (sodium tri-citrate vs. ascorbic acid) and graphene matrix type (GO vs. RGO), with particular attention to whether plasmonic integrity is preserved upon composite formation and with an explicit perspective on radiosensitization application. This paper addresses that gap.

3. Materials and Methods

3.1 Synthesis of Gold Nanoparticles (AuNPs)

The Turkevich method was performed to produce AuNPs with the help of sodium tri-citrate as a reducing and capping agent [25]. Gold(III) chloride hydrate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$) was dissolved to prepare a 0.25 mM working solution (50 mL). Trisodium citrate (0.0438 g) was dissolved in 5 mL of deionised water to prepare a 34 mM citrate solution. The HAuCl_4 solution was boiled with stirring. The citrate solution was added quickly, and stirring was done until the ruby-red colour was obtained, which indicated the formation of nanoparticles. The size of particles was controlled with a change in the molar ratio of citrate to HAuCl_4 .

A room temperature single-step process that used ascorbic acid as the reductant was also used to prepare AuNPs [26]. The following reaction describes the process,



Stock addition of HAuCl_4 solution to ascorbic acid solution at room temperature resulted in an immediate colour change to red, attesting to the formation of nanoparticles without heating.

3.2 Synthesis of Graphene Oxide (GO)

Graphite powder was used to prepare GO through the Modified Hummers Method [27]. There was a 9:1 (v/v) mixture of H_2SO_4 and H_3PO_4 . KMnO_4 , weighing 1.32 g, was gradually added to the mixture, and then the graphite powder, weighing 0.225 g, was added. The mixture was mixed for 6 h until dark green appeared. The surplus oxidant was reduced by 30% H_2O_2 dropwise addition. Cooling was followed by washing of the product with 1:3 (v/v) HCl /deionised water, followed by centrifugation of the product at 11,000 rpm up to a pH of 6. Drying of the product was carried out at 60 °C for 24 h.

3.3 Synthesis of Reduced Graphene Oxide (RGO)

GO was dispersed in distilled water (1:1, w/v) by sonication. While the ascorbic acid was added as a green reductant, the suspension was stirred at 60°C for 30 min [29]. The product was centrifuged, then washed three times with ethanol and distilled water, and dried at 60°C for 24 h.

3.4 Synthesis of Composite Materials

There were four composites prepared: GO–AuNP (sodium tri-citrate), GO–AuNP (ascorbic acid), RGO–AuNP (sodium tri-citrate), and RGO–AuNP (ascorbic acid). For each composite, 20 mg of GO or RGO was sonicated in deionised water over a 30-min period. HAuCl_4 solution (40 mL) was added to the suspension and shaken (sonicated)

Online ISSN

3007-3197

Print ISSN

3007-3189

<http://amresearchreview.com/index.php/Journal/about>

for 2 h. Under the stirring condition, the reducing agent (8 mL) was added, and the mixture was heated in an oven at 60 °C for 2 h. The mixture was centrifuged and washed in distilled water and ethanol at 7,000 rpm for 6 min and dried at 60 °C [30].

3.5 Characterisation

XRD characterization of GO and RGO was done to confirm the purity of the phase and interlayer d-spacing. Surface morphology was examined using SEM. The pristine AuNPs and the four composites were subjected to UV-Visible spectroscopy at 5 percent and 20 percent in terms of V/V in order to identify the positions of LSPR peaks. D-band and G-band features in all of the composites were characterised by Raman spectroscopy [32]. GO was subjected to TGA/DSC to a maximum temperature of 350 °C.

4. Results

4.1 XRD Analysis

As shown in Figure 1, the XRD analysis of GO showed a prominent (001) diffraction peak at low 2θ , which is consistent with oxygen-intercalated interlayer expansion of 8-9 Å d-spacing. Minor humps around 20°, 30°, and 40° indicate residual ionic species from the H_2SO_4 and H_3PO_4 oxidant system. These peaks are consistent with findings reported by Zaaba et al. [27]. The XRD analysis of RGO, as shown in Figure 2, showed the characteristic (002) peak confirming partial restoration of graphitic stacking, with a residual hump near 43°.

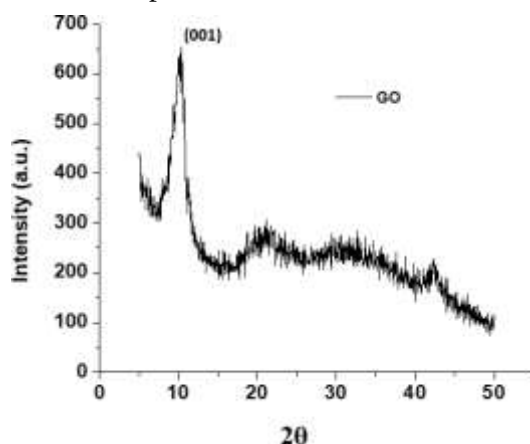


Figure 1: XRD pattern of GO. The (001) peak confirms interlayer expansion; humps at 20°-40° indicate residual acid-derived ionic species

Online ISSN

3007-3197

Print ISSN

3007-3189

<http://amresearchreview.com/index.php/Journal/about>

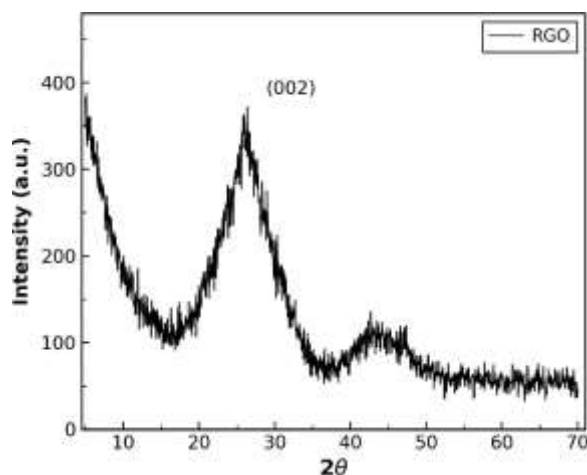


Figure 2: XRD pattern of RGO. The (002) peak confirms partial restoration of graphitic stacking order following ascorbic acid reduction.

