

# Terahertz spectroscopic studies of quantum dots–conjugated gold nanoparticles

## Abstract

Composite structures of metal nanoparticles and semiconductor nanomaterials present unique properties that have made them candidates for various applications. The properties of these hybrid structures to a large extent depend on the design and specific material used in to produce them. Here, we present work on the synthesis and characterization of CdSeS/ZnS quantum-dot–gold nanoparticles hybrids (denoted as QD–GNP) and studies on their interaction with terahertz radiation. The prepared QD–GNPs were characterized using UV–vis spectroscopy (UV–vis), Dynamic Light Scattering (DLS), Transmission Electron Microscopy (TEM), Fluorescence Spectrometry, and Photoluminescence Lifetime measurement. The wavelength of maximum absorption of the gold nanoparticles was 519 nm while that of the quantum dot was 609 nm. The peak absorption band of the hybrid solution was around 519 nm. Transmission electron microscopy imaging revealed the surface morphological features of the quantum dot and gold nanoparticle. Strong photoluminescence quenching was observed upon the conjugation of the quantum dots with gold nanoparticles. The observed difference in the lifetime of free quantum dot and the hybrid QD–GNP was an indication of the bonding between the quantum dot and gold nanoparticles. A biexponential decay was observed with a lifetime of 3.57 ns for bare quantum dots and 1.05 ns for QD–GNP as for the faster component and the slower component 15.09 ns and 8.30 ns QD AND QD–GNP, respectively. Unique features were observed on the terahertz spectra of the composite structures in comparison with that of the either the QD or the GNP.

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## Introduction

Due to their unique electronic properties, quantum dots exhibit broad absorption spectra, size–tunable band gap, narrow and symmetrical emission spectra, tunable and sized–dependent emission wavelengths and long–term photochemical stability.<sup>1</sup> To make soluble in aqueous media, quantum dots are capped with various hydrophilic agents for application in various biochemical systems. Quantum dots have currently been explored for use in immunosassays, in vivo studies and various cellular studies.<sup>2</sup> They have also been employed in FRET studies. Most of the studies on FRET involving the quantum dots also employ other fluorescent agents in which the depending on the wavelength of emission<sup>3</sup> only a few studies has explored the FRET phenomenon in other metallic nanoparticles. There are a few reports in which other metallic nanoparticles actually enhance the fluorescence of quantum mostly due to surface Plasmon. Mostly metal nanoparticle tend to quench the fluorescence of various fluorophore.<sup>4</sup> Quantum dots however have been applied in dye sensitized solar cell in which they acted as dye sensitizers.<sup>5–7</sup>

A number of procedures have been reported for the syntheses of quantum dots.<sup>8</sup> This method of synthesis is usually dependent on the type of quantum dot being synthesized. The synthesis of quantum dot is normally carried out in organic solvent before the ligand exchange is carried out to replace the hydrophobic groups stabilizing them with hydrophilic groups. Hydrophilic ligand in addition enhancing the solubility of the quantum dot also impact the quantum dot the functionality for conjugation with other materials. One of the agents that quantum dot could be conjugated to for various studies is the gold nanoparticles. Gold nanoparticles like quantum dot have unique features that make them versatile for various biomedical applications.<sup>9–12</sup> First their large surface area allows for the attachments of various linkers and agent.<sup>13</sup> This attachment could be hydrophilic

molecules that enhance their solubility in aqueous media. The preparation of gold nanoparticles is flexible and could be synthesized in either aqueous medium or organic medium.<sup>14–16</sup>

This studies focus on the conjugation of gold nanoparticles with quantum dot and energy transfers that occur within them. The conjugate are also characterized by Terahertz spectroscopy. Whereas other forms of electromagnetic radiation have been explored for the studies involving FRET, there is not much of literature on how Terahertz plays in the FRET phenomena. Terahertz spectroscopy is a relatively new field of spectroscopy compared with visible and infrared spectroscopy.<sup>17,18</sup> However, in recent times, the material need for producing and detecting terahertz are becoming abundant and consequently work on the that spectroscopy is also booming. For example, nanostructures<sup>19,20</sup> such as quantum dots and dendrimers<sup>21,22</sup> have been used for the generation and detection of terahertz radiation. These nanostructures are significantly smaller in size than conventional sources of terahertz radiation and thus make terahertz devices compact and relatively low cost.

