



Tuning of photoluminescence behavior of gold coated chitosan-polyvinyl alcohol binding with graphene quantum dots

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ABSTRACT

In this work, Gold coated Chitosan-Polyvinyl Alcohol binding with Graphene Quantum Dots (Au/CTS/PVA/GQDs) nanoparticles were reported by chemical reduction method. The Au/CTS/PVA/GQDs nanocomposite prepared with various reaction duration further used for physiochemical study. The Fourier Transformation Infrared Spectroscopy (FTIR) and the UV-Vis spectrophotometer were used for further analysis. The FTIR study revealed the hydrogen bonding interaction between PVA polymer and GQDs nanoparticles. In optical properties, photoluminescence study presented blue shift effect for the different reaction time duration. The average size of the nanocomposites was measured by DLS data, and nanoparticle size decreased between 172.2 nm and 134.8 nm with reaction time.

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1. Introduction

Nanomaterials (NPs) have a great interest in bulk materials due to their unique optical, magnetic and electrical properties [1]. The size of nanoparticles reduced below a certain level (>10 nm) changes the magnetic properties, further if drops less than 1 nm, metallic nature vanishes [2]. A quantum mechanical effect changes the physiochemical properties of nanoparticles due to higher surface area comparatively to bulk material [3,4]. However, this effect not observed while going from macro to micro dimensions. Precious nanoparticle catalysis has been presenting great properties in electronics, medicine energy conversion and storage [5–10].

Presently, carbon based material attracting more attention may be due to maximum physical and chemical durability, huge surface to mass ratio and less price [11,12]. The graphene quantum dots (GQDs), is a 0-dimensional carbon structure with several prospective applications in many areas such as energy conversion, biomedical, industrial water usage and optoelectronic devices. Additionally, GQDs have been playing most significant role in optoelectronics properties due to well surface attaching properties due to the p-p conjugated linkages [13–15]. The precious metal (gold,

platinum and silver) nanoparticles are shown the great absorption to visible light property at low size. The Chitosan-GQDs polymer matrix presented the significantly improved the absorption performance [16,17]. For catalysis application, metal nanoparticles are highly used in hydrolyzation reactions, oxidation, C-C coupling reaction, and hydrogenation [18,19]. Now, the Gold nanoparticles are applied in nano biotechnology, biosensor studies, visualization and identification of cell structure, targeted drug delivery system.

Last decades, great efforts have been developed to synthesize nanoparticles using Chitosan, PVA, GQDs, and Gold with various methods. Additionally, size and growth are controlled by changing solvent, PH, reaction temperature, time, and concentration of solution [20]. Siegel et al. prepared the gold nanoparticles by direct sputtering of liquid medium and studied the stability in diluted aqueous solution [21]. Agnihotri et al. reported silver nanoparticles using the chitosan-PVA-based hydrogel matrix for the promising antibacterial applications by repeated freeze-thaw treatment and reported the antibacterial activity [22]. Hajji et al. prepared the CTS-Ag NPs by the electron beam irradiation method and illustrated various medical applications. Further, CTS-Ag NPs exhibited the great response for capped silver nanoparticles [23]. Menazea et al. reported the Au doped PVA/Chitosan (CTS) nanoparticles for different concentrations by laser ablation route. Additionally, The Au NPs presented the best for AC conductivity in electronic use

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[24]. Chen et al. used the green synthesis route and prepared the Au nanoparticles on graphene quantum dots by doping nitrogen (NGQDs). The Au-NPs-NGQDs nanocomposite with high catalytic activity for polluted industrial wastewater [25].

