Distinct optical response of colloidal gold-cinnamon nanocomposites: Role of pH sensitization

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Abstract. Nanocomposites (NCPs) with excellent physical, chemical and optical properties have been broadly used for commercial products and industrial applications. Based on these features of the NCPs, we prepared colloidal gold (Au) and organic cinnamon (Cin) NCPs by laser irradiated Au and Cin targets separately immersed in glass container fulfilled with different pH solutions (5.0 to 8.0). A Q-switched pulse laser ablation in liquid (PLAL) technique was employed to customize morphology, structural and optical characteristics of these grown nanoparticles inside various pH solutions at room temperature. Colloidal solution of gold-cinnamon nanocomposites (Au-Cin NCPs) was characterized via Transmission electron microscopy (TEM), Ultraviolet-visible (UV-Vis) spectrometer and CIE 1931 chromaticity diagram. TEM image and SAED patterns revealed spherical shaped Au-Cin NCPs with a particle diameters of 5.19 ± 1.23 nm and a nanocrystalline face centred cubic (FCC) nucleation. These plasmonic Au-Cin NCPs very strong UV-Vis absorbance bands at (270 nm and 522 nm) and CIE color coordinate (color temperature of 6437.001 K and color purity of 11.9130 %). It is established that the PLAL made-up Au-embedded Cin NCPs may be useful for the formulation of nanobiomedicine drugs.

1. Introduction
Molecular nanoparticles (NPs) are fundamentally distinct from their larger counterparts in that they are molecular species with specific well-defined structures [1-3]. The optical characteristics of molecular metal and organic NPs are quite different than those of the bulk form due to fundamental variations in their electronic structures [3,4]. Noble metallic NPs such as gold (Au) and silver (Ag), and organic nanocomposites (NCPs) have gained growing interest in the field of nanoscience and nanotechnology, especially in nanomedicine sector due to their size effect, localized surface plasmon resonance (LSPR), plasmon enhanced fluorescence and physicochemical properties [5-9]. Among the topic of concern, plasmonic-mediated fluorescence (FL) is of the precise significance because fluorescence spectroscopy is commonly utilized in large numbers of optoelectronic and biomedical sciences as a sensing device [6]. Recently, fluorescent inorganic-organic NPs have fascinated considerable research interests due to their unique chemical formulation and optical properties originating from quantum-size effects [3,10]. Few-atom gold (Au) and cinnamon (Cin) nanocomposites are fluorophores with a desirable set of properties such as sub-nanometre scale, high fluorescence quantum yield and photo-stability, those are...
exhibiting nontoxicity and lack of blinking [3,10,11]. The past few years, many significant reports relied on Au NPs and Cin NPs synthesis and potentials, mostly attempt to customize morphology (size and shape), size distribution, purity, structure and stability of these NPs [3,7,12]. Chemical approach with desirable control of NPs development with different chemical agents are commonly used as a single-step, environmental compatibility and low cost effectiveness. However, the long-term procedures, high toxicity of the used extra chemical purifications are commonly used as a single-step, environmental compatibility and low cost effectiveness. However, the long-term procedures, high toxicity of the used extra chemical purifications is one of the unsolved environmental problems [13,14].

Presently, pulse laser ablation in liquid (PLAL) approach is used to process materials and promote many chemical processes [15-17]. Pulsed laser irradiation of a target immersed in a liquid generates cavitation bubble, shock waves, and secondary photons followed by NP growth, solution reduction, and the target-solution combination [17]. Major advantages of laser-based methods are producing surfactant-free long-term stable colloidal solutions of NPs, functional NPs for in situ functionalization, and highly purified products [18]. John et al. [19] have established the synthesis of gold NPs embedded silica using a femtosecond laser irradiation in solution with their attributions as a reduction agent.

In this research, the influence of various pH solutions on the growth of Au and Cin NCPs produced via the pulse laser ablation in liquid (PLAL) method is determined by morphology, structural, and optical features. A colloidal solution of gold-cinnamon nanocomposites (Au-Cin NCPs) with customized growth parameters was characterized using TEM, SAED and UV–Vis analytical tools obtained to determine the physiochemical and optical properties of NCPs. Our overall investigations are helpful to develop new nanomaterial for biomedical applications.

2. Methodology

2.1. Preparation and characterisations

Gold (Au) and cinnamon (Cin) NPs were prepared using the laser pulse irradiation of the separately ablated Au and Cin targets immersed in different pH buffer solutions (5.0, 6.0, 7.0 and 8.0) at 8 mL. The gold target of purity 99.999 % with a dimension of 25 mm × 25 mm was purchased from Merck, Sigma Aldrich. While the natural cinnamon stick target was acquired from local supermarket, with a dimension of 40 mm × 10 mm × 2 mm. Prior to the laser irradiation process, both targets were well-cleaned with ethanol liquid media and used for NPs growth. A Q-switched Nd:YAG pulse laser irradiation with a \( \lambda = 1064 \text{ nm} \), pulse width \( \tau = 10 \text{ ns} \), laser fluence (LF) = 1.29 J/cm\(^2\), spot size = 2.2 mm\(^2\) and 10 Hz repetition rate was normally centred through a planoconvex lens (focal length = 8 cm) onto the target. The optimum laser parameters were selected according to our previous reports [3,12,20]. Next, the suspension containing Au and Cin NPs was mixed at the ratio of 1.5 mL to 1.5 mL. Finally, the resulting colloidal solution was rotated using a magnetic stirrer (at 20 rpm) to boost the yield by avoiding the sedimentation. In the PLAL process, the mechanism of plasma plume formation can be ascribed to the effect of confined interaction between the target-liquid interface and intense laser irradiations. The ejected hot plasma plume was expanded unceasingly at a supersonic speed and caused the formation of a shock wave that quenched underneath the sequestration of the pH medium. The morphology (size and shape) and crystallinity (SAED) pattern of the as-synthesized Au-Cin NCPs were obtained using a biological-transmission electron microscope (Bio-TEM, Hitachi HT7700), performed at an accelerated voltage of 120 kV. Prior to the analysis process, a little drop of colloidal Au-Cin NCPs suspension was poured onto a carbon coated-copper grid and allowed to fade at room temperature. The particles size distribution of Au-Cin NCPs was obtained from the Bio-TEM image analyses. The absorption spectra, color chromaticity and color temperature of samples were observed in the range of 200 to 1000 nm via the UV-Vis spectrometer (PerkinElmer Lambda 25 Spectrometer) wherein the colloidal sample was placed in a quartz cuvette having path-length of 0.5 cm.
3. Results and discussion

