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Polyethyleneglycol diacrylate hydrogels with plasmonic gold nanospheres incorporated via functional group optimization

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Abstract

We present a facile method for the preparation of polyethyleneglycol diacrylate (PEG-DA) hydrogels with plasmonic gold (Au) nanospheres incorporated for various biological and chemical sensing applications. Plasmonic Au nanospheres were prepared ex situ using the standard citrate reduction method with an average diameter of 3.5 nm and a standard deviation of 0.5 nm, and evaluated for their surface functionalization process intended for uniform dispersion in polymer matrices. UV-Visible spectroscopy reveals the existence of plasmonic properties for pristine Au nanospheres, functionalized Au nanospheres, and PEG-DA with uniformly dispersed functionalized Au nanospheres (hybrid Au/PEG-DA hydrogels). Hybrid Au/PEG-DA hydrogels examined by using Fourier transform infra-red spectroscopy (FT-IR) exhibit the characteristic bands at 1635, 1732 and 2882 cm^{-1} corresponding to reaction products of OH^- originating from oxidized product of citrate, $-\text{C}=\text{O}$ stretching from ester bond, and $\text{C}-\text{H}$ stretching of PEG-DA, respectively. Thermal studies of hybrid Au/PEG-DA hydrogels show three-stage decomposition with their stabilities up to 500 °C. Optical properties and thermal stabilities associated with the uniform dispersion of Au nanospheres within hydrogels reported herein will facilitate various biological and chemical sensing applications.

Keywords: Au nanospheres, Functional groups, Hydrogels, Plasmonic, Polyethyleneglycol diacrylate (PEG-DA)

Background

The field of materials science has been developing steadily over the years, and has today become invaluable in helping us to reach the scientific horizons by providing solutions for bio-medical, sensors, catalysis, pharmaceutical, petrochemical, and mechanical industries, to name a few [1]. An avenue of research that has progressed a great deal in the past few decades in the chemo-sensors via hybrid nanostructured materials by integration of organic, inorganic and biomolecules [2]. Initially, these could only be administered in scant manner, partially due to their limitations in material characterizations and real time applications. Whereas in the current scenario, advancement in analytical instrumentation had made a new paradigm in the development of hybrid materials, which is smart, enough to sense the external stimuli

and respond rapidly thus enables the easy access towards hazardous environments [3]. Promising candidates include hydrogel-based hybrid materials, which possess exceptional sensitivity, selectivity, and stability for various external stimuli especially toxic and hazardous gases [4]. As hydrogels replicate the natural systems existing inside the biological organism with three-dimensional (3D) structures, they can be more sensitive towards certain external environments with very high degree of responsivity and selectivity in general. These 3D polymer matrices are capable of imbibing large amounts of water, chemical moieties, large molecules, drugs and biological fluids [5]. The aforementioned properties of hydrogels are the main reasoning behind their diverse applications ranging from sensors, drug delivery, food additives to pharmaceuticals and clinical applications [5, 6]. Synthetic hydrogels provide an effective and controlled way to incur selective target chemical analytes which administer chemo-sensing. The special chemical moieties were used

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to selectively pick up the hazardous molecules thereby altering their mechanical, optical, electrical, and calorimetric signals which can be read out once integrated with microelectromechanical systems (MEMS) devices [7]. Preparing such smart polymeric hydrogels for sensing applications can be achieved by combining inorganic/organic networks of 3D materials with higher degree of stability obtained via cross-linking. However, the addition of polymer layers with inorganic materials such as Au, platinum (Pt), zinc oxide (ZnO), iron oxide (Fe_2O_3) etc., can alter the intrinsic properties of the resulting functional inorganic particles [8]. Polymer hydrogel with 3D support should provide enhanced molecular interactions with the functional inorganic materials, thereby creating a hydrophilic environment with more favorable solution kinetics [9]. These kinds of highly oriented molecular interactions were achieved by utilizing the structural property relationship of nanostructured materials *in-lieu* with their synthetic strategy. It was reported that, anisotropic nanostructures with controlled dimensions and additional functionalities would improve the intrinsic properties of the hybrid materials and make them efficient chemo-sensors [8, 9].