Researchers synthesized metal NPs using various methods like chemical reduction [26], thermal decomposition [27], electrochemical synthesis [28], and sonochemical synthesis [29]. Additionally, Gold-Chitosan NPs as catalysis prepared with different metallic chitosan polymer nanocomposites (NCs) by various reducing salt and acids in aqueous solution [30,31]. Further, reported the synthesis of Chitosan-PEG Nanoparticles [32–35] with carbon dots [36,37] using the stirring method. First time, we reported the gold coated Chitosan-Polyvinyl alcohol (PVA) anchored Graphene Quantum Dots nanocomposite using ascorbic acid as a reducing agent by moderate temperature and stirring. The optoelectronic properties have been studied with change reaction duration between nanocomposites. The structure, morphology and charge of gold nanoparticles was characterized by the Fourier Transform Infrared Spectroscopy (FTIR), Scanning Electron Microscopy (SEM), Ultraviolet-Visible (UV-Vis) Spectroscopy, Photoluminescence(PL), and Dynamic Light Scattering (DLS).

2. Materials

All chemicals were brought from Sigma-Aldrich analytical grade, Gold (III) chloride, citric acid, Polyvinyl Alcohol (Mw 9000–10,000), Chitosan, ascorbic acid, acetic acid, and NaOH. The solution made with double-distilled (dd) water without further purification.

2.1. Synthesis of GQDs and AU/CTS/PVA/GQDS nanocomposite

To synthesis the GQDs, 2 g of citric acid was treated at 433 K to get an orange liquid. Next, 10 mg of NaOH was dissolved in 100 mL water, finally stirred up to yellow solution [38]. The Au/CTS/PVA/GQDs nano composite was synthesized by dissolving the 100 mg Chitosan in 1.0 wt% of acetic acid at 35 °C and stirred for a 5 hr (as organic Phase); 1.0 wt% was PVA added in GQDs solution (aqueous phase) to get 8 mL solution for 1 hr stirring [39]. Organic phase was slowly added to the aqueous phase and make a homogenous solution. For metallic coating, Gold (III) chloride was dissolved and maintained the 338 K temperature through oilbath. Lastly, ascorbic acid was added for reduction process to get tiny particles. Further, the bath was maintained at constant temperature for the different time duration, 2 hrs, 3 hrs, 4 hrs, 5 hrs, 6 hrs and 7 hrs and named as 2 h, 3 h, 4 h, 5 h, 6 h and 7 h, respectively.

2.2. Characterization of nanocomposites

The FTIR (Bruker alpha 100508 series) was used to identify the functional groups of nanocomposites. The SEM (SU 8000 Hitachi) used to study the morphological properties. The optical properties were studied by using UV-Visible spectrophotometer (Shimadzu, UV-1800). The photoluminescence (PL) study of Au/CTS/PVA/GQDs nanocomposite was obtained at excitation wavelength 380 nm. The Zetasizer Nano ZS 90 DLS (Malvern Instruments Ltd., England) system was used to determine the nanoparticle diameter. From average scattered light intensity particle size is reported.

3. Results and discussion

3.1. Fourier-transform infrared (FT-IR) spectroscopy

To obtain the chemical functional group the FT-IR spectra of the nano-composite were studied at room temperature are shown in

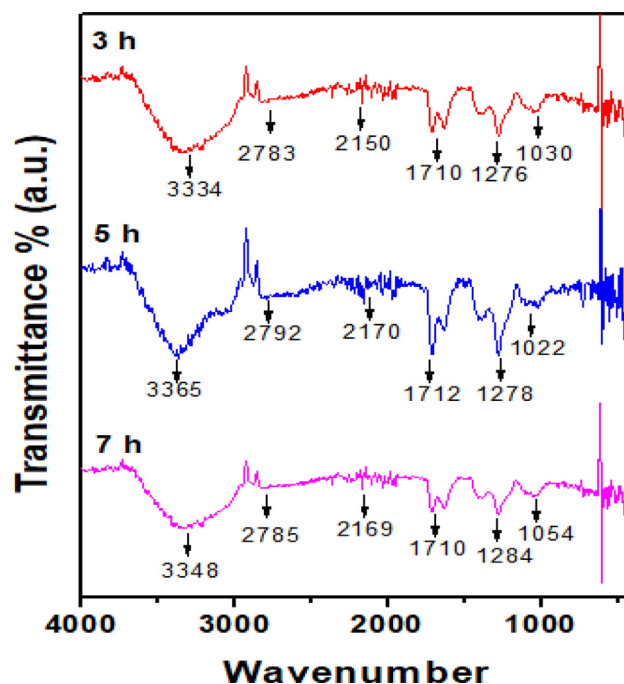


Fig. 1. (a): FT-IR Spectra of nanocomposites with various time duration (3, 5, 7 h). (b): FT-IR Spectra of graphene quantum dots (GQDs).