## Experimental section

### Materials

All chemicals, reagents and solvents used for this report were of analytical grade and were used without further purification. Tetrachloroauric acid trihydrate (HAuCl<sub>4</sub>·3H<sub>2</sub>O) and trisodium citrate (C<sub>6</sub>H<sub>5</sub>Na<sub>3</sub>O<sub>7</sub>) were purchased from Electron Microscopy Services (Fort Washington, PA). The TEM carbon–coated 200 mesh copper grids were purchased from Ted Pella, Inc. (Redding, CA). Doubly purified deionized water from an 18 M Millipore system was used for aqueous solutions. All glassware used for GNPs syntheses was cleaned with freshly prepared aqua regia solution (3 parts HCl, 1

part  $\text{HNO}_3$ ) and rinsed with Milli-Q water ( $\rho > 18 \text{ M}\Omega$ ). Carboxy functionalized CdSeS/Zn quantum dot alloy was purchased from Sigma Aldrich.

### Synthesis of gold nanoparticles

The gold nanoparticles solution was synthesized using a modified protocol reported elsewhere.<sup>14,16,23</sup> The starting materials for the synthesis were gold salt and sodium citrate. A gold salt stock solution was prepared by dissolving 0.1 g of gold salt in 10 mL of pure water. Separately, 5% citrate solution, equivalent to 0.17 M, was prepared by dissolving 0.5 g of sodium citrate in 10 mL of pure water. Part of the gold salt stock solution was further diluted to obtain 100 mL of 0.3 mM solution. In a flask equipped with a magnetic stir bar, the gold salt solution was brought to boil with continuous stirring. Next, 2 mL sodium citrate solution ( $n_{\text{citrate}}/n_{\text{Au}} = 12$ ) was quickly added to the gold salt solution and the mixture kept under continuous stirring for 20 min. During this period the color of solution changed from light yellow to dark grey, purple, and finally deep ruby red. The reaction was then stopped and the solution was cooled to room temperature. Subsequently, the sizes of the gold nanoparticles in this solution were determined using different techniques described below.

### Preparation of gold nanoparticle–quantum dot conjugated (GNP–CdSeS/Zn)

The gold nanoparticle–quantum dot conjugate (denoted as GNP–CdSeS/Zn) was prepared using a method reported earlier by Huang et al (REF) with few modifications. Briefly the carboxy capped CdSeS/Zn was diluted 10-fold and to 1 ml of this solution, 1 ml of the synthesized gold nanoparticle was added. The reaction mixture was subsequently stirred at room temperature for five hours to complete the reaction.

### Characterizations

The size and morphology of the gold nanoparticles (GNPs) were analyzed using Transmission Electron Microscopy (TEM; JEM–1400 Plus) (JEOL USA, Peabody, Massachusetts). The images were viewed using Digital Micrograph software from (Gatan, Inc, Pleasanton, CA). The micrographs were analyzed using Origin software to obtain the mean size of the GNP cores (160 particles were measured) and their associated standard deviations were calculated. The hydrodynamic diameter and size distributions of the GNPs were determined using Dynamic Light Scattering (DLS) (HORIBA, Version LB–550 program). Absorption spectroscopy was carried out with UV–3600 Plus from Shimadzu, MD, USA.

### Fluorescence lifetime measurements

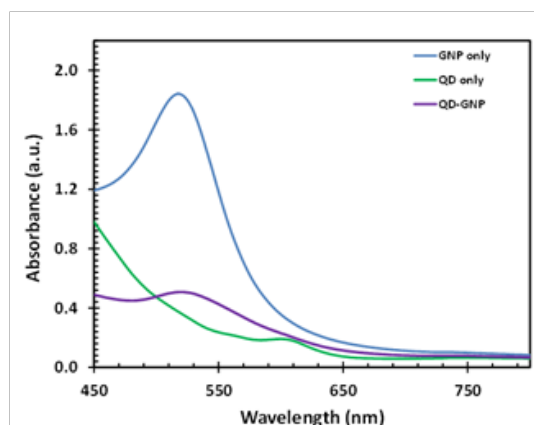
A known concentration of the quantum dots and also the composite hybrid were measured. For each reading, an instrument response (prompt) was run first before measurement of the decay. To prevent inner filter effect, absorption measurements were carried out to ensure the absorbance of the dyes was less or equal to 0.15 absorbance unit. Fluorescence decays were measured using Horiba deltaflex fluorescence lifetime system using the time–correlated single–photon counting (TCSPC) technique with the PPD–850 picosecond photon detection module. The excitation source was 340 nm light–emitting diodes (Delta LED) with 340 nm. The fluorescence decays were fitted to a two–exponential function.