One inorganic material used extensively as chemo-sensors is Au, owing to its high catalytic and sensitization phenomenon [10]. Perhaps, its well-established synthesis procedure for uniform, structural and anisotropic nanostructures with high surface-to-volume ratio makes them well suited for preparing hybrid nanostructures. Integration of polymeric supports with the inorganic nanostructures for preparing functional hybrids mainly depends on the nature of polymer, i.e. chain length, mesh size, etc. [11]. In this context, PEG-DA based materials had shown very promising applications by preparing highly stable hydrogels which were used as mechanical sensors, piezo actuating devices, stimuli response materials and so on [12]. Moreover, polyethyleneglycol diacrylate (PEG-DA) is non-volatile, non-toxic, environmentally benign and tailor made into various shapes, enabling to act as potential stabilizers and matrices for the formation of functional hydrogels [13]. In this paper, a facile method was demonstrated to incorporate functionalized Au nanospheres into PEG-DA polymer matrices by an *ex situ* approach for the preparation of hybrid Au/PEG-DA hydrogels to further accelerate applications based on PEG-DA and Au hybrids.

Experimental details

Gold chloride (HAuCl_4 , 99.9%), polyethylene glycol (PEG-200 M_n , 99.9%), polyethyleneglycol diacrylate (PEG-DA-700 M_n , 95.9%), sodium borohydride (NaBH_4 , 95.9%), 2-hydroxy-2-methylpropiophenone (99.9%) (Darocur 1173, photo-initiator, PI) and tri sodium citrate

(99.9%) were purchased from Aldrich and used for the synthesis without further purification. Lysine ($\geq 98\%$), thioglycolic acid ($\geq 98\%$) and glutathione ($\geq 98\%$) were purchased from Merck Millipore, Korea and used without further purification. Ultra-high pure water (Merck Millipore) with resistivity of $18.2 \text{ M}\Omega\text{-cm}$ was used for the overall synthesis.

Synthesis of Au nanospheres

Au nanospheres were synthesized using the well-established citrate reduction method [14], where, 20 mL of 2.5 mM of HAuCl_4 and tri sodium citrate were taken in a 50 mL round-bottom flask and stirred under ice cold conditions. 0.6 mL of 0.1 M NaBH_4 was added as an indicator for the formation of Au nanospheres showing the solution color change from yellow to pink. The synthesized Au nanospheres were purified and washed several times by centrifugation with the ultra-high pure water. Next, the surface of purified Au nanospheres was functionalized with three amino acids [lysine (10%), glutathione (10%) and thioglycolic acid (10%)] individually by magnetic stirring at room temperature. Finally, after 12 h of stirring, the functionalized Au nanospheres solutions were centrifuged and washed several times using the ultra-high pure water to remove the un-reacted amino acids. As it was an *ex situ* approach, the bonds between Au surface and electron-donating end group of ligand molecules (thiol or amine) undergo dynamic binding and un-binding processes. The ligand molecules bound to the surface of Au nanoparticles by some attractive interactions, such as chemisorption, electrostatic attraction or hydrophobic interactions provided by the head group.

Synthesis of Au/PEG-DA hydrogel

550 μL of functionalized Au nanospheres solution was mixed with 150 μL of PEG in a 1-mL centrifuge tube. Similarly, 250 μL of PEG-DA solution was mixed with 50 μL of PI in another 1-mL centrifuge tube. Then, two solutions mixed separately in different centrifuge tubes were slowly mixed and sonicated for 10 min to achieve uniform dispersion. The final volumetric ratio of each constituent in the Au/PEG/PEG-DA/PI hybrid solution was 55/15/25/5. The prepared mixture was used to fabricate Au/PEG-DA hydrogels by using the UV light emitting diode (CBT-90-ultraviolet-C31-M400-22, Luminus Devices; 8 W and 365 nm) for 3 min to initiate photo-polymerization.

Characterization techniques

The synthesized materials were characterized using electron microscopy and other analytical techniques. The structure and morphology of the Au nanospheres were

examined by using high-resolution transmission electron microscope (HR-TEM) JEOL, JEM-2010 (Japan). UV-Visible absorbance spectra were acquired by using Jasco UV-660 UV-VIS-NIR spectrophotometer (Japan). The FT-IR analysis was performed by using Nicolet Impact 400 FT-IR spectrophotometer with the KBr pellet method. Thermal gravimetric analysis (TGA) was performed by using a STA N-650 simultaneous thermal analyzer (SCINCO) with a heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$ under Ar (99.999%, 5 N) flow.

Results and discussion

Au nanospheres, synthesized by the standard citrate reduction method [14], and surface functionalization using amino acids to enhance the dispersion ability in the polymer matrix and to avoid agglomeration are schematically shown in Fig. 1. Three functional compounds (lysine, glutathione, and thioglycolic acid) were used for the surface functionalization process.

