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FUNCTIONALIZED PLASMONIC NANOPARTICLES: SYNTHESIS, SURFACE ENGINEERING AND EMERGING BIOMEDICAL APPLICATIONS

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ABSTRACT

Functionalized plasmonic nanoparticles have attracted significant attention in biomedical research due to their unique optical properties, high surface reactivity, and versatile surface chemistry. In this study, gold nanoparticles (AuNPs) were synthesized via the Turkevich citrate reduction method and subsequently functionalized using (3-glycidyloxypropyl) trimethoxysilane (GPTMS) to enhance their stability and surface reactivity. The synthesized and functionalized nanoparticles were comprehensively characterized using multiple analytical techniques. Morphological features and particle size distribution were investigated by transmission electron microscopy (TEM) and scanning electron microscopy (SEM), while elemental composition was confirmed by energy-dispersive X-ray spectroscopy (EDS). The crystalline structure was analysed using X-ray diffraction (XRD), and the average crystallite size was estimated using the Scherrer equation. Fourier-transform infrared spectroscopy (FTIR) was employed to identify surface functional groups and confirm successful GPTMS functionalization. Additionally, UV–Vis spectrophotometry was used to evaluate the optical properties of the nanoparticles and to assess their localized surface plasmon resonance (LSPR) behavior. The results demonstrate that the functionalized AuNPs exhibit stable colloidal properties, controlled morphology, and modified optical responses due to surface engineering. The presence of additional absorption features in the UV region highlights the influence of GPTMS on the interfacial environment of the nanoparticles. The obtained results underscore the potential of GPTMS-functionalized gold nanoparticles for applications in nanomedicine, including biosensing, drug delivery, and optical bioimaging.

KEYWORDS: plasmonic nanoparticles; gold nanoparticles; surface functionalization; GPTMS; biomedical applications

1. Introduction

Nanotechnology has significantly transformed biomedical research by enabling the development of materials with size-dependent properties that interact efficiently with biological systems at the molecular and cellular levels. Among these materials, plasmonic nanoparticles - particularly gold- and silver-based systems - have attracted considerable attention due to their unique optical properties, chemical stability, and high biocompatibility [1-3].

The defining feature of these nanostructures is localized surface plasmon resonance (LSPR), which arises from the collective oscillation of conduction electrons under electromagnetic excitation. This phenomenon leads to strong light absorption and scattering which can be precisely tuned by controlling nanoparticle size, shape, and composition [2-4]. Notably, the ability to shift the LSPR into the near-infrared (NIR) region makes these systems particularly attractive for biomedical applications as NIR light exhibits deeper tissue penetration and reduced biological absorption [3, 5].

Recent advances have demonstrated that plasmonic nanoparticles can be engineered for a wide range of biomedical applications, including imaging, biosensing, and minimally invasive therapies such as photothermal treatment [4-6]. However, their performance is determined not solely by the core structure but also by the surface properties which govern interactions with biological environments.

Surface functionalization plays a critical role in enhancing colloidal stability, reducing toxicity, and enabling targeted delivery. Strategies such as ligand conjugation, polymer coating, and silane-based modification have been extensively explored to tailor nanoparticle behavior in complex biological systems [6-8].

In this context, the present work provides a comprehensive overview of the synthesis and solution-chemical surface functionalization of gold nanoparticles, highlighting the role of the silane-based compound (3-glycidyloxypropyl) trimethoxysilane (GPTMS), as well as the biomedical applications of plasmonic nanoparticles with a particular focus on gold-based systems. Special attention is paid to the interplay between structural design, surface functionalization, and plasmonic behavior as well as their implications for next-generation biomedical applications.

2. Experimental procedure

2.1. Synthesis of gold nanoparticles by the Citrate Method (Turkevich method)

Gold nanoparticles (AuNPs) were synthesized via the classical citrate reduction method (Turkevich method [9]), which enables the formation of relatively monodisperse spherical nanoparticles in aqueous media.