3.1. Optical traits
Noble metallic NPs integrated with organic nanostructure have typically been known to have unique optical characteristics under electromagnetic radiation [3, 21]. This report clarifies the impact of different pH buffers from 4.0 to 8.0 on the growth of NPs/NCPs through laser irradiation and the effects of physical and optical properties (in particular the LSPR position). The optical properties of samples were tabulated in Table 1. Figure 1 (a-c) spectacles the UV-visible absorption spectra with the corresponding CIE-1931 chromaticity diagram (Figure 1 (a1-c1)) of the as-synthesized Au NPs, Cin NPs and Au-Cin NCPs. Observed NPs and their color variations (insets) based pH buffer solution exhibited the prominent SPR peaks of Au NPs (Figure 1a) in the visible region of 526-536 nm and absorption peaks of Cin NPs in the UV region of 267-277 nm respectively. While the colloidal solution of Au-Cin NCPs showed two absorption peaks in the range of 522-535 nm and 265-281 nm with minor alteration in band position and intensity which was obviously confirmed by the SPR interaction of Au NPs with organic compounds in the Cin NPs. The shifting and broadening of the bands are due to the transitions between benzenoid rings ($\pi \rightarrow \pi^*$) and the localized exciton in the cinnamaldehyde rings that responsible for the stabilization and enhancement of the absorption band intensities of NCPs [22,12]. The stability of the colloidal Au-Cin NCPs solution was proved by storing them inside glass containers for more than 10 days in the darkness at room temperature and then the optical UV-Vis absorption spectra were measured. The absorption spectra were found to be same in the spectral profiles without any alteration in the wavelength peak positions, demonstrating their stability due to the complex interaction mechanisms of pH buffer molecules with the gold and cinnamon matrix.

The corresponding Figures 1 (a1-c1) display the luminescence color modification of the as-synthesized Au NPs, Cin NPs and Au-Cin NCPs were assessed from the chromaticity coordinates (x,y) following the CIE 1931 guidelines [23]. The CIE 1931 chromaticity diagram of the as-proposed samples which were observed in the white regions [24,25]. The color coordinates including color purities (CP) and color temperatures (CCT) of these samples are summarized in Table 1.

Table 1. Various UV-Vis absorption properties and CIE-1931 chromaticity coordinates, colour purities (CP) and color temperature (CCT) of the prepared samples (with their codes).

| Sample Code | UV-Vis Spectra of Au NPs (nm) | UV-Vis Spectra of Cin NPs (nm) | UV-Vis Spectra of Au-Cin NCPs (nm) | CP (%) /CCT (K) of Au NPs | CP (%) /CCT (K) of Cin NPs | CP (%) /CCT (K) of Au-Cin NCPs |
|-------------|-----------------------------|-----------------------------|---------------------------------|------------------------|------------------------|-------------------------------|
| pH 5        | 530                         | 275                         | 281 and 530                     | 14.0418/5028.99        | 1.289/6667.164          | 12.2505/5028.99             |
| pH 6        | 536                         | 271                         | 265 and 532                     | 14.3881/5062.686       | 1.065/6765.017          | 8.2565/5692.184             |
| pH 7        | 535                         | 267                         | 272 and 535                     | 17.4029/4885.296       | 1.403/7053.29           | 11.8676/5348.702            |
| pH 8        | 526                         | 277                         | 270 and 522                     | 9.0875/6356.966        | 3.339/7166.667          | 11.9130/6437.001            |
Figure 1. UV-Vis absorption spectra of as-synthesized NPs with corresponding CIE-1967 (a) Au NPs, (b) Cin NPs and (c) Au-Cin NCPs (Insets: color variation)

3.2. Surface structural
Figure 2 (a) illustrates the TEM image of Au-Cin NCPs at optimum pH 5.0 sample that exposed a spherical nanoshape with a particle diameter of 5.19 ± 1.23 nm. The TEM micrograph clearly showed poly-dispersed, followed by a slight agglomeration of Au-Cin NCPs, which could be attributed to the self-assembly of protein-adsorbed from organic cinnamon compounds (cinnamaldehyde, cinnamate and cinnamic acid) [3]. The presence of strong bright circular spots and concentric rings in the SAED pattern (inset) has confirmed the crystalline existence of Au-Cin NCPs. Figure 2 (b) exemplifies the narrow size distribution of the corresponding TEM image in the range from 1 nm to 14 nm.
4. Conclusion

The easy production, scalable and eco-friendly PLAL technique was utilized to produce high quality Au NPs, Cin NPs and colloidal solution of Au-Cin NCPs in different pH solutions (4.0 up to 8.0). Through laser parameters optimization it was possible to lessen the SPR of the Au-Cin NCPs very close to the Au-NPs. This tailored SPR properties of the Au-Cin NCPs was essentially decided by the synergistic spectral overlap between the SPR bands. Based on these findings, it was established that the proposed Au-Cin NCPs may contribute towards the development of future nanomedicine.

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