Figure 2 shows the TEM images of synthesized Au nanospheres. Highly spherical Au nanospheres with an average diameter of $3.5 \pm 0.5\text{ nm}$ (Additional file 1) were observed, depicting the controlled citrate reduction method performed at the ice-cold condition. The HR-TEM image of Au nanospheres (Fig. 2d) reveals the lattice fringes with the inter-planar spacing of 0.236 nm

corresponding to (111) plane of face centered cubic (FCC) Au crystal [15].

Figure 3 represents the UV-Visible spectroscopic studies of pristine and functionalized Au nanospheres. The surface plasmon peak centered at the wavelength of 517 nm was observed for pristine Au nanospheres, ensembles the smaller cluster size of nanospheres as evident from the TEM studies. It was observed that, after functionalization with amino acids such as lysine, glutathione, and thioglycolic acid had made appreciable plasmonic peak shifts (Fig. 3b) owing to the interfacial electron transfer and charge separation processes [16]. As known, Au can accept electrons and mediate the electron transfer process with functional groups thereby generating charge separation and drastic re-arrangement of surface electrons [16, 17]. This process clearly implies the successful immobilization of functional groups over the Au nanospheres surface, which improves the stability of functional nanospheres.

Thus, functionalized Au nanospheres were mixed with PEG, PEG-DA and PI to prepare the pre-polymer solution as shown in Fig. 4a. The addition of PEG with Au nanospheres and followed by PEG-DA/PI solution ensures the homogenous dispersion of Au in the polymer solution which can be easily identified by varying the PEG-DA and PI ratio from 10 to 35% (Fig. 4b). Among the various ratios prepared, 25% was chosen for further