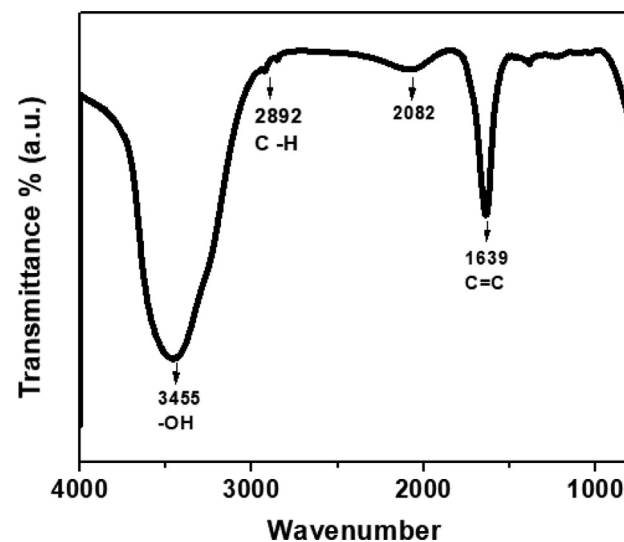


Fig. 1 (continued)

Fig. 1 (a) and (b). The FT-IR spectra of the GQDs shows strong absorption stretching bonds, O-H absorption at 3455 cm^{-1} , C=C at 1639 cm^{-1} and GQD confirmed the hydroxyl, epoxy and carbonyl group [38]. Additionally, the peaks observed at 2892 cm^{-1} and 1382 cm^{-1} consistent to C-H bonds. The sharp peaks obtained at 3348 cm^{-1} bonds of -NH₂ and -OH group [39]. The peak at 2892 cm^{-1} , 1382 cm^{-1} associated to C-H bonds of the GQDs and peak at 285 cm^{-1} linked to -CH₂ stretching of PVA [39] as shown Fig. 1 (b). The chitosan crystallization peak observed at 1054 and 882 cm^{-1} [40].

3.2. Scanning electron microscopy (SEM)

The Fig. 2 shows the surface morphology study for Au/CTS/PVA/GQDs nanocomposite. The nanocomposite shows the particles size