Initially, an aqueous solution of chloroauric acid ($HAuCl_4$) with a concentration of 1.0 mM was prepared by dissolving the appropriate amount of precursor in deionized water. Separately, a 1% (w/v) sodium citrate solution was prepared by dissolving sodium citrate in deionized water under continuous stirring.

For the synthesis, the $HAuCl_4$ solution was transferred into a round-bottom flask and heated to approximately 80 °C under constant magnetic stirring to ensure a homogeneous temperature distribution. Once the desired temperature was reached, the sodium citrate solution was rapidly added to the reaction mixture under continuous stirring.

The addition of sodium citrate initiates the reduction of Au^{3+} ions to metallic gold (Au^0), while simultaneously acting as a stabilizing agent. Upon the addition of the reducing agent, the solution undergoes a sequence of colour changes, ultimately turning ruby red, which is characteristic of gold nanoparticle formation and is attributed to localized surface plasmon resonance (LSPR).

The reaction was maintained under heating and stirring until a stable ruby-red colloidal suspension was obtained, indicating the successful synthesis of gold nanoparticles (Figure 1, a-e).

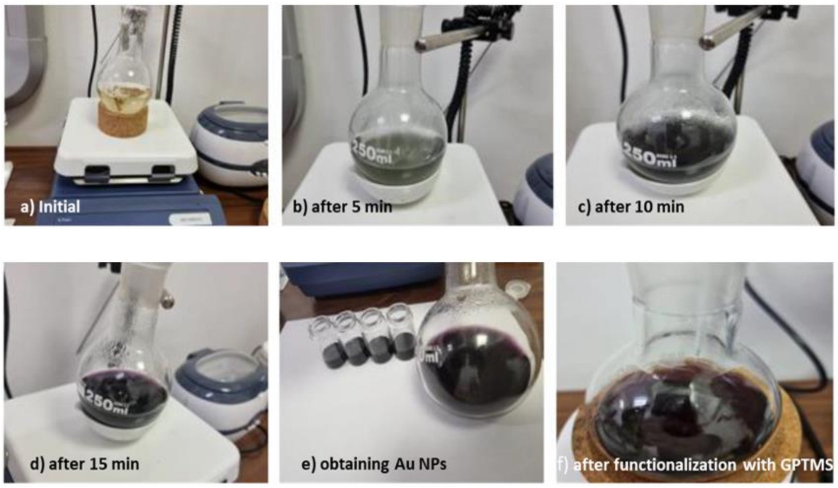


Fig. 1. *Steps of the synthesis of gold nanoparticles functionalized with GPTMS*

Following the formation of gold nanoparticles, the reaction mixture was allowed to cool naturally to room temperature under continuous magnetic stirring. This step ensures the stabilization of the colloidal system and prevents uncontrolled aggregation during temperature equilibration.

Subsequently, the obtained gold nanoparticles were purified to remove excess reagents and by-products. The colloidal suspension was subjected to multiple washing cycles using deionized water followed by centrifugation. After each centrifugation step, the supernatant was discarded and the nanoparticles were redispersed in fresh deionized water. This purification process was repeated several times to ensure the removal of unreacted citrate ions and residual impurities, resulting in a stable and purified nanoparticle suspension.

2.2. Surface Functionalization with GPTMS

Surface functionalization of the synthesized gold nanoparticles was carried out using (3-glycidyloxypropyl) trimethoxysilane (GPTMS) to introduce reactive functional groups and enhance their applicability in biomedical systems (Figure 2).