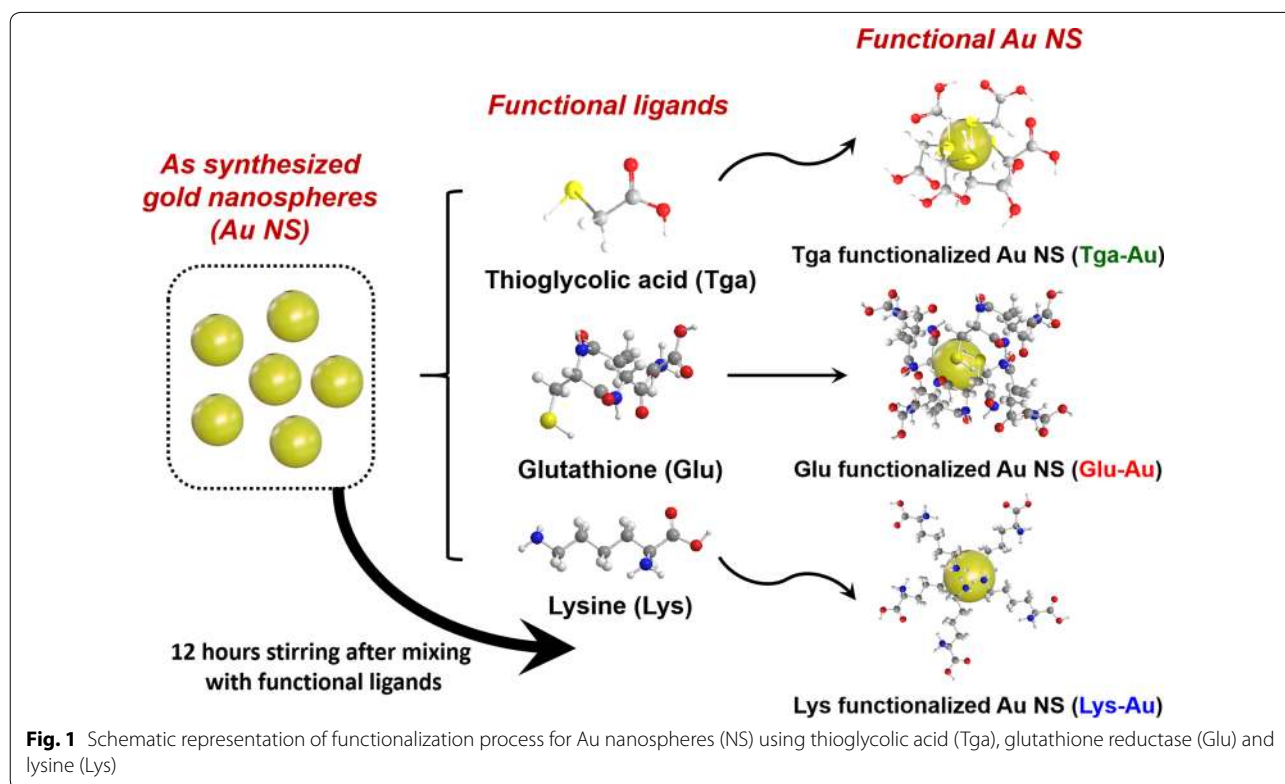


Fig. 1 Schematic representation of functionalization process for Au nanospheres (NS) using thioglycolic acid (Tga), glutathione reductase (Glu) and lysine (Lys)

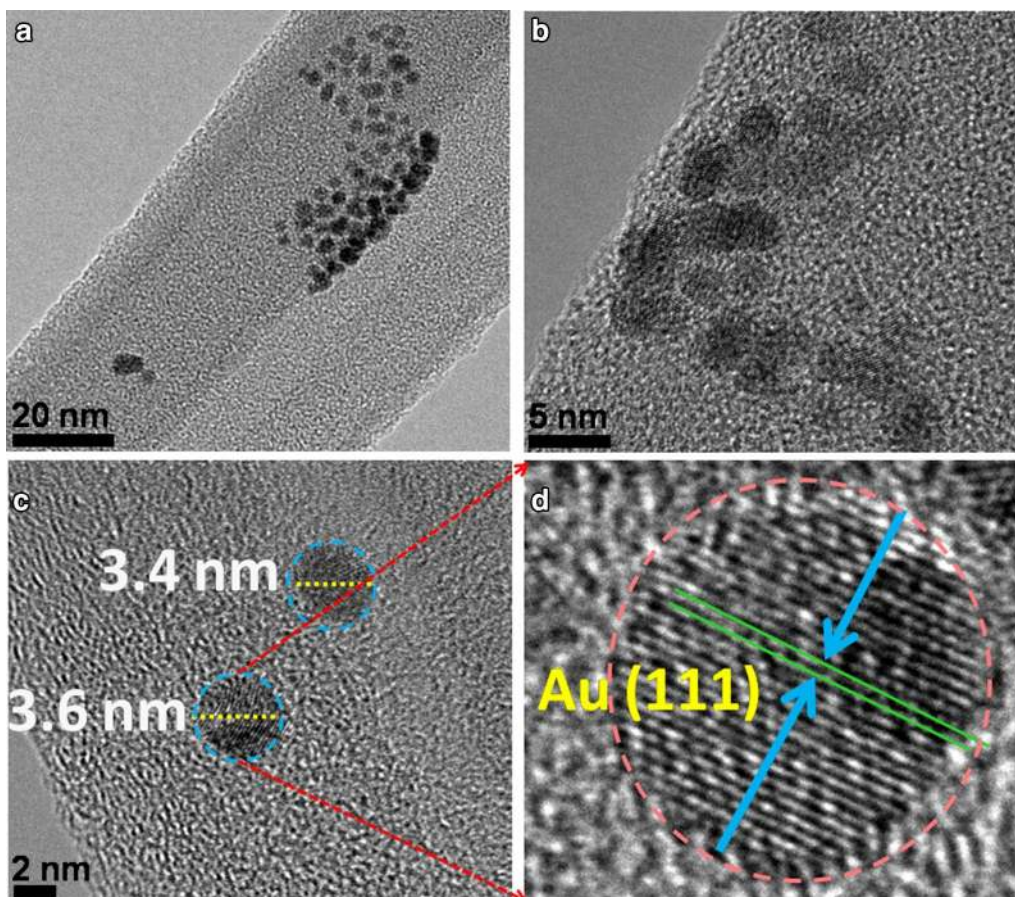


Fig. 2 a, b TEM images of Au nanospheres, and c, d HR-TEM images of Au nanospheres