## Results and discussion

The GNP–CdSeS/ZnS used in the investigation was prepared based on an earlier report with few modifications.<sup>24</sup> Firstly, citrate stabilized gold nanoparticles were synthesized following the Frens–Turkevich citrate method with slight modification. Gold salt solution with a concentration of 0.3 mM was brought to boil after which 4 mL of 0.17 M sodium citrate solution was added. The citrate solution served a dual purpose of reducing the gold salt and capping the synthesized gold nanoparticles to keep them from aggregating. The commercially available CdSeS/ZnS was diluted and made to react with the gold nanoparticles. In the process of the reaction, the carboxylic acid capping the quantum dots react with the hydroxyl groups of the of the citrate molecules capping the gold nanoparticles and thus form ester bonds. The reaction is carried out in aqueous solution at room temperature. The quantum dot is positively charged in water due to due to the functional groups while the gold nanoparticles are negatively charged. The synthesized gold nanoparticles and the gold nanoparticle–quantum dot conjugate were characterized using Absorption spectroscopy, dynamic light scattering, and Transmission Electron Microscopy, Steady state Fluorescence, and Fluorescence lifetime measurement.

### Absorption spectrometry

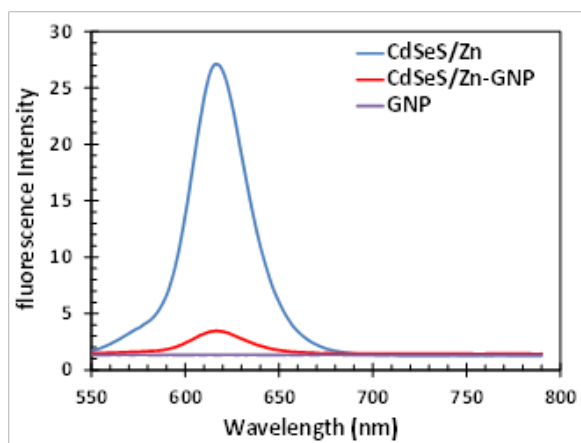
UV–vis absorption spectrometry was used to characterize the gold nanoparticles, CdSeS/Zn quantum dot and the composite CdSeS/Zn–GNP. The optical absorption spectra of these samples were collected and analyzed accordingly. The gold nanoparticles showed a strong absorption of 519 nm in keeping with the absorption band of aqueous gold nanoparticles of that size. Figure 1 shows the UV–vis spectra of the synthesized gold nanoparticles, CdSeS/ZnS quantum dot and the composite CdSeS/ZnS–GNP. The absorption shows the first excitonic transition peak for CdSeS/ZnS quantum dot in aqueous solution to be at 610 nm. The peak absorption of the gold nanoparticles remains unchanged when the quantum dot are added to it. There is however a shift in the absorption maximum of the quantum dots when they are added to the gold nanoparticles. The peak of absorption of the quantum dot located at 610 nm disappear and the peak of the gold nanoparticle on the other hand is enhances. The spectra peak of both gold nanoparticle and quantum dot are consistent with what have already been reported.



**Figure 1** UV-vis spectra of gold nanoparticles (GNP only), quantum dot (QD only) and the hybrid gold nanoparticle and quantum dot (GD-GNP).