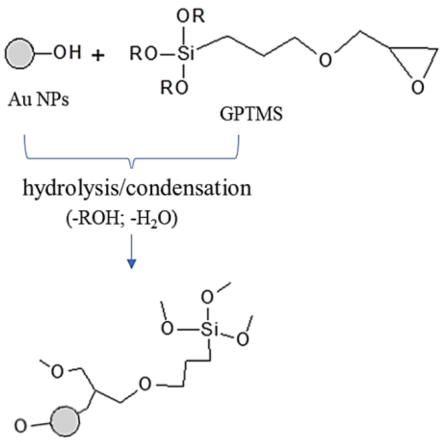


Fig. 2. *Proposed scheme for the functionalization of Au nanoparticles with (3-glycidyloxypropyl) trimethoxysilane (GPTMS)* [10]

A 1% GPTMS solution was added to the purified gold nanoparticle suspension under continuous magnetic stirring at room temperature. The reaction was allowed to proceed for 4 hours to ensure uniform surface coverage of the nanoparticles. During this time, the silane groups of GPTMS undergo hydrolysis and condensation forming a siloxane network on the nanoparticle surface, while the epoxide groups remain available for further functionalization (Figure 2f).

After the functionalization step, the nanoparticles were thoroughly washed multiple times with ethanol followed by deionized water to remove unbound GPTMS and residual impurities. The purified, functionalized nanoparticles were then redispersed in deionized water for further analysis.

2.3. Characterization Techniques

The morphological characteristics of the synthesized nanoparticles were investigated using both transmission electron microscopy (TEM) and scanning electron microscopy (SEM). TEM analysis was performed using a JEOL JEM-1010 instrument to evaluate particle size and morphology at the nanoscale. Samples for TEM were prepared by depositing a few drops of the nanoparticle suspension onto carbon-coated copper grids, followed by drying at room temperature under ambient conditions.

Complementary morphological analysis was carried out using a scanning electron microscope (SEM, Quanta Inspect F, FEI Company). The chemical composition of the samples was determined by energy-dispersive X-ray spectroscopy (EDX), coupled with the SEM system, allowing for elemental analysis and confirmation of the presence of gold in the synthesized nanoparticles.

The crystalline structure of the gold nanoparticles was analysed by X-ray diffraction (XRD) using a Rigaku SmartLab diffractometer (9 kW) with Cu Kα radiation (λ = 0.154 nm) in a parallel beam configuration. Powder X-ray diffraction (PXRD) measurements were conducted in θ–2θ scanning mode.

The average crystallite size was estimated using the Scherrer equation (1):

$$D = \frac{K\lambda}{\beta\cos\theta} \qquad (1)$$

where D represents the crystallite size, K is the shape factor (typically ~0.9), λ is the X-ray wavelength, β is the full width at half maximum (FWHM) of the diffraction peak expressed in radians, and θ is the Bragg diffraction angle.

Fourier-transform infrared (FTIR) spectroscopy was performed using a Bruker Optics Tensor 27 spectrometer to investigate the chemical bonding configuration of the samples. The measurements were carried out at room temperature over the spectral range of 4000–400 cm^{-1}, with 64 scans collected for each sample. The KBr pellet method was employed for sample preparation. The obtained spectra were analysed by assigning the observed absorption bands to the corresponding vibrational modes of the molecular functional groups.

The optical absorption properties of the samples were evaluated using a UV–Vis spectrophotometer (Cary 5000, Agilent Technologies, Santa Clara, CA, USA) at room temperature. The absorption spectra of the gold nanoparticle suspensions were recorded to confirm nanoparticle formation and to assess their optical characteristics.

For gold nanoparticles synthesized via the citrate reduction method in aqueous solution with typical sizes in the range of 20–30 nm, a characteristic localized surface plasmon resonance (LSPR) peak is generally observed around 520 nm.

Following surface functionalization, additional absorption features were detected in the ultraviolet region (250–350 nm), which can be attributed to modifications in the surface chemistry and the presence of functional groups introduced during the functionalization process.