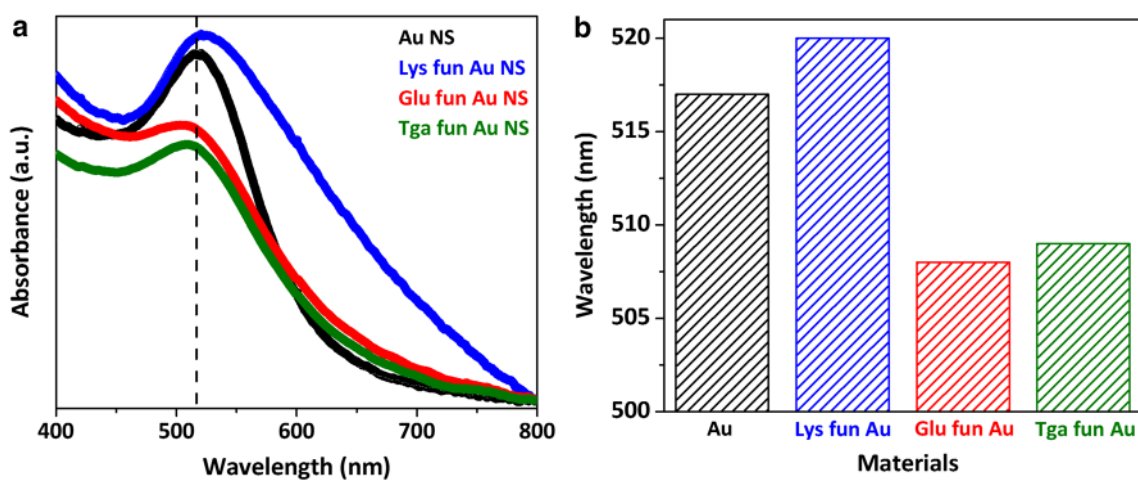
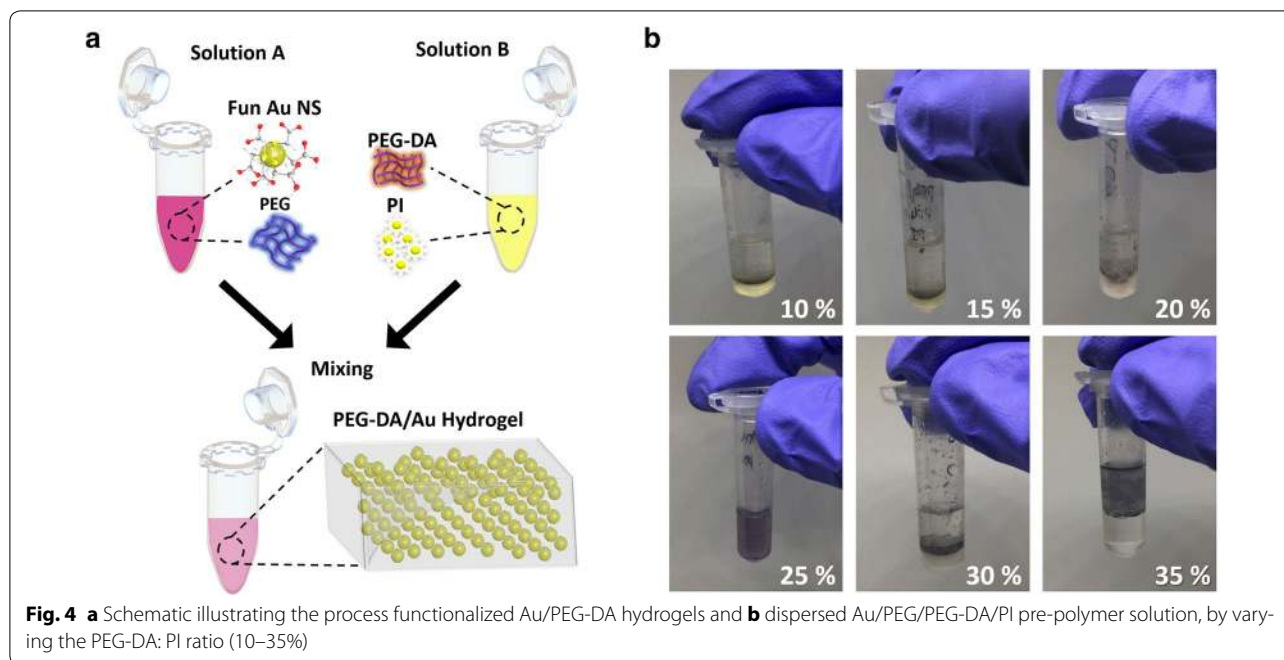


Fig. 3 a UV-Visible spectra and b SPR peak positions of the pristine and functionalized Au (lysine, glutathione, and thioglycolic acid) nanospheres



studies with the aid of its high mono-dispersity observed. To obtain functionalized Au/PEG-DA hydrogels as explained in the schematic (Fig. 4a), the selected 25% pre-polymer solution was photo-polymerized by the UV LED (8 W and 365 nm).