## Fluorescence measurements

The Emission characteristic of the gold nanoparticles, CdSeS/ZnS quantum dot and the composite CdSeS/Zn–GNP were measured to investigate their emission characteristics. The spectra were measured in ethanol by scanning the excitation from 500 to 800 nm with fixed excitation at 400 nm. The emission of the quantum dot was quenched when conjugated to the gold nanoparticle to form the hybrid CdSeS/ZnS. The emission peak of both the quantum dot and gold nanoparticle–quantum dot conjugate was located at 620 nm and remain at the same wavelength upon further dilution of the conjugate. The phenomenon of the fluorescence quenching is clearly seen from the fluorescence measurements. The peak of the quantum dot clearly decreases upon the addition of the gold nanoparticles which is as a result of the charge and energy transfer between quantum dot and gold nanoparticles. In addition to the charge and energy transfer processes, non–radiative decays could also cause a decrease in the intensity of the gold–quantum dot conjugates (Figure 2). Others have reported that the fluorescence enhancement could occur when a small amount of the gold nanoparticles is added to the quantum dot solution. It's been shown that when quantum dots are decorated with gold nanoparticles, electrons migrate from the gold to the conduction band of the quantum dots owing to the fact that the work function for gold nanoparticles is lower than that of quantum dots. The attainment of Fermi level equilibration as a result of this leads to an increase in the surface exciton emission. This process eventually results in photoluminescence quenching. Conversely, migration of electrons from gold nanoparticle to quantum dots defects occur when the gold nanoparticles and quantum dot are in close proximity. These enhance the defect–related emission and thus promote photoluminescence quenching as well.

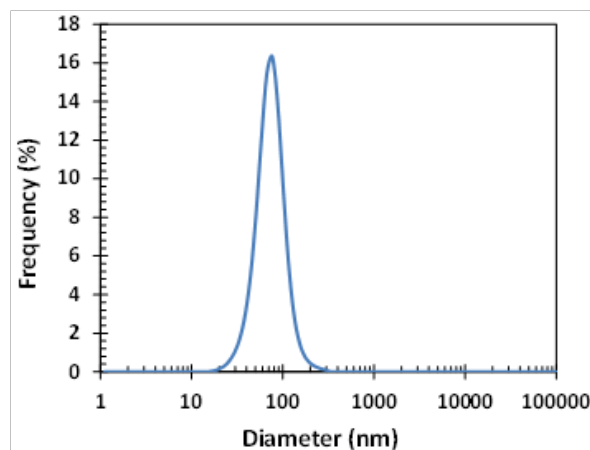


**Figure 2** Fluorescence measurement of gold nanoparticles (GNP), quantum dot (CdSeS/Zn) and the hybrid gold nanoparticle and quantum dot (CdSeS/Zn-GNP).

## Dynamic light scattering

The size of the gold nanoparticles, CdSeS/ZnS quantum dot and the composite CdSeS/Zn–GNP were determined using the dynamic light scattering technique. Thus Dynamic Light Scattering measures the hydrodynamic diameter (HD) or the size of the particles in solution. Particle size obtained using from DLS measurement are usually bigger than those obtained from TEM and FESEM since the electron microscope provides an estimation of the particles in the dry state. Figure 3 shows the DLS measurement of the gold nanoparticles. The

average size of gold nanoparticles as determined by DLS was 22.40 nm with a standard deviation of 4.4 nm. The DLS measurement shows only one peak which is indicative of a homogeneous or monodispersed gold nanoparticles in solution with negligible agglomeration.



**Figure 3** Dynamic light scattering measurement of the hybrid gold nanoparticle and quantum dot (GD-GNP).

## Photoluminescence lifetime measurements

Photoluminescence lifetime measurements were carried out on the free quantum dot and CdSeS/ZnS–GNP composites to study the photoluminescence properties on the samples and to investigate their optical properties. The excitation wavelength of the LED was 340 nm and the photoluminescence lifetime measurements were restricted to the emission peak of the quantum dot. The photoluminescence decays with the impulse response function along with exponential fits are displayed in Figure 3. The photoluminescence lifetimes of the quantum dot were significantly higher than that of the hybrid. The lifetime of bare quantum dots 3.57 ns and that nanocomposite was found to 1.05 ns. The colloidal solution also exhibited a second exponential decay with a fast decay followed by a slower long decay. Thus the lifetime of the CdSeS/ZnS and CdSeS/ZnS–GNP composites shows a significant decrease in the presence of gold nanoparticles compared to the absence of the gold nanoparticles. These results further corroborate with the steady state fluorescence data that quenching is as a result of energy transfer from the CdSeS/ZnS quantum to the gold nanoparticles.