4.2 SEM Analysis

Figure 3 shows the SEM analysis of GO. A characteristic layered, sheet-like morphology with partial layer fracture from lattice strain induced by oxygen functional group insertion can be observed. Moreover, the structure is consistent with the previously reported structure for Hummers-derived GO [27,28]. Figure 4 shows the SEM analysis of RGO and it similarly exhibited a layered structure with improved structural integrity, consistent with partial sp^2 network restoration [34].

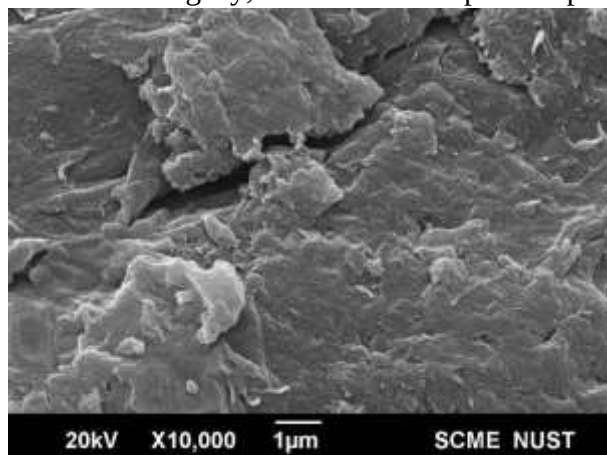


Figure 3: SEM micrograph of GO showing layered sheet morphology with partial layer fracture. Scale bar: 1 μ m.

Online ISSN

3007-3197

Print ISSN

3007-3189

<http://amresearchreview.com/index.php/Journal/about>

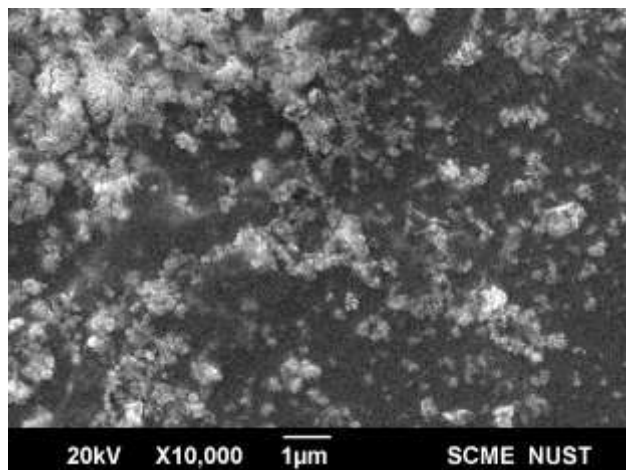


Figure 4: SEM micrograph of RGO showing improved structural integrity relative to GO. Scale bar: 1 μm .

4.3 UV-Visible Spectroscopy

The HAuCl_4 precursor solution showed no LSPR feature, as shown in Figure 5, confirming the unreduced state of the gold salt. The expected LSPR peak at approximately 525 nm for non-aggregated AuNPs in the 20–40 nm size range [31,50] is instead observed in the four composite formulations, as discussed below.

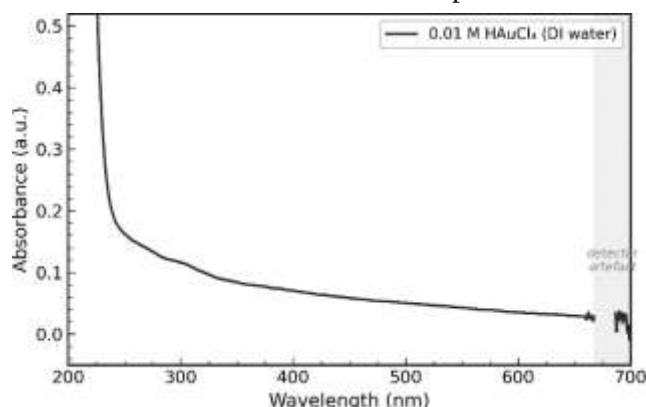


Figure 5: UV-Visible spectrum of HAuCl_4 precursor solution (0.01 M, DI water), showing monotonically decreasing absorbance with no LSPR feature, confirming the unreduced state of the gold precursor

All four composites showed a well-defined LSPR peak retained in the 525–537 nm range, as shown in Figures 6–8. This is consistent with the LSPR position expected for non-aggregated AuNPs in the 20–40 nm size range [31,50]. The preservation of the LSPR peak position across all formulations is independent of reducing agent identity and composite concentration which confirms that AuNPs are successfully deposited on the graphene surface without significant aggregation. Aggregation of AuNPs typically causes a pronounced broadening and redshift of the LSPR peak beyond 600 nm [31]; the absence of such features in all four composites is therefore a positive indicator of colloidal stability and well-dispersed nanoparticle decoration.