The functionalized Au/PEG-DA hydrogels were examined for its surface plasmon resonance (SPR) effect by spectroscopically to confirm the incorporation and bonding of Au nanospheres into the PEG-DA polymer matrix. The functionalized Au/PEG-DA hydrogels showed the characteristic SPR peak, which appears due

to the coherent oscillation of the surface conduction electrons as induced by the incident electro-magnetic radiation as shown in Fig. 5. Peak broadening observed for the absorbance maximum in hydrogels due to the presence of acrylic group and dispersion of Au nanospheres, which confirms the interaction of functionalized Au nanospheres with the surrounding polymer matrix [18, 19]. From the UV–Visible spectra, an appreciable red shift (Fig. 5b) was observed for the functionalized Au/PEG-DA hydrogels (lysine, glutathione, and thioglycolic acid) as compared to the pristine Au/PEG-DA hydrogel owing

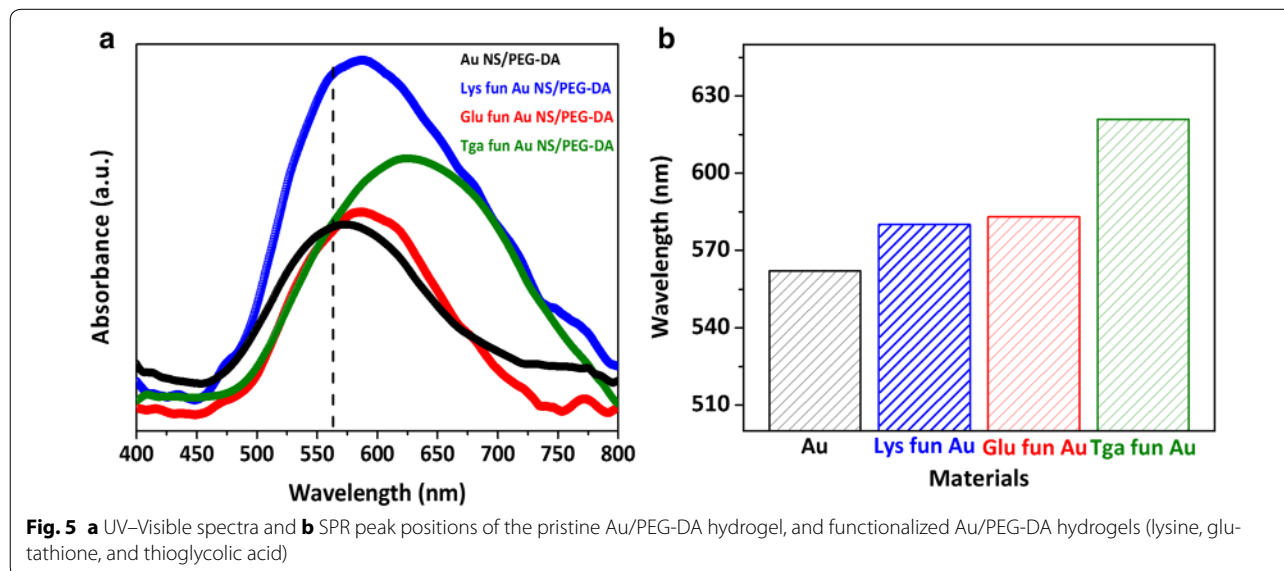


Fig. 5 a UV–Visible spectra and b SPR peak positions of the pristine Au/PEG-DA hydrogel, and functionalized Au/PEG-DA hydrogels (lysine, glutathione, and thioglycolic acid)