3. Results and discussion

3.1. Morphological and Elemental Analysis (SEM–EDS and TEM)

Energy-dispersive X-ray spectroscopy (EDS) is an analytical technique widely used to determine the elemental composition of materials. It is commonly coupled with scanning electron microscopy (SEM) or transmission electron microscopy (TEM), enabling both qualitative and semi-quantitative analysis as well as spatial mapping of elemental distribution across the sample surface or within its volume. This technique allows the identification of regions with varying elemental concentrations and facilitates correlation with morphological features observed in electron microscopy images.

The particle size and morphology were further evaluated using transmission electron microscopy (TEM) (Figure 3.). The images reveal the formation of gold nanoparticles with sizes ranging between 20 and 30 nm. The nanoparticles exhibit a polydisperse distribution and display a variety of shapes, including spherical, tetragonal, and pentagonal morphologies.

The observed polydispersity reflects variations in both size and shape within the nanoparticle population and is influenced by several synthesis parameters, including precursor concentration, reducing agent, stabilizing agents, pH, and reaction conditions. Higher precursor concentrations may accelerate nucleation and growth processes, leading to a broader size distribution. Additionally, the presence of surface-modifying agents such as GPTMS can influence nanoparticle growth dynamics by selectively interacting with specific crystal facets, thereby affecting both morphology and stability.

As shown in Figure 3, the semi-quantitative EDS analysis confirms the presence of gold as the dominant element in the synthesized samples. The elemental distribution appears relatively homogeneous, indicating a uniform composition of the nanoparticles.

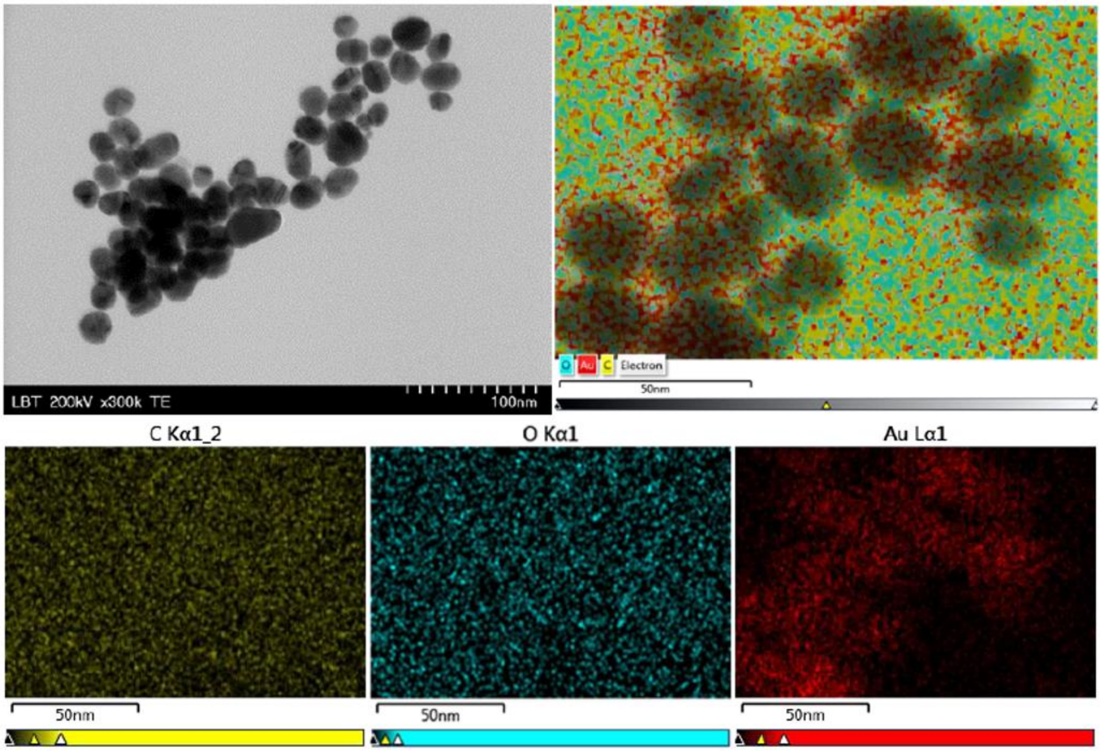
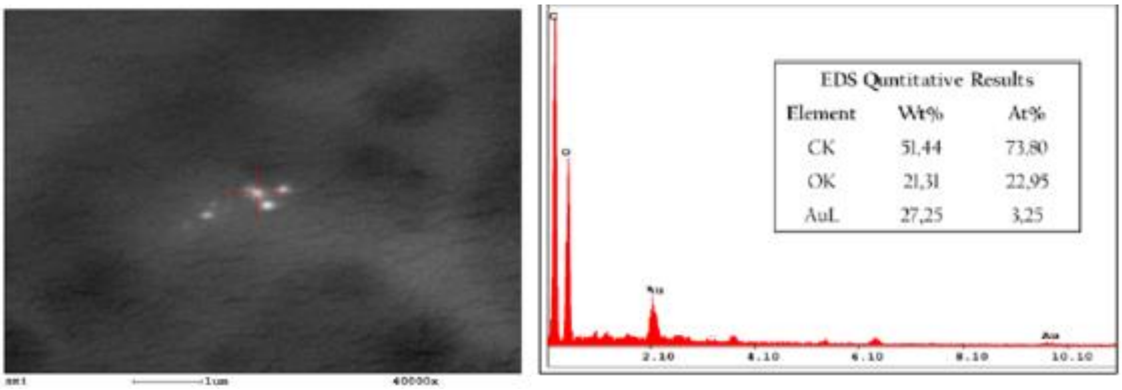