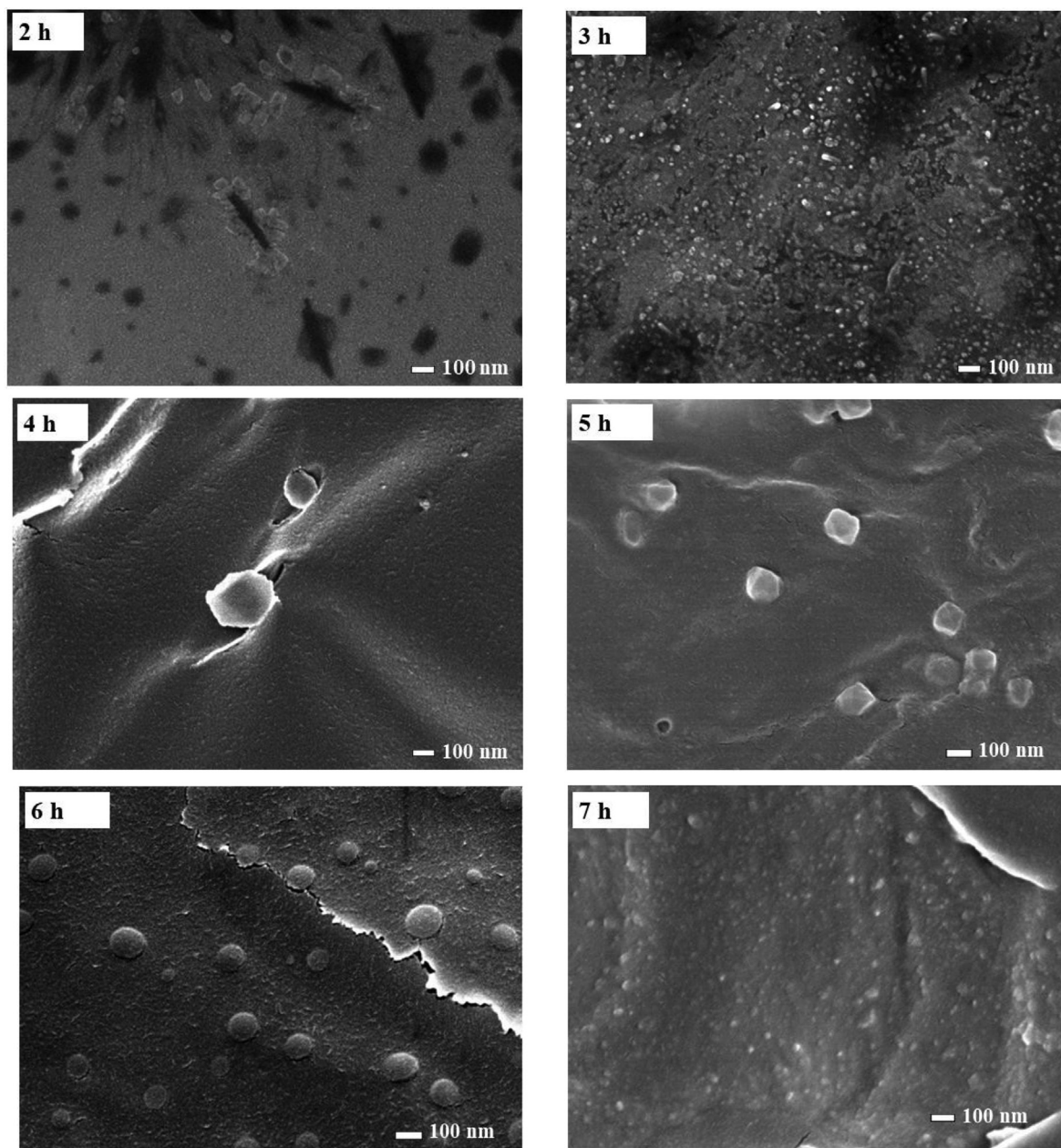


Fig. 2. Scanning electron microscopy (SEM) of nanocomposites for various time duration.

and shapes are changing with time. The nanocomposite of 2 h shows the smooth surface and little white particles are observed for 3 h duration. The Au/CTS/PVA/GQDs nanocomposite for 4 h, 5 h and 6 h reaction time shows the typical size and shaped nanoparticles. These large nanoparticles are produced may be due to the agglomerations of GQDs in the polymer matrix. Further, particle size decreased with increase in time of reaction for 7 h.

3.3. Ultraviolet–visible (UV–Vis) spectroscopy:

The change in light yellow to red brown color results represents formation of AuNPs and confirmed UV spectra. UV–visible spectra of GQDs, Au-Cts-PVA NPs and Au-Cts-PVA-GQDs for various time (2, 3, 4, 5, 6 and 7 h) nanocomposite (Fig. 3 (a) and (b)) GQDs exhibit absorption peak at 340 nm which consistent to $n-\pi^*$ transition of C=O bond [38]. There was a strong absorption peak at around 275–325 nm due to the $n-\pi^*$ transition of C=O, N-H, O-H bond

shows the formation of Chitosan nanoparticles [40]. Further, little blue shift indicates the probability in aspect ratio of AuNPs after binding with GQDs compared with AuNPs cumulative structure. The Au Nanoparticles showed a broad absorbance at a peak value of 485–650 nm. The reaction was studied with 1:1 concentration of gold and chitosan by various time (2, 3, 4, 5, 6 and 7 h) and absorption vs wavelength as shown in Fig. 3(a). The Fig. 3 (b). shows wavelength shift graph with time duration resulted in blue shift with reduction in particle size [41].