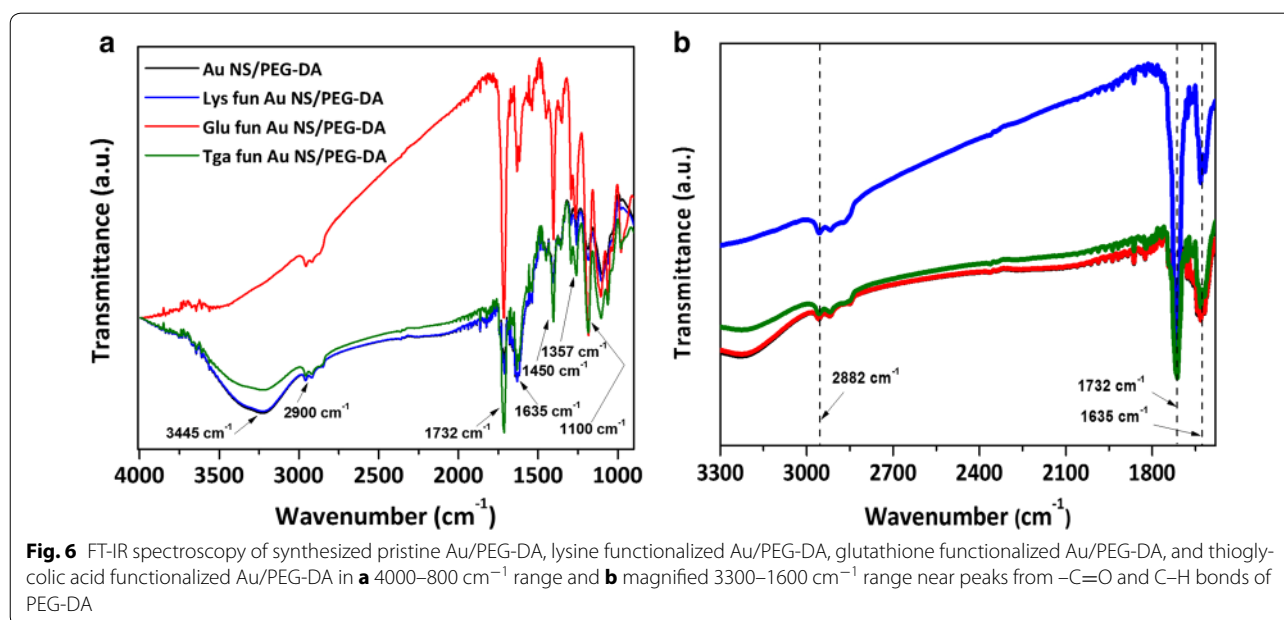
to the interfacial electron transfer process and proving the colloidal stability of functionalized Au nanospheres in the PEG-DA polymer matrix. Thus, functionalization process improved the stability of Au nanospheres inside the PEG-DA, as revealed with the characteristic SPR peak after photo-induced polymerization.

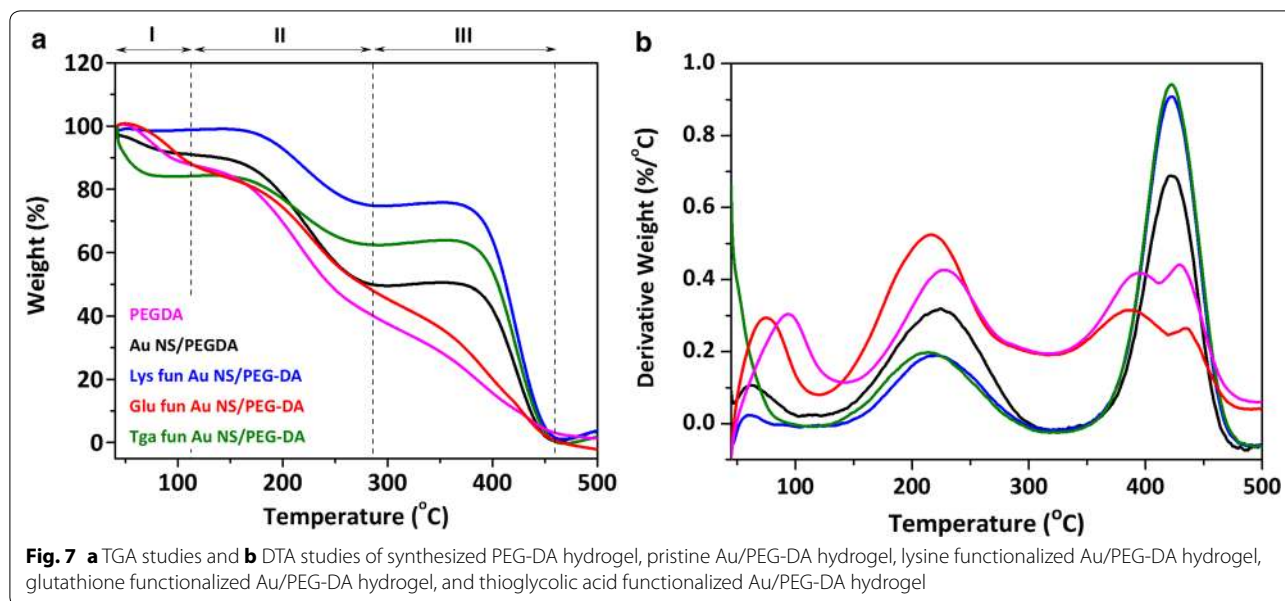
Fourier transform infrared spectroscopy with an attenuated total reflection assembly (FT-IR-ATR) mode was employed to study the molecular and structural changes in the hydrogels. Figure 6a shows the FT-IR spectra in the range of 4000–800 cm^{-1} for the pristine Au/PEG-DA hydrogel and functionalized Au/PEG-DA hydrogels (lysine, glutathione, and thioglycolic acid). The spectrum of the pristine Au/PEG-DA hydrogel (Fig. 6a) shows the absorption bands for acrylic vinyl groups at 810 cm^{-1} ($\text{CH}_2=\text{CH}$), 1410 cm^{-1} ($\text{CH}_2=\text{CH}$ bond) and 1198 cm^{-1} ($\text{C}=\text{O}$) [20]. Similarly, strong peaks at the wavenumber of 1732 and 2882 cm^{-1} observed correspond to $-\text{C}=\text{O}$ stretching from ester bonds and $\text{C}-\text{H}$ stretching vibrations, respectively [21]. The band at 1635 cm^{-1} corresponds to the reaction product of OH^- which comes from H_2O and oxidized products of citrate produced during the Au^{3+} reduction [13, 22]. Figure 6b shows that the interactions of Au with PEG-DA were confirmed by presence of intense absorption bands at 1732 and 2882 cm^{-1} with their difference in intensity after functionalization process and dispersion in the PEG-DA matrix [23]. The FT-IR spectra confirm the molecular structural changes between PEG-DA chains and functionalized Au nanospheres, ensuing by van der Waals interactions inside the polymeric matrix.