Online ISSN

3007-3197

Print ISSN

3007-3189

<http://amresearchreview.com/index.php/Journal/about>

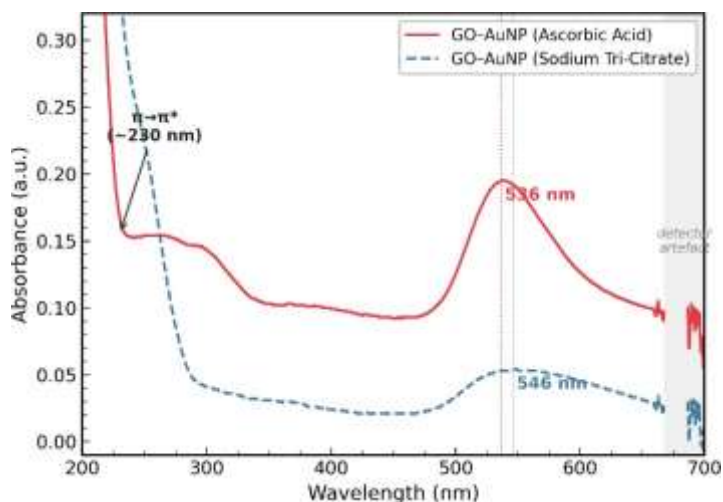


Figure 6: UV-Visible spectrum of GO–AuNP composites (Ascorbic Acid and Sodium Tri-Citrate) showing preserved LSPR peak at approximately 527 nm.

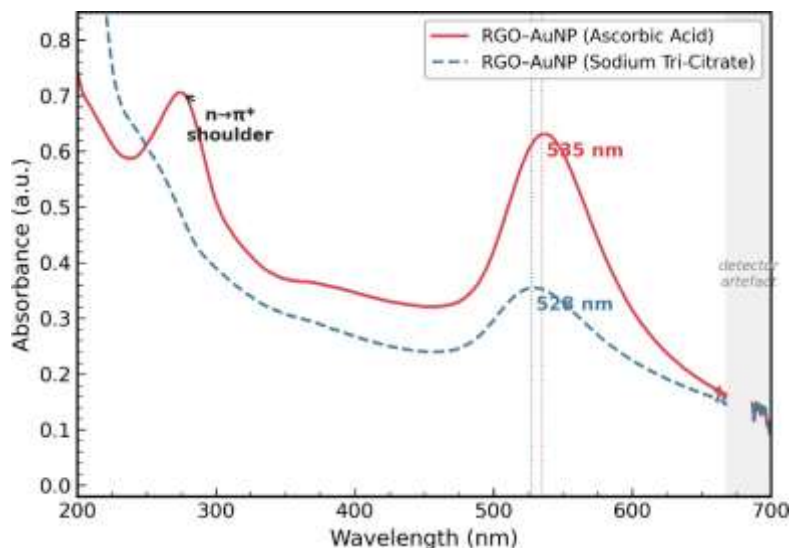


Figure 7: Comparison of UV-Visible spectra of RGO–AuNP composites: sodium tri-citrate vs. ascorbic acid reduction, showing preserved LSPR peaks in the 525–537 nm range and graphene UV signatures below 400 nm.

Online ISSN

3007-3197

Print ISSN

3007-3189

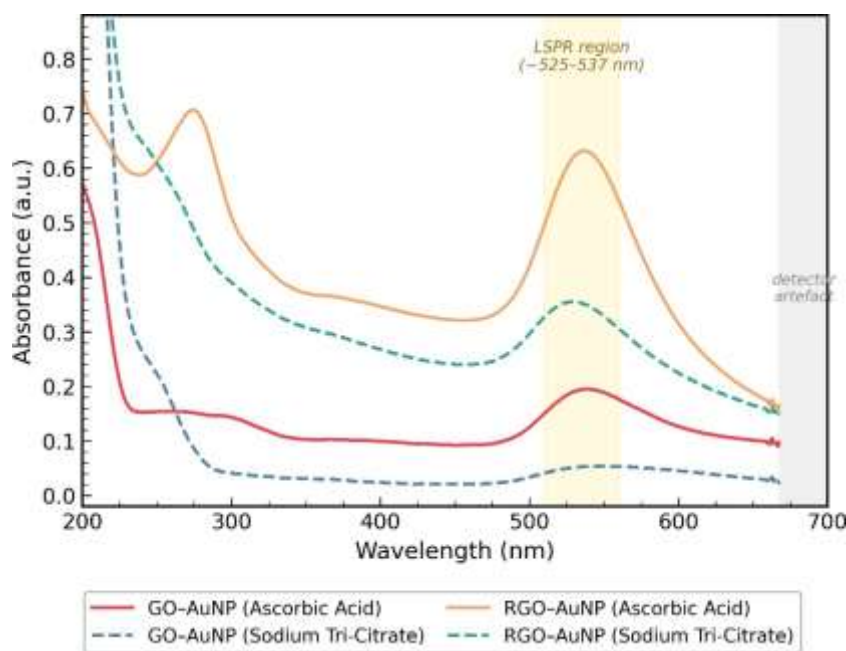
<http://amresearchreview.com/index.php/Journal/about>

Figure 8: Comparison of UV-Visible spectra of GO–AuNP and RGO–AuNP composites: sodium tri-citrate vs. ascorbic acid reduction, showing preserved LSPR peaks and elevated broadband absorbance from the RGO matrix.

It was observed that the peak absorbance intensities were substantially higher in the RGO–AuNP composites compared to the corresponding GO–AuNP formulations. This is attributable to the broadband visible-range absorption of the RGO matrix arising from its partially restored sp^2 conjugation network, which superimposes on the AuNP plasmonic signal [34]. The GO–AuNP composites showed comparatively lower absorbance, consistent with GO's more disrupted carbon lattice and lower visible-range extinction. Below 400 nm, composites retained distinct graphene component signatures: the π to π^* transition near 230 nm in GO and the n to π^* shoulder near 300 nm, and RGO's redshifted, broadened absorption edge characteristic of partial sp^2 restoration [34,52].