***Fig. 3.** TEM image of gold nanoparticles and EDS analysis of the distribution of chemical elements*

Figure 4 presents point-based EDS analysis where the acquired spectrum was processed using dedicated software to identify characteristic peaks corresponding to the elements present. The presence of gold is further confirmed by the detection of its characteristic peaks at approximately 2.12 keV and 9.71 keV, which are consistent with the known X-ray emission lines of gold.



EDS Qumtitative Results

Element	Wt%	At%
CK	51,44	73,80
OK	21,31	22,95
AuL	27,25	3,25

***Fig. 4.** EDAX analysis for gold nanoparticles*

It should be noted that the signals corresponding to carbon and oxygen detected in the EDS analysis originate primarily from the supporting substrate used during the measurements rather than from the intrinsic composition of the gold nanoparticles.

Overall, the combined SEM–EDS and TEM analyses confirm the successful synthesis of gold nanoparticles, providing insight into their morphology, size distribution and elemental composition.

3.2. Structural characterization of functionalized gold nanoparticles

To evaluate the structural characteristics of the samples studied, X-ray diffraction investigations were performed (Figure 5). The typical diffractogram of gold nanoparticles shows four peaks corresponding to the standard Bragg reflections characteristic of the (111), (200), (220) and (311) planes of the face-centered cubic crystal structure. The peak with the highest intensity at the angle 2θ = 38.1 represents a preferential growth in the (111) direction.

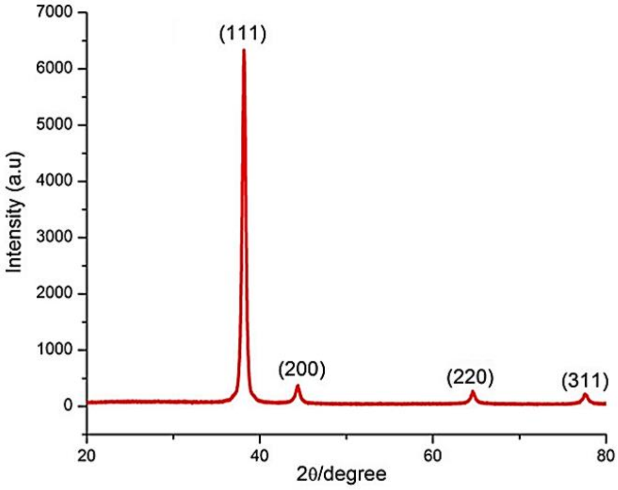


***Fig. 5.** XRD analysis of gold nanoparticles*

Other diffraction peaks corresponding to impurities or sodium citrate were not found, suggesting the high purity of the synthesized nanomaterials.