It's been shown that the photoluminescence intensity of the quantum dot–gold nanoparticles hybrid is dependent on the photoluminescence quenching due to the energy and the charge transfer between and the quantum dot or other non–radiative processes. It is also dependent on the enhancement due to the enhanced absorption and radiative rate that is by the localized surface plasmon resonance (LSPR). There the photoluminescence of the hybrid of gold nanoparticle CdSeS/ZnS is therefore the competing results of the two aforementioned processes.

According to studies reported earlier, the energy transfer efficiency of the quenching resulting from energy transfer from CdSeS/ZnS to gold nanoparticles is given by the equation illustrated below:

$$E = 1 - \left( \frac{\tau_{DA}}{\tau_D} \right) \quad (1)$$

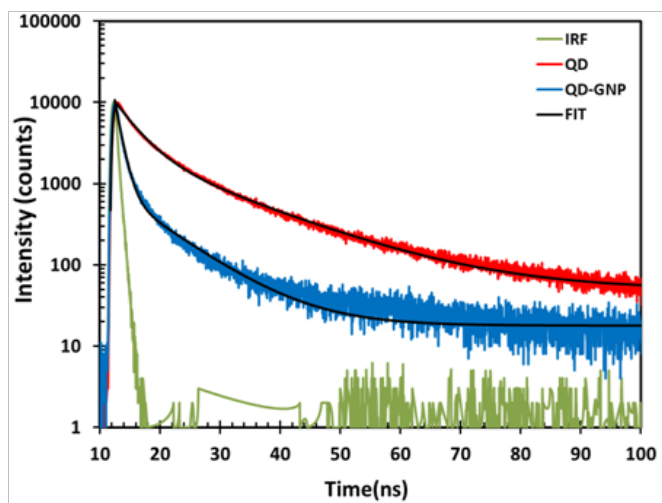
$\tau_D$  and represent the lifetimes of the CdSeS/ZnS quantum dot in the absence of the gold nanoparticle and  $\tau_{DA}$  represent the lifetime of



CdSeS/ZnS quantum dot in the presence of the gold nanoparticles. In carrying out the analysis, the decay time as the fluorescence intensity drops to  $1/e$  is applied. Therefore with  $\tau_D$  being 3.57 and  $\tau_{DA}$  being 1.05 ns, the energy transfer efficiency is computed to be 87%. The biexponential obtained for the quantum dots in the presence and in the absence of the gold nanoparticle or quencher shows the faster and slower component. Qin et al.,<sup>25</sup> proposed that the faster component of the lifetime trace is due to the trion photoluminescence of charged QDs and the slower decay originates from the he photoluminescence of neutral QDs, the relative ratio of which can be tuned by electrochemistry.<sup>25</sup> Trion lifetime traces could be obtained by subtracting the exponential trace extrapolated from long times (Figure 4). CdSeS/ZnS QDs shows a trion decay evidently slower, with a lifetime of 8.17 ns. Others have concluded that the CdSeS/ZnS QDs have a slower trion decay rate than CdSe/ZnS QDs, which is consistent with the slower biexciton recombination rate (Table 1).

**Table 1** Fluorescence Lifetime Measurement of CdSeS/Zn Quantum dot (QD), and CdSeS/ZnS conjugated with gold nanoparticle (QD-GNP) in aqueous media

Sample name	Lifetime (ns)	
	$\tau_1$	$\tau_2$
QD	3.57	15.09
QD-GNP	1.05	8.3

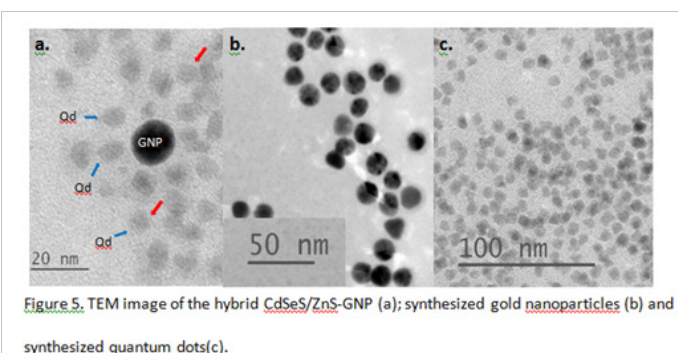


**Figure 4** Photoluminescence decay of quantum dot (QD only) and the hybrid gold nanoparticle and quantum dot (GD-GNP) measured with 340 nm excitation beam. The fluorescence lifetime for hybrid was 1.78 ns and that of only quantum dot was 8.17 ns.