4.4 Raman Spectroscopy

Figure 9 shows the Raman spectra of 5% V/V RGO–AuNP composites for both reducing agents. D-band and G-band features are clearly observed at approximately 1320 cm^{-1} and 1601 cm^{-1} , respectively, consistent with published values for graphene-based materials [32]. The D-band intensity exceeds the G-band for both composites, indicating a high degree of lattice disorder. Maximum intensities were approximately 12,950 counts for RGO–AuNP (ascorbic acid) and 4,405 counts for RGO–AuNP (sodium tri-citrate). The higher Raman intensities in the ascorbic acid composite may reflect differences in AuNP distribution and local electromagnetic field enhancement. High D/G ratios are indicative of sp^3 carbon defects and oxygen functional group attachment sites [32]. It should be noted that complete Raman data for GO–AuNP composites could not be acquired over the full spectral range required to resolve the D and G bands, owing to a spectrometer range limitation during data collection. Raman

Online ISSN

3007-3197

Print ISSN

3007-3189

<http://amresearchreview.com/index.php/Journal/about>

characterisation of GO–AuNP composites across the full spectral window is acknowledged as a limitation of the present study and is prioritised for future work.

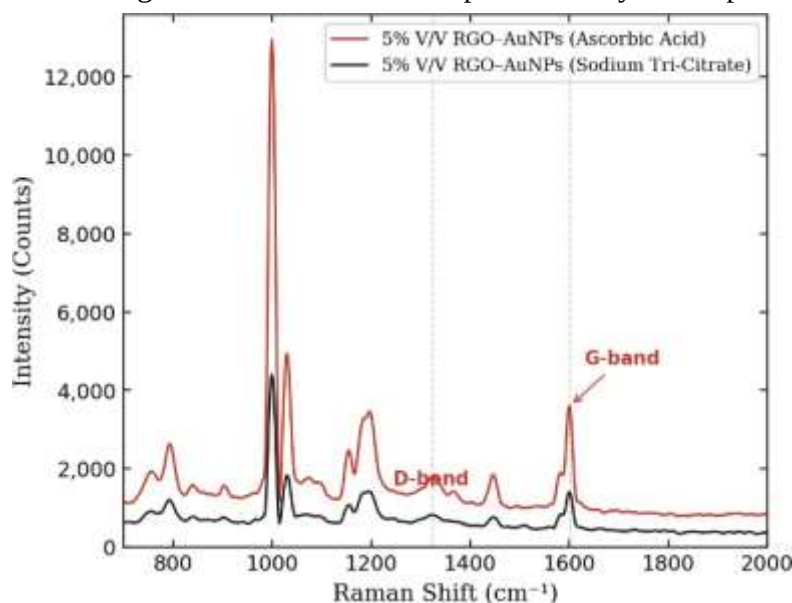


Figure 9: Raman spectra of 5% V/V RGO–AuNP composites (both reducing agents) in the 700–2000 cm^{-1} region, showing D-band ($\sim 1320 \text{ cm}^{-1}$) and G-band ($\sim 1601 \text{ cm}^{-1}$) features.

4.5 TGA and DSC

Figure 10 shows the TGA of GO in which a two-stage mass loss can be observed. Gradual weight loss to around 215 °C corresponds to desorption of physisorbed water and decomposition of labile epoxy/hydroxyl groups. Above 215 °C, sudden mass loss is related to pyrolytic decomposition of stable carbonyl/carboxyl groups with CO/CO₂ evolution [34]. DSC showed maximum exothermic heat flow around 215 °C. GO is thermally stable at the physiological temperature of 37 °C.

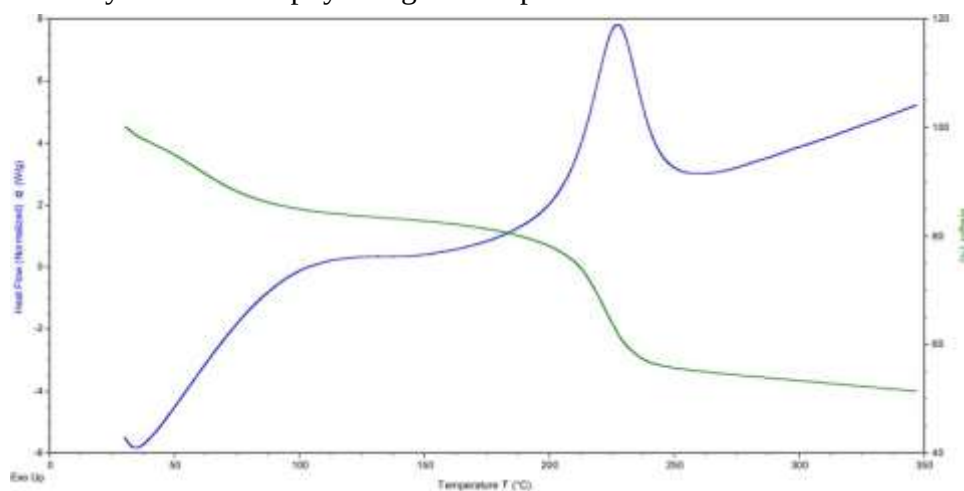


Figure 10: TGA and DSC curves of GO up to 350 °C. Two-stage mass loss and exothermic heat flow are clearly seen to peak around 215 °C

Online ISSN

3007-3197

Print ISSN

3007-3189

<http://amresearchreview.com/index.php/Journal/about>

5. Discussion

The central finding of this study is the preservation of the AuNP LSPR peak at approximately 525–537 nm across all four composite formulations, independent of reducing agent identity and graphene matrix type. This is a significant and practically meaningful result: aggregation of AuNPs — the most common failure mode in nanoparticle–substrate composite synthesis — produces a characteristic broadening and redshift of the LSPR peak beyond 600 nm [31]. The absence of such features in any of the four formulations confirms that the synthesis protocol successfully achieves non-aggregated AuNP decoration of the graphene surface. The invariance of peak position across all conditions further indicates that the plasmonic response is governed by the intrinsic properties of the AuNPs rather than by inter-particle coupling or capping agent interactions.