3.4. Photoluminescence (PL)spectra

The Fig. 4 shows the photoluminescence study of Au/CTS/PVA/GQDs nanocomposite for the various time duration (2, 3, 4, 5, 6 and 7 h) were collected in photoluminescence at room temperature. PL spectra of Au at 408 nm are reported [41]. However, in this paper, excitation wavelength of Au at 460 nm and Au band appear

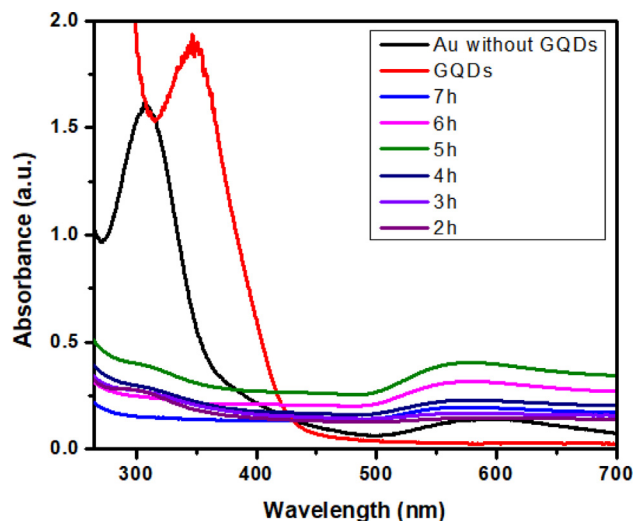


Fig. 3. (a):UV-Vis spectra of GQDs, Au without GQDs and with GQDs for various time duration. (b): Relation between wavelength and time for Au.

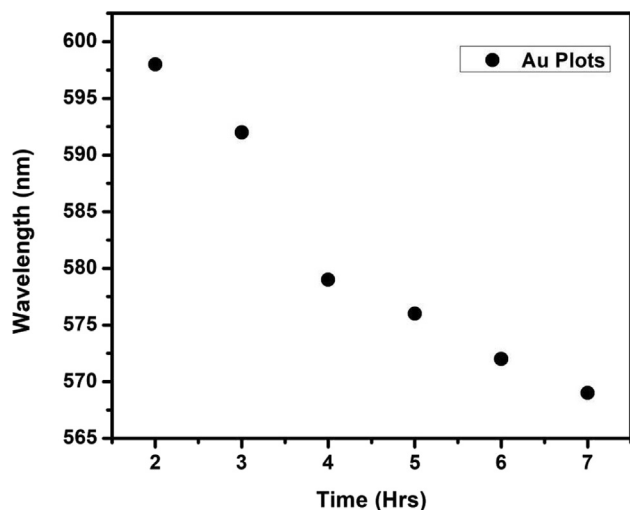


Fig. 3 (continued)

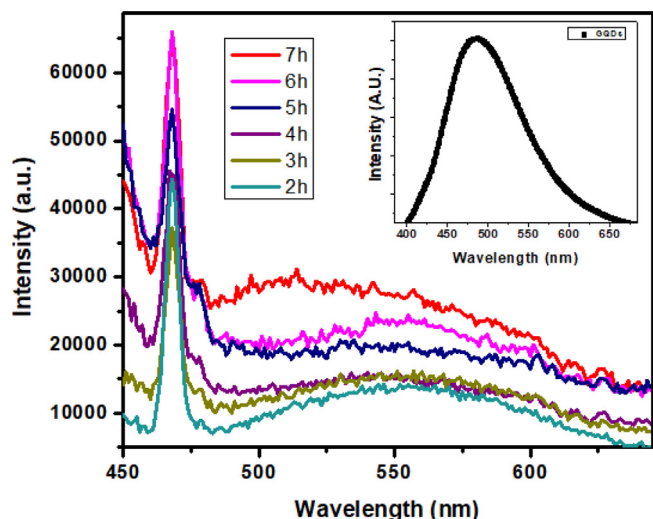


Fig. 4. Photoluminescence (PL) of Au-GQDs nanocomposites for various time duration.