### Transmission electron microscopy

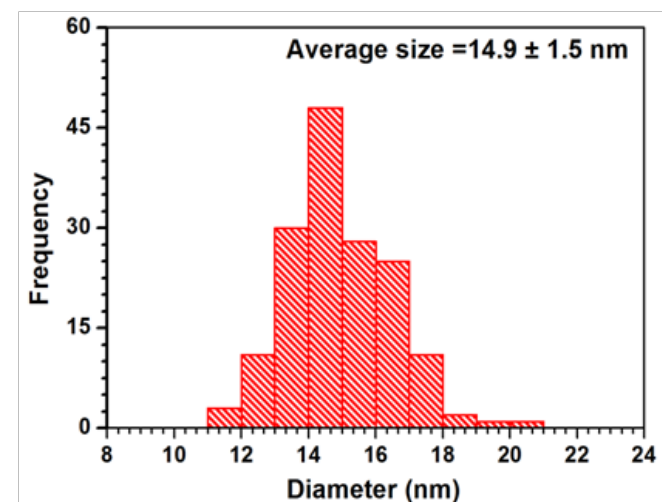
The quantum dot, citrate stabilized gold nanoparticles and the hybrid CdSeS/ZnS–GNP were further characterized by transmission electron microscopy to obtain the size distribution of the particles. To carry out the TEM imaging, a drop of each of quantum dot, citrate stabilized gold nanoparticles and the hybrid CdSeS/ZnS–GNP were each dropped on a carbon-coated copper grids and each sample dried overnight. In general the gold nanoparticles are darker in color than the quantum dots. This could be attributed to the higher density of the gold and also the large size of the gold nanoparticle compared to

the quantum dots. Figure 5 shows a representative TEM images of hybrid CdSeS/ZnS–GNP (a) synthesized gold nanoparticles (b) and synthesized quantum dots (c). The gold nanoparticles, dark in color, are seen surrounded by quantum dots which are lighter in color. The distance between the attached QDs and the gold nanoparticle is below 3 nm as shown in the Figure 6. In addition, the typical crystal patterns were clearly observed from some QDs around the gold nanoparticle (the red arrow marks). The average size of the gold nanoparticles calculated from 160 particles was 14.9 nm with a standard deviation of  $\pm 1.5$  nm. The average size of the quantum dot was about 6 nm. All the three types of nanoparticle were moderately monodisperse particles.



**Figure 5** TEM image of the hybrid CdSeS/ZnS-GNP (a); synthesized gold nanoparticles (b) and synthesized quantum dots (c).

**Figure 5** TEM image of the hybrid CdSeS/ZnS-GNP (a); synthesized gold nanoparticles (b) and synthesized quantum dots (c).