Figure 6 presents the FTIR spectrum of the synthesized gold nanoparticles. The presence of distinct absorption bands at approximately 3400 cm^{-1} and 2916 cm^{-1} can be attributed to N–H stretching vibrations of primary and secondary amines and C–H stretching vibrations, respectively. These features may also indicate the presence of hydroxyl (-OH) functional groups on the nanoparticle surface.

Additionally, absorption bands observed in the range of 1600–1400 cm^{-1} are associated with O–H bending and stretching vibrations, which can be attributed to surface hydroxyl groups and adsorbed moisture. These findings suggest the presence of surface-bound species and functional groups that may play a role in nanoparticle stabilization and subsequent surface functionalization processes.

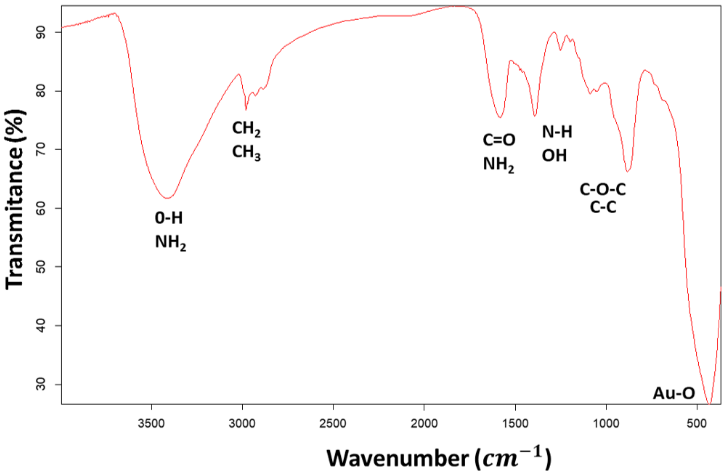


Fig. 6. *FTIR spectrum - Fourier transform infrared spectroscopy of functionalized gold nanoparticles*

A distinct absorption band observed around 1100 cm^{-1} corresponds to Si–O stretching vibrations, indicating the presence of siloxane bonds and suggesting that the silane fragment is successfully anchored onto the surface of the gold nanoparticles [11]. This feature provides strong evidence for the formation of a silane layer following GPTMS functionalization.

Furthermore, the absorption peak located at approximately 820 cm^{-1} can be attributed to Si–O–CH_3 vibrations, characteristic of GPTMS-derived structures [12]. The presence of this band further confirms the successful incorporation of the silane coupling agent onto the nanoparticle surface.

Overall, the FTIR results demonstrate the formation of a hybrid organic–inorganic interface, confirming that GPTMS functionalization was successfully achieved and that reactive functional groups are present on the nanoparticle surface for potential subsequent modifications.

3.3. Analysis of additional SPR bands in GPTMS-functionalized AuNPs

Gold nanoparticles (AuNPs) are well known for their plasmonic properties, which are manifested through localized surface plasmon resonance (LSPR) bands in the UV–Vis spectrum. These optical features arise from the collective oscillation of conduction band electrons induced by an external electromagnetic field, leading to strong and selective light absorption and scattering.

For spherical gold nanoparticles with sizes in the range of 20–30 nm, a characteristic LSPR band is typically observed around 520 nm. However, following surface functionalization with (3-glycidyloxypropyl) trimethoxysilane (GPTMS), additional absorption features were observed in the ultraviolet region, specifically at approximately 230, 270, and 312 nm (Figure 7).