The substantially higher broadband absorbance observed in RGO–AuNP composites relative to GO–AuNP composites across the visible range is consistent with the partially restored sp^2 conjugation of the RGO lattice, which significantly increases the visible-range extinction coefficient of the graphene component [34,52]. This distinction between GO and RGO composites has practical implications: the higher optical cross-section of RGO–AuNP composites may be advantageous in photothermal applications, while GO–AuNP composites offer a cleaner spectral window around the AuNP LSPR peak, which may benefit LSPR-based biosensing. For the RGO–AuNP composites, the ascorbic acid sample exhibited higher Raman intensities (~12,950 counts at the D-band) compared to the sodium tri-citrate sample (~4,405 counts), which may reflect differences in AuNP surface coverage and associated electromagnetic field enhancement [33]. High D/G ratios in both RGO–AuNP composites confirm the presence of sp^3 defects and oxygen functional group attachment sites in the RGO lattice. These defect sites likely serve as anchoring points for AuNP decoration and do not compromise optical performance, as evidenced by the sharp, well-defined LSPR peaks observed across all UV-Visible spectra.

The data presented by TGA/DSC support the physiological thermal stability of GO that is constant up to 215 °C, much higher than the body temperature of 37 °C. This thermal stability is an important prerequisite for any in vivo application. This sudden loss of mass at temperatures exceeding 215 °C agrees with other frequently reported GO thermal profiles, which are due to quick CO/CO₂ loss of oxygen functional groups during the pyrolysis process [34].

The preserved LSPR peak at approximately 525–537 nm across all composite formulations is located in the visible range where AuNPs are known to generate photoelectrons, Auger electrons, and reactive oxygen species (ROS) upon photon irradiation, which is the mechanistic basis for radiosensitization [5,8,11]. The AuNP–graphene composite platform demonstrated here maintains this plasmonic activity while incorporating a high-surface-area graphene carrier that can be further functionalised with targeting ligands, therapeutic agents, or surface coatings for in vivo delivery [18,19,42]. The thermal stability of GO, confirmed up to 215 °C by TGA/DSC, is well above physiological temperature (37 °C), satisfying a basic prerequisite for biological application [34]. Several limitations of the present study are acknowledged.

Online ISSN

3007-3197

Print ISSN

3007-3189

<http://amresearchreview.com/index.php/Journal/about>

Particle size, morphology, and AuNP distribution on the graphene sheets were not directly characterised by transmission electron microscopy (TEM); the inferred 20–40 nm size range is based on LSPR peak position and literature precedent rather than direct measurement. Colloidal stability and hydrodynamic diameter, which are critical for biomedical translation, were not assessed by dynamic light scattering (DLS) or zeta potential measurements. Additionally, Raman characterisation of GO–AuNP composites over the full spectral window was not achievable within the present study due to spectrometer range constraints. Future research will cover particle size and distribution characterisation using TEM and DLS, in vitro cytotoxicity tests to determine biocompatibility, and irradiation experiments using both X-ray and visible photon sources to quantitatively determine radiosensitization enhancement factors. The structurally and optically characterised composite platform described here provides a well-defined experimental foundation for those studies.

6. Conclusion

This study demonstrates the successful synthesis of GO–AuNP and RGO–AuNP nanocomposites using two reducing agents (sodium tri-citrate and ascorbic acid) and reports the preservation of the AuNP LSPR peak at approximately 525–537 nm across all four composite formulations, independent of reducing agent identity or graphene matrix type. The retention of the LSPR peak position without aggregation-induced broadening or redshift confirms successful non-aggregated AuNP decoration of the graphene surface in all formulations. RGO–AuNP composites exhibited substantially higher broadband visible-range absorbance than GO–AuNP composites, attributable to the partially restored sp^2 conjugation of the RGO lattice. XRD and SEM confirmed the structural integrity and characteristic morphologies of GO and RGO. Raman spectroscopy of RGO–AuNP composites confirmed defect-rich graphene lattices with D- and G-band features at ~ 1320 and ~ 1601 cm^{-1} , respectively; GO–AuNP Raman characterisation over the full spectral range remains to be completed. TGA/DSC confirmed GO thermal stability up to 215 °C, well above physiological temperature. These results establish GO–AuNP and RGO–AuNP composites as structurally and optically well-characterised platforms, with preserved AuNP plasmonic activity upon graphene functionalisation, warranting further investigation as radiosensitization candidates, pending cytotoxicity evaluation and in vitro irradiation studies.

Author's Contribution

Faizan Azmat contributed to the conceptualization of the study, experimental design, synthesis of nanocomposites, UV-Visible and Raman spectroscopy characterization, data analysis, interpretation of results, and original manuscript preparation. Muhammad Umair Arshad performed X-ray diffraction (XRD) analysis and contributed to the structural characterization and interpretation of diffraction data. Aftab Ahmad was responsible for data visualization, including preparation of all figures and graphical representations of experimental results.

Acknowledgement

The authors gratefully acknowledge the Department of Physics, School of Natural Sciences, National University of Sciences and Technology (NUST), Islamabad, for

Online ISSN

3007-3197

Print ISSN

3007-3189

<http://amresearchreview.com/index.php/Journal/about>

generously making their laboratory and characterisation facilities available for this work. The SCME NUST facility is acknowledged for SEM imaging.

Funding Statement

This research did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors.

Conflict of Interest

The authors declare no conflict of interest regarding the publication of this paper.

Data Availability

The data supporting the findings of this study are available from the corresponding author upon reasonable request.