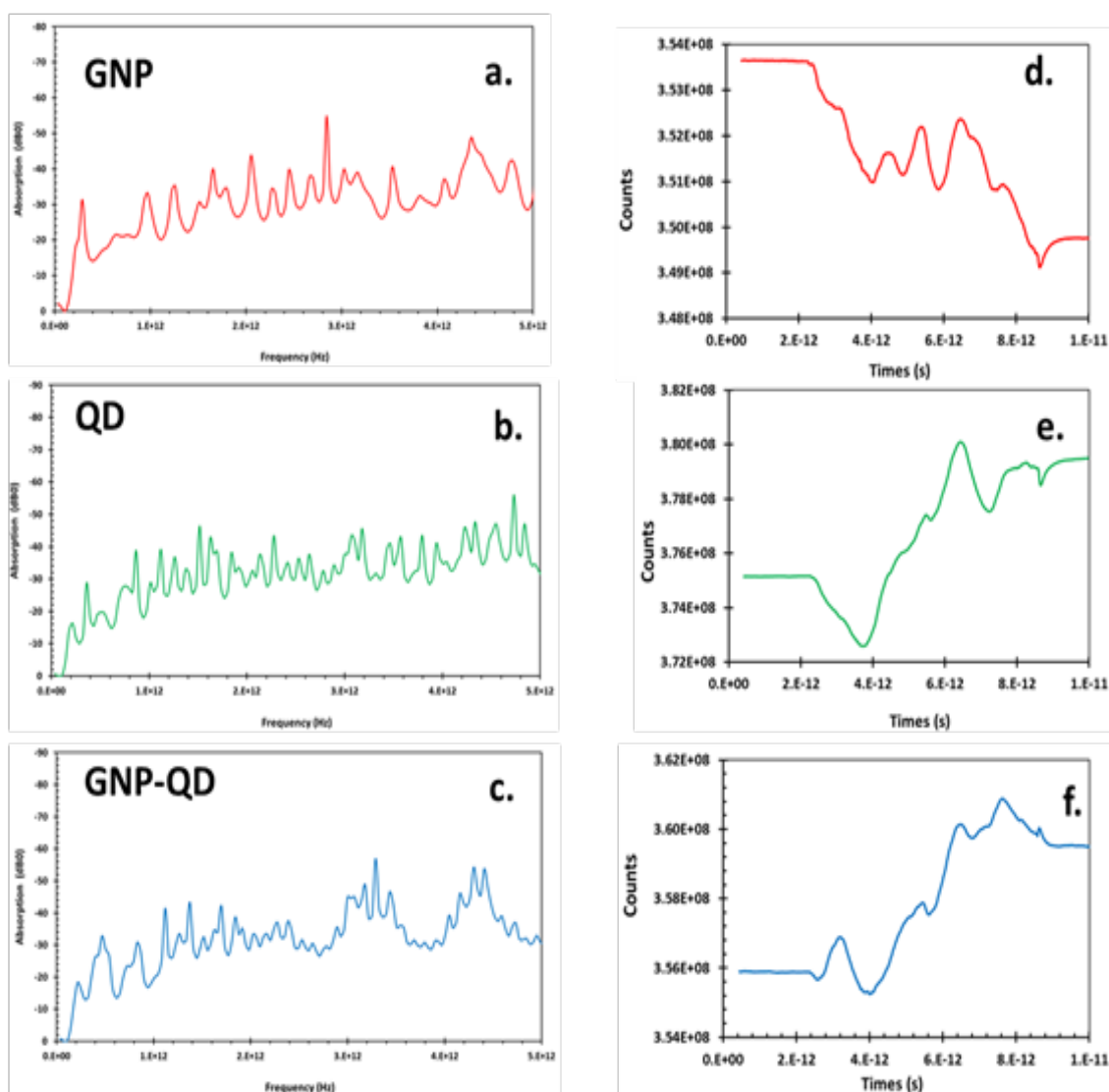
**Figure 6** Histogram of gold nanoparticle size distribution.

### Terahertz studies

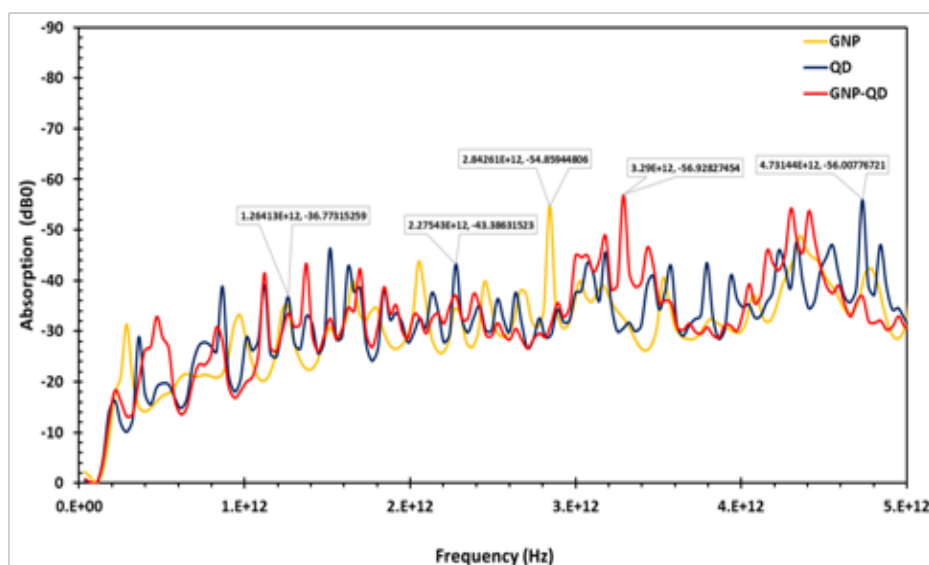
In this work, we used terahertz spectroscopy to investigate energy transfer processes between the CdSeS/ZnS quantum dots with gold nanoparticles. Terahertz was the least popular of all regions of the electromagnetic spectrum. The reasons being that Spectroscopic features in the terahertz regime are inadequate for most materials. Their long wavelength in comparison with the wavelength of most important biological structure also limits its application in biology and medicine. Terahertz is known to be very sensitive to water which could sometime make it difficult to analyze biological samples. With new technologies, terahertz has become a non-invasive technique for probing vibration modes of various materials and the timescales for