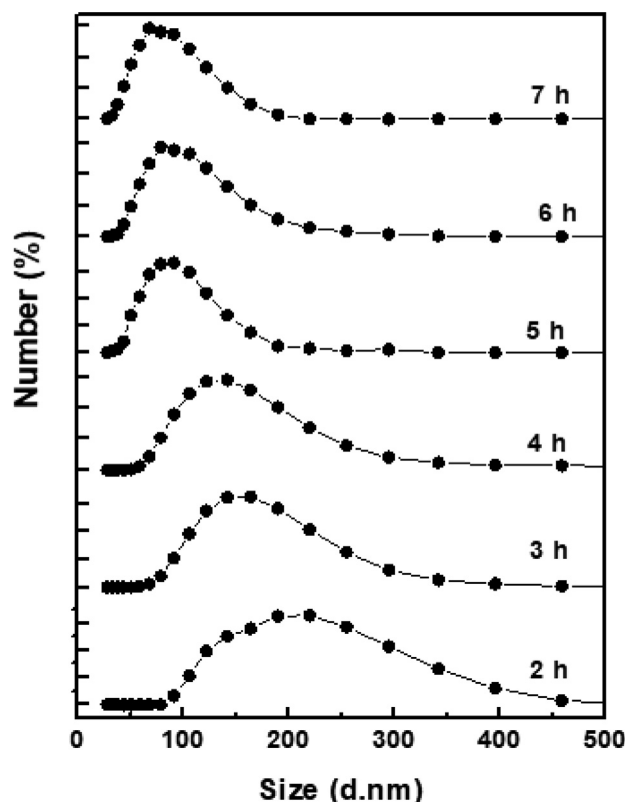


Fig. 5. Intensity-weighted size distribution curves of Au coated Cts-PVA.

Table 1
Dynamic light scattering.

Sample No.	Time (Min)	Temperature (°C)	DLS average particle size (nm)
1	120 min	65 °C	172.2
2	180 min	65 °C	152.4
3	240 min	65 °C	145.5
4	300 min	65 °C	137.9
5	360 min	65 °C	135.7
6	480 min	65 °C	134.8

468 nm were confirmed. In Fig. 4, there is a broad spectrum of Chitosan is excited from wavelength 483 nm. It has been observed as a PL intensity increased with increase in reaction time and in 7 h reaction band center was largely shifted at 534 nm as compared to 2 h reaction which indicates that the particle size was smaller than other reaction. The inset figure shows the typical PL peak of GQDs and shown the blue shift property after reaction with Chitosan [42].

3.5. Dynamic lights Scattering (DLS)

The sizes of the Au/CTS/PVA/GQDs nanocomposite were studied using DLS study as shown in Fig. 5. The nanocomposite prepared at 2 h shows the maximum size of 172.2 nm whereas for 7 h reaction time obtained the minimum size of 134.8 nm. The reduction in size of nanoparticles with time may due to increase in concentration of GQDs with PVA. The average size for all the nanoparticles are shown in Table 1.

4. Conclusions

The chemical reduction method was successfully used to prepare Au/CTS/PVA/GQDs nanocomposite. The FT-IR results con-

firmed all the functional groups in Au/CTS/PVA/GQDs nanocomposite. The absorption spectra represented the presence of formation of Chitosan nanoparticles in nanocomposite. Chitosan-based nanocomposites were shown spherical nanoparticle surface morphology overall. The Au/CTS/PVA/GQDs nanocomposite enhanced the performance towards the photoluminescence with reaction duration and π -conjugated interaction between nanocomposites. The dynamic light scattering (DLS) for Au/CTS/PVA/GQDs characterization exhibited average hydrodynamic diameter between 134.8 and 172.2 nm for nanocomposite. Overall, the physicochemical properties of nanocomposites were totally depending upon reaction time with GQDs and PVA.

CRedit authorship contribution statement

Amol S. Salunke: Writing-Original draft preparation, Methodology. **Shrikrishna T. Salunke:** Reviewing and editing. **Ramesh J. Deokate:** Reviewing and editing. **Bharat B. Kale:** Supervision, Writing, reviewing and editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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