References

- [1] Bray, F., Laversanne, M., Sung, H., Ferlay, J., Siegel, R. L., Soerjomataram, I., & Jemal, A. (2024). Global cancer statistics 2022: GLOBOCAN estimates of incidence and mortality worldwide for 36 cancers in 185 countries. *CA: A Cancer Journal for Clinicians*, 74(3), 229–263. <https://doi.org/10.3322/caac.21834>
- [2] Baskar, R., Lee, K. A., Yeo, R., & Yeoh, K. W. (2012). Cancer and radiation therapy: Current advances and future directions. *International Journal of Medical Sciences*, 9(3), 193–199. <https://doi.org/10.7150/ijms.3635>
- [3] Baskar, R., Dai, J., Wenlong, N., Yeo, R., & Yeoh, K. W. (2014). Biological response of cancer cells to radiation treatment. *Frontiers in Molecular Biosciences*, 1, 24. <https://doi.org/10.3389/fmolb.2014.00024>
- [4] Durante, M., & Loeffler, J. S. (2010). Charged particles in radiation oncology. *Nature Reviews Clinical Oncology*, 7(1), 37–43. <https://doi.org/10.1038/nrclinonc.2009.183>
- [5] Butterworth, K. T., McMahon, S. J., Currell, F. J., & Prise, K. M. (2012). Physical basis and biological mechanisms of gold nanoparticle radiosensitization. *Nanoscale*, 4(16), 4830–4838. <https://doi.org/10.1039/C2NR31227A>
- [6] Her, S., Jaffray, D. A., & Allen, C. (2017). Gold nanoparticles for applications in cancer radiotherapy: Mechanisms and recent advancements. *Advanced Drug Delivery Reviews*, 109, 84–101. <https://doi.org/10.1016/j.addr.2015.12.012>
- [7] Hainfeld, J. F., Slatkin, D. N., & Smilowitz, H. M. (2004). The use of gold nanoparticles to enhance radiotherapy in mice. *Physics in Medicine and Biology*, 49(18), N309–N315. <https://doi.org/10.1088/0031-9155/49/18/N03>
- [8] Jain, S., Hirst, D. G., & O'Sullivan, J. M. (2012). Gold nanoparticles as novel agents for cancer therapy. *British Journal of Radiology*, 85(1010), 101–113. <https://doi.org/10.1259/bjr/59448833>
- [9] Liu, Y., Zhang, P., Li, F., Jin, X., Li, J., Chen, W., & Li, Q. (2018). Metal-based nanoenhancers for future radiotherapy: Radiosensitizing and synergistic effects on tumor cells. *Theranostics*, 8(7), 1824–1849. <https://doi.org/10.7150/thno.22172>
- [10] Zhang, X. D., Wu, D., Shen, X., Liu, P. X., Yang, N., Zhao, B., Zhang, H., Sun, Y. M., Zhang, L. A., & Fan, F. Y. (2011). Size-dependent in vivo toxicity of

Online ISSN

3007-3197

Print ISSN

3007-3189

<http://amresearchreview.com/index.php/Journal/about>

- PEG-coated gold nanoparticles. *International Journal of Nanomedicine*, 6, 2071–2081. <https://doi.org/10.2147/IJN.S21657>
- [11] Chen, Y., Yang, J., Fu, S., & Wu, J. (2020). Gold nanoparticles as radiosensitizers in cancer radiotherapy. *International Journal of Nanomedicine*, 15, 9407–9430. <https://doi.org/10.2147/IJN.S272902>
- [12] Zhang, X., Liu, C., Li, G., Zhao, L., Ma, X., Yang, H., & Zhu, X. (2019). Enhanced radiosensitization by gold nanoparticles with acid-triggered aggregation in cancer radiotherapy. *Advanced Science*, 6(8), 1801806. <https://doi.org/10.1002/advs.201801806>
- [13] Laprise-Pelletier, M., Simao, T., & Fortin, M. A. (2018). Gold nanoparticles in radiotherapy and recent progress in nanobrachytherapy. *Advanced Healthcare Materials*, 7(16), 1701460. <https://doi.org/10.1002/adhm.201701460>
- [14] Butterworth, K. T., Coulter, J. A., Jain, S., Forker, J., McMahon, S. J., Schettino, G., Prise, K. M., Currell, F. J., & Hirst, D. G. (2010). Evaluation of cytotoxicity and radiation enhancement using 1.9 nm gold particles: Potential application for cancer therapy. *Nanotechnology*, 21(29), 295101. <https://doi.org/10.1088/0957-4484/21/29/295101>
- [15] Novoselov, K. S., Geim, A. K., Morozov, S. V., Jiang, D., Zhang, Y., Dubonos, S. V., Grigorieva, I. V., & Firsov, A. A. (2004). Electric field effect in atomically thin carbon films. *Science*, 306(5696), 666–669. <https://doi.org/10.1126/science.1102896>
- [16] Idisi, D. O., Oke, J. A., & Bello, I. (2021). Graphene oxide/Au nanoparticles: Synthesis, properties, and applications: A mini-review. *International Journal of Energy Research*, 45(11), 15993–16010. <https://doi.org/10.1002/er.7073>
- [17] Georgakilas, V., Tiwari, J. N., Kemp, K. C., Perman, J. A., Bourlinos, A. B., Kim, K. S., & Zboril, R. (2016). Noncovalent functionalization of graphene and graphene oxide for energy materials, biosensing, catalytic, and biomedical applications. *Chemical Reviews*, 116(9), 5464–5519. <https://doi.org/10.1021/acs.chemrev.5b00620>
- [18] Liu, L., Ma, Q., Cao, J., Gao, Y., Han, S., Liang, Y., Zhang, T., & Song, W. (2021). Recent progress of graphene oxide-based multifunctional nanomaterials for cancer treatment. *Cancer Nanotechnology*, 12, 18. <https://doi.org/10.1186/s12645-021-00087-7>
- [19] Sharma, H., & Mondal, S. (2020). Functionalized graphene oxide for chemotherapeutic drug delivery and cancer treatment: A promising material in nanomedicine. *International Journal of Molecular Sciences*, 21(17), 6280. <https://doi.org/10.3390/ijms21176280>
- [20] Wong, L. J., Kaminer, I., Ilic, O., Joannopoulos, J. D., & Soljacic, M. (2016). Towards graphene plasmon-based free-electron infrared to X-ray sources. *Nature Photonics*, 10(1), 46–52. <https://doi.org/10.1038/nphoton.2015.223>
- [21] Serafinelli, C., Fantoni, A., & Reymao, M. S. (2018). Effect of graphene layer on the localized surface plasmon resonance (LSPR) and the sensitivity in periodic nanostructure. *Optik*, 163, 100–108. <https://doi.org/10.1016/j.ijleo.2018.01.083>
- [22] Chuang, M. K., Chen, F. C., & Chu, C. W. (2014). Gold nanoparticle-graphene