Thermo-gravimetric studies of PEG-DA hydrogel, pristine Au/PEG-DA hydrogel and functionalized Au/PEG-DA hydrogels (lysine, glutathione, and thioglycolic acid) were shown in Fig. 7a. It was observed that, all materials ensemble the characteristic III stage decomposition. The I stage corresponds to the removal of adsorbed water molecules on the hydrogels surface and the II and III stage decompositions are directly related with the cross-linked PEG and PEG-DA molecules, respectively, formed by the photo-initiation process. Among the five materials, the pristine Au/PEG-DA hydrogel shows lower stability than the functionalized Au/PEG-DA hydrogels, owing to the addition of functional groups and Au nanospheres which favours the cross linking percentage of polymers by chemical bonds and electronic interaction as revealed by FT-IR and UV-Visible studies, respectively [24–26]. Thus, functionalized Au/PEG-DA hydrogels can be used for temperature based sensing applications without altering their chemical compositions. Functionalization process of Au nanospheres further improves the dispersion inside the PEG-DA matrix owing to their higher thermal stability. The derivative thermo-gram (Fig. 7b) also reveals the presence of three stage decomposition, corresponding to the removal of water molecule, functional moieties and decomposition of di-acrylate molecules.

Conclusions

In this study, a facile and rapid chemical method for the uniform dispersion of plasmonic Au nanospheres into the PEG-DA matrix has been developed. Optical and spectroscopic analyses reveal the mono-dispersion





of plasmonic nanostructures into the polymer matrix, resulting in the formation of hybrid Au/PEG-DA hydrogels. Au nanospheres with an average diameter of 3.5 ± 0.5 nm and surface plasmon resonance band were confirmed by TEM and UV-Visible spectroscopic studies, respectively. Chemical functionalization of the PEG-DA with functionalized Au nanospheres were observed from the FT-IR studies by the existence of characteristic $-C=O$ stretching and $C-H$ stretching peaks. Thermal stability of the PEG-DA hydrogel had shown significant enhancement after the incorporation of functionalized Au nanospheres owing to the formation of interfacial region and successful dispersion of Au inside the polymer matrix. Thus, functionalized Au/PEG-DA hydrogels would find multiple uses for chemo-sensing applications.

Additional file

Additional file 1: Figure S1. Size histogram for synthesized gold nanospheres characterized by TEM.

Authors' contributions

VPD and JL developed the main idea and designed experiments. VPD and SBK performed experiments and data analysis. VPD, SBK and JL drafted the manuscript. All authors read and approved the final manuscript.

Competing interests

The authors declare that they have no competing interests.

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