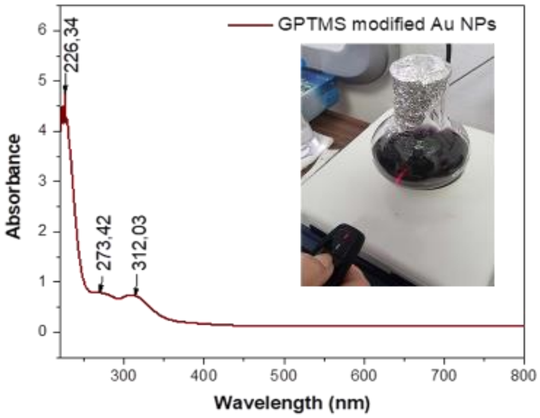


Fig. 7. *UV-Vis absorption spectrum of functionalized gold nanoparticles*

These supplementary bands are not directly associated with the classical plasmonic resonance of gold nanoparticles but rather can be attributed to electronic transitions related to the organic moieties introduced by GPTMS, as well as to interfacial effects arising from nanoparticle–ligand interactions [13]. The attachment of GPTMS onto the nanoparticle surface modifies the local dielectric environment, which can influence the optical response of the system.

Moreover, surface functionalization may promote partial aggregation or clustering of nanoparticles, leading to plasmonic coupling effects. Such interactions between closely spaced nanoparticles can give rise to additional optical features due to dipole–dipole interactions and the emergence of new plasmonic modes. However, these effects should be interpreted with caution as the presence of UV bands alone does not conclusively indicate plasmonic coupling.

The presence of multiple absorption features may also suggest a certain degree of structural and morphological heterogeneity, consistent with the polydisperse nature of the synthesized nanoparticles [14]. Variations in size, shape, and surface chemistry can contribute to the broadening or modification of the optical response.

Importantly, no significant changes in colour or absorption intensity were observed over a period of 45 days, indicating good colloidal stability of the functionalized nanoparticles at room temperature (Figure 7). This stability can be attributed to the presence of surface-bound GPTMS, which provides steric and chemical stabilization.

Overall, the UV–Vis analysis confirms that surface functionalization with GPTMS influences the optical properties of gold nanoparticles, primarily through modification of the interfacial environment and potential nanoparticle interactions, while preserving the overall colloidal stability of the system.

4. Conclusions

Gold nanoparticles (AuNPs) were successfully synthesized using the Turkevich citrate reduction method resulting in particles with sizes below 30 nm and exhibiting a polydisperse distribution. The structural analysis performed by X-ray diffraction confirmed the formation of a face-centered cubic (fcc) crystalline structure, with characteristic Bragg reflections corresponding to the (111), (200), (220), and (311) planes. The most intense diffraction peak observed at $2\theta \approx 38.1°$ indicates a preferential growth orientation along the (111) crystallographic plane.

The formation of gold nanoparticles was initially indicated by the characteristic ruby-red colour of the colloidal solution which arises from the excitation of localized surface plasmon resonance (LSPR). This observation was further confirmed by UV–Vis spectroscopic measurements which revealed the presence of the typical plasmonic absorption band associated with gold nanoparticles in the visible region. Additional absorption features observed in the ultraviolet region (250–350 nm) are attributed to surface functionalization effects and interfacial interactions, rather than intrinsic plasmonic modes.

Surface functionalization with GPTMS was successfully achieved as confirmed by FTIR analysis, indicating the formation of a hybrid organic–inorganic interface on the nanoparticle surface. This modification enhances the chemical versatility and stability of the nanoparticles, enabling further functionalization and integration into complex systems.

Considering their tuneable optical properties, surface adaptability, and demonstrated stability, the synthesized AuNPs represent promising platforms for a wide range of biomedical applications. These include targeted drug and gene delivery, biosensing, detection, and optical bioimaging. The results highlight the importance of controlled synthesis and surface engineering in tailoring nanoparticle properties for advanced applications in nanomedicine.

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