Online ISSN

3007-3197

Print ISSN

3007-3189

<http://amresearchreview.com/index.php/Journal/about>

- oxide nanocomposites that enhance the device performance of polymer solar cells. *Journal of Nanomaterials*, 2014, 736879. <https://doi.org/10.1155/2014/736879>
- [23] Naeem, H., Ajmal, M., Muntha, S. T., Ambreen, J., & Siddiq, M. (2018). Synthesis and characterization of graphene oxide sheets integrated with gold nanoparticles and their applications to adsorptive removal and catalytic reduction of water contaminants. *RSC Advances*, 8(8), 3599–3610. <https://doi.org/10.1039/C7RA12030C>
- [24] Li, C., Guo, T., Liang, X., Guo, K., & Li, Z. (2020). LSPR optical fiber biosensor based on a 3D composite structure of gold nanoparticles and multilayer graphene films. *Optics Express*, 28(5), 6071–6083. <https://doi.org/10.1364/OE.383793>
- [25] Dong, J., Carpinone, P. L., Pyrgiotakis, G., Demokritou, P., & Moudgil, B. M. (2020). Synthesis of precision gold nanoparticles using the Turkevich method. *KONA Powder and Particle Journal*, 37, 224–232. <https://doi.org/10.14356/kona.2020011>
- [26] Annur, S. (2018). Rapid synthesis of gold nanoparticles without a heating process. *Asian Journal of Chemistry*, 30(11), 2399–2403. <https://doi.org/10.14233/ajchem.2018.21386>
- [27] Zaaba, N. I., Foo, K. L., Hashim, U., Tan, S. J., Liu, W. W., & Voon, C. H. (2017). Synthesis of graphene oxide using modified Hummers method: Solvent influence. *Procedia Engineering*, 184, 469–477. <https://doi.org/10.1016/j.proeng.2017.04.118>
- [28] Surekha, G., Krishnamoorthi, C., Ravi, P., & Santhosh, C. (2020). FTIR, Raman, and XRD analysis of graphene oxide films prepared by the modified Hummers method. *International Journal of Nanoscience*, 19(1–2), 1941026. <https://doi.org/10.1142/S0219581X19410268>
- [29] Rodriguez-Gonzalez, B., Vazquez-Vazquez, C., Garcia-Rio, L., & Solla-Gullon, J. (2020). One-step synthesis of reduced graphene oxide/gold nanoparticles under ambient conditions. *Arabian Journal of Chemistry*, 13(1), 2800–2812. <https://doi.org/10.1016/j.arabjc.2017.07.013>
- [30] Mahesh, V., & Zhitomirsky, I. (2019). Synthesis and characterization of hybrid graphene oxide/gold nanoparticle composites. *Materials Letters*, 255, 126575. <https://doi.org/10.1016/j.matlet.2019.126575>
- [31] Liu, X., Atwater, M., Wang, J., & Huo, Q. (2007). Extinction coefficient of gold nanoparticles with different sizes and different capping ligands. *Colloids and Surfaces B: Biointerfaces*, 58(1), 3–7. <https://doi.org/10.1016/j.colsurfb.2006.03.006>
- [32] Ferrari, A. C., & Robertson, J. (2000). Interpretation of Raman spectra of disordered and amorphous carbon. *Physical Review B*, 61(20), 14095–14107. <https://doi.org/10.1103/PhysRevB.61.14095>
- [33] Muszynski, R., Seger, B., & Kamat, P. V. (2008). Decorating graphene sheets with gold nanoparticles. *Journal of Physical Chemistry C*, 112(14), 5263–5266. <https://doi.org/10.1021/jp800977b>
- [34] Stankovich, S., Dikin, D. A., Piner, R. D., Kohlhaas, K. A., Kleinhammes, A., Jia,