various processes. Energy transfer between quantum dots (QDs) and gold nanoparticle has been studied and in the visible region of the electromagnetic spectrum. Our goal was to determine if the samples under consideration could exhibit electromagnetic responses and also to study the relationship between the responses and the how the transfer of energy could be characterized using the terahertz spectroscopic techniques. To probe the energy transfer, terahertz spectra was acquired for gold nanoparticles, quantum dots and gold nanoparticle–quantum dot conjugates. Figure 7 shows the time-domain temporal signal for gold nanoparticle, quantum dot, and gold nanoparticle–quantum dot conjugate and their corresponding Fourier transform broadband terahertz absorbance spectra. The time-domain temporal signals are first measured and the resulting data are Fourier transformed to determine phonon vibrational modes absorption frequencies of the samples. An overlay of all three samples show

unique strong absorption peaks for each of the samples at different wavelength. Gold nanoparticles show a prominent peak at 2.84 THz and another peak at around 2.15 THz. The quantum dot spectra on the other hand show prominent peaks at 4.73 THz and around 0.8 THz. In the spectra of the conjugate overlaid with gold nanoparticle and quantum dot, some overlapping peaks are overserved. These overlapping peaks occur at 1.26 THz and 2.28 THz. There were also unique peaks for just the gold nanoparticles–quantum dot with the prominent of them occurring at 3.29 THz. It is been shown that quenching of quantum dot in the presence of gold nanoparticles is dependent on the spectra overlap of the separation distance between the quantum dot and gold nanoparticles.<sup>26,27</sup> Therefore by using terahertz, it could be possible to study the extent of overlap that result in the quenching of the emission of quantum dot.



**Figure 7** Time-domain temporal signal (d–f); its corresponding Fourier transform broadband terahertz absorbance spectra (a–c) of gold nanoparticle (a,d) quantum dot (b,e) and gold nanoparticle–quantum dot conjugate (c,f).



**Figure 8** Fourier transform frequency spectra of three samples (gold nanoparticles, quantum dot and gold nanoparticle-quantum dot conjugate) showing distinct absorbance characteristics.

## Conclusion

Energy transfer has very important application in various scientific fields. Most of the energy transfer studies involve the use of two different fluorophores— a donor and an acceptor. This study focuses on the synthesis and characterization of CdSeS/ZnS quantum dot–gold nanoparticles hybrids (denoted as CdSeS/ZnS–GNP) and their interaction with terahertz radiation. The prepared CdSeS/ZnS–GNP hybrids were characterized using UV–vis spectroscopy (UV–vis), Dynamic Light Scattering (DLS), Transmission Electron Microscopy (TEM), Fluorescence Spectrometry and Photoluminescence Lifetime measurement (Figure 8). The wavelength of maximum absorption of the gold nanoparticles was 519 nm while that of the quantum dot was 609 nm. The peak absorption band of the hybrid solution was around 519 nm. Transmission electron microscopy and imaging revealed interaction between the quantum dot and gold nanoparticle. Strong photoluminescence quenching was observed upon the conjugation of the quantum dots with gold nanoparticles. The observed Lifetime difference in the lifetime of free CdSe/ZnS quantum dot and the CdSeS/ZnS–GNP is indicative of the bonding between the quantum dot and gold nanoparticles. The lifetime of bare quantum dots was 8.17 ns and that nanocomposite was found to be 1.78 ns. The unique terahertz signal of the unconjugated gold nanoparticles and quantum dots versus the conjugated forms shows that terahertz could be used to characterize such material. The result indicate that the hybrid gold nanoparticle and quantum dot will have great potential for other optical application.

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## Conflict of interest

Author declares there is no conflict of interest.

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