Online ISSN

3007-3197

Print ISSN

3007-3189

<http://amresearchreview.com/index.php/Journal/about>

- Y., Wu, Y., Nguyen, S. T., & Ruoff, R. S. (2007). Synthesis of graphene-based nanosheets via chemical reduction of exfoliated graphite oxide. *Carbon*, 45(7), 1558–1565. <https://doi.org/10.1016/j.carbon.2007.02.034>
- [35] Hummers, W. S., & Offeman, R. E. (1958). Preparation of graphitic oxide. *Journal of the American Chemical Society*, 80(6), 1339. <https://doi.org/10.1021/ja01539a017>
- [36] Marcano, D. C., Kosynkin, D. V., Berlin, J. M., Sinitskii, A., Sun, Z., Slesarev, A., Alemany, L. B., Lu, W., & Tour, J. M. (2010). Improved synthesis of graphene oxide. *ACS Nano*, 4(8), 4806–4814. <https://doi.org/10.1021/nn1006368>
- [37] Jiricková, A., Jankovský, O., Sofer, Z., & Sedmidubský, D. (2022). Synthesis and applications of graphene oxide. *Materials*, 15(3), 920. <https://doi.org/10.3390/ma15030920>
- [38] Song, S., Shen, H., Wang, Y., Chu, X., Xie, J., Zhou, N., & Shen, J. (2020). Biomedical application of graphene: From drug delivery, tumor therapy, to theranostics. *Colloids and Surfaces B: Biointerfaces*, 185, 110596. <https://doi.org/10.1016/j.colsurfb.2019.110596>
- [39] Hoseini-Ghahfarokhi, M., Mirkiani, S., Mozaffari, N., Abdolahi Sadatlu, M. A., Ghasemi, A., Abbaspour, S., Akbarian, M., Farjadian, F., & Karimi, M. (2020). Applications of graphene and graphene oxide in smart drug/gene delivery: Is the world still flat? *International Journal of Nanomedicine*, 15, 9469–9496. <https://doi.org/10.2147/IJN.S265876>
- [40] Maiti, D., Tong, X., Mou, X., & Yang, K. (2019). Carbon-based nanomaterials for biomedical applications: A recent study. *Frontiers in Pharmacology*, 9, 1401. <https://doi.org/10.3389/fphar.2018.01401>
- [41] Yin, T., Liu, J., Zhao, Z., Zhao, Y., Dong, L., Yang, M., Zhou, J., & Huo, M. (2017). Redox-sensitive hyaluronic acid-decorated graphene oxide for photothermally controlled tumor-cytoplasm-selective rapid drug delivery. *Advanced Functional Materials*, 27(14), 1604620. <https://doi.org/10.1002/adfm.201604620>
- [42] Yang, K., Feng, L., Hong, H., Cai, W., & Liu, Z. (2013). Preparation and functionalization of graphene nanocomposites for biomedical applications. *Nature Protocols*, 8(12), 2392–2403. <https://doi.org/10.1038/nprot.2013.131>
- [43] Guo, J., & Guo, S. (2017). Graphene-gold nanostructures. In *Graphene-Based Energy Devices*. Wiley-VCH. <https://doi.org/10.1002/9783527690374.ch4>
- [44] Feng, J., Gao, J., Yang, W., Liu, R., Shafi, M., Zha, Z., Liu, C., Xu, S., Ning, T., & Jiang, S. (2022). LSPR optical fiber sensor based on 3D gold nanoparticles with monolayer graphene as a spacer. *Optics Express*, 30(6), 10187–10198. <https://doi.org/10.1364/OE.453806>
- [45] Turkevich, J., Stevenson, P. C., & Hillier, J. (1951). A study of the nucleation and growth processes in the synthesis of colloidal gold. *Discussions of the Faraday Society*, 11, 55–75. <https://doi.org/10.1039/DF9511100055>
- [46] Daniel, M. C., & Astruc, D. (2004). Gold nanoparticles: Assembly, supramolecular chemistry, quantum-size-related properties, and applications

Online ISSN

3007-3197

Print ISSN

3007-3189

<http://amresearchreview.com/index.php/Journal/about>

- toward biology, catalysis, and nanotechnology. *Chemical Reviews*, 104(1), 293–346. <https://doi.org/10.1021/cr030698+>
- [47] Huang, X., El-Sayed, I. H., Qian, W., & El-Sayed, M. A. (2006). Cancer cell imaging and photothermal therapy in the near-infrared region by using gold nanorods. *Journal of the American Chemical Society*, 128(6), 2115–2120. <https://doi.org/10.1021/ja057254a>
- [48] Dreaden, E. C., Alkilany, A. M., Huang, X., Murphy, C. J., & El-Sayed, M. A. (2012). The golden age: Gold nanoparticles for biomedicine. *Chemical Society Reviews*, 41(7), 2740–2779. <https://doi.org/10.1039/c1cs15237h>
- [49] Amendola, V., Pilot, R., Frascioni, M., Marago, O. M., & Iatì, M. A. (2017). Surface plasmon resonance in gold nanoparticles: A review. *Journal of Physics: Condensed Matter*, 29(20), 203002. <https://doi.org/10.1088/1361-648X/aa60f3>
- [50] Huang, X., Jain, P. K., El-Sayed, I. H., & El-Sayed, M. A. (2007). Gold nanoparticles: Interesting optical properties and recent applications in cancer diagnostics and therapy. *Nanomedicine*, 2(5), 681–693. <https://doi.org/10.2217/17435889.2.5.681>
- [51] Guerrero-Contreras, J., & Caballero-Briones, F. (2015). Graphene oxide powders with different oxidation degrees, prepared by variations of the Hummers method. *Materials Chemistry and Physics*, 153, 209–220. <https://doi.org/10.1016/j.matchemphys.2015.01.006>
- [52] Pei, S., & Cheng, H. M. (2012). The reduction of graphene oxide. *Carbon*, 50(9), 3210–3228. <https://doi.org/10.1016/j.carbon.2011.11.010>
- [53] Kuila, T., Bose, S., Khanra, P., Mishra, A. K., Kim, N. H., & Lee, J. H. (2011). Recent advances in graphene-based biosensors. *Biosensors and Bioelectronics*, 26(12), 4637–4648. <https://doi.org/10.1016/j.bios.2011.05.039>
- [54] Pérez-Jiménez, A. I., Lyu, D., Lu, Z., Liu, G., & Ren, B. (2020). Surface-enhanced Raman spectroscopy: Benefits, trade-offs and future developments. *Chemical Science*, 11(18), 4563–4577. <https://doi.org/10.1039/d0sc00809e>