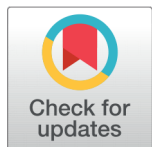


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Synthesis and characterization of gold (Au): Fullerene (C₆₀)-Poly (vinyl pyrrolidone) nanofluids in an alcoholic medium

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Abstract

Objectives: To synthesize gold (Au) doped fullerene (C₆₀)-Poly (vinyl pyrrolidone) PVP nanofluids in an alcoholic medium. **Methods:** A simple chemical reduction method was adopted to synthesize Au nanoparticles and then these NPs were doped into the C₆₀-PVP NFs by ultra-sonication. The samples were characterized using spectrophotometer, rheometer and microscope. **Findings:** We reported Surface Plasmon Resonance enhanced $\pi \rightarrow \pi^*$ C₆₀ (sp²) electron transition in PVP molecules upon insertion of NG into C₆₀ NFs with PVP in butanol. Electron transfer PVP \rightarrow Au(NG) causes a drastic decrease in the light emission in PVP moieties in a Au:C₆₀-PVP complex. A noticeable red shift of the C=O stretching band of PVP reveals surface interaction between $>C=O$ and Au-atom. Rheological study of NFs reveals non-Newtonian behavior with an enhanced yield stress and follows a typical Bingham type flow characteristics. High resolution transmission electron micrograph shows formation of Au-C₆₀ metal-non metal NPs of hexagonal shape. **Novelty:** Decrease in light emission intensity of PVP molecules in presence of Au NPs hints that it could be a candidate for sensing applications.

Keywords: Nanogold; nanofluids; surface plasmon resonance; light emission; rheological properties

1 Introduction

Fullerene (C₆₀) nanofluids (NFs) are engineered colloidal suspensions of C₆₀ nanoparticles (NPs) dispersed in medium such as water, mineral oils, ethylene glycol, polymer solutions, and biofluids. C₆₀ NFs finds applications in various areas like photovoltaics, catalysis, sensors, biomedical, etc. (1-8). Usually, four strategies were widely used in developing C₆₀ in aqueous or non-aqueous medium: (1) surface functionalization; (2) solvent exchange method; (3) mechano-chemical method; and (4) surface modification method (2-10). Since the last seven years, we are actively involved in developing C₆₀ NFs with and without gold NPs in aqueous and non-aqueous media using method-4 (2-10). Owing to possession of excellent properties by C₆₀ and noble metal NPs like gold

(Au), fullerene-gold NP combination is preferred to harvest the unique electron or energy transfer properties useful for photovoltaics, sensing and biomedical applications that cannot be obtained either with individual metals or with C₆₀ in an efficient manner.

A lot of research is going on in developing C₆₀-Au NPs by various routes⁽¹¹⁻¹⁶⁾. In⁽¹¹⁾ reported that 3D-nano-assembled Au-C₆₀ clusters are capable of efficient electro-catalytic reduction of hydrogen peroxide in an aqueous solution as they get chemisorbed on the surface of NG. C₆₀-Au NPs synthesized by⁽¹²⁾ via chemical modification route are capable of enhancing photovoltaic efficiency by providing a large number of donor-acceptor interfaces of large surface area. In⁽¹³⁾ synthesized highly stable organo-soluble thiol-protected Au-nanorods via a functionalization route which exhibits exceptional optical properties different from their corresponding spherical ones. They further reported that thiol compounds not only acts a stabilizer but also provides space for inclusion of insertion of C₆₀ molecules to develop hybrid nanostructures. The thin films prepared by⁽¹⁴⁾ reaches a maximum value quantum yield of light emission and results in huge enhancement in the signal of film because of a strong local field induced by surface plasmon resonance (SPR) excitation in the NG. The synthesized piperidine-based Au-C₆₀ nano-composites by⁽¹⁵⁾ reported to perform catalytic oxidation of some selected primary & secondary alcohols to their corresponding aldehyde and ketone derivatives. In⁽¹⁶⁾ synthesized graphene/C₆₀-capped Au nanocomposite film which can be used to construct supercapacitor electrodes. In⁽¹⁷⁾ stabilized NG with C₆₀ molecules via multiple binding modes and van der Waals interactions.

In this report we discuss on synthesis of Au doped C₆₀-PVP NFs in a non aqueous medium by a simple chemical method and studied their optical, microstructural and rheological properties.

2 Synthesis route and characterization techniques

Toluene was obtained from Merck and was used as received. Fullerene (C₆₀) of 99.9% purity and gold hydroxide Au(OH)₃ of 79% Au were obtained from Alfa Aesar. Poly(vinyl pyrrolidone) PVP was purchased from Alfa Aesar. At first we prepared three stock solutions, i.e., C₆₀ solution, PVP solution and water soluble Au(NO₃)₃ solution. C₆₀ solution is prepared by dissolving 10.0 mg of C₆₀ in 5.0 mL of toluene by stirring in a beaker covered with a watch glass and then stirring for 1 h at room temperature. PVP solution was prepared by dissolving PVP powder in water and then stirring for 3h at 60 °C. As Au(OH)₃ is very difficult to dissolve in water or other common solvents, it was dissolved in HNO₃ to form water soluble gold nitrate Au(NO₃)₃. We prepared a 5 mL stock solution of 1.27 mM Au(NO₃)₃ solution by dissolving 2.43 mg of Au(OH)₃ salt in 5.0 mL HNO₃ (5 N). Then we prepared PVP-C₆₀ NFs in butanol and to this we added Au(NO₃)₃ solution in various volume (e.g., 0.10 mL, 0.15 mL, 0.2 mL, 0.25 mL, 0.30 mL, 0.35 mL, 0.40 mL) to obtain a series of C₆₀-Au-PVP NFs in butanol. UV-Vis spectra were recorded in the wavelength region of 300 to 1000 nm using UV-Vis spectrophotometer from Thermo Scientific. The FTIR data studied in this work were measured in the 400 to 4000 cm⁻¹ region of the vibrational frequencies for the various samples. Liquid solutions were studied in an attenuated total reflectance (ATR) mode using a ZnSe crystal as a sample holder with a Perkin-Elmer FTIR Spectrometer (Spectrum 65). The rheological properties of the synthesized Au:C₆₀-PVP NFs of varied compositions in butanol were measured using a rotational rheometer (TA instruments, model: AR-1000) of parallel plate geometry, with a upper plate of diameter 40 mm. The morphology and size of obtained NFs were studied from micrographs obtained using a Libra Transmission Electron Microscope TEM (Carl Zeiss) operating at 120 kV.

3 Results and Discussion

3.1 Absorption and infrared spectra in Au:C₆₀-PVP NFs

We studied absorption spectra (Figure 1 A) in the 250-900 nm region in the NFs, which consists of (a) 0, (b) 1, (c) 2, (d) 3, (e) 5, (f) 10.0, (g) 30.0, and (h) 50.0 μM Au along with 10.0 μM C₆₀ in the presence of 40.0 g/L PVP in butanol. The optical absorption spectrum exhibits surface plasmon resonance (SPR) enhanced dipole allowed transition near

300 nm in $C(sp^2)$ electrons when Au attached to C_{60}/PVP ^(3-10,18). In the presence of Au, a characteristic Au-SPR band group exhibits over 500–900 nm with an average wavelength maxima $\lambda_{max} = 535$ nm. FTIR results show that a non-covalent interaction occurs between Au and “>C=O” (PVP) sites. It can be seen from the spectra in Figure 1B that the Au brings a substantial change and red-shift in the PVP (>C=O) vibrational band. It shows that Au interacts with carbonyl group in an Au: C_{60} -PVP complex⁽⁵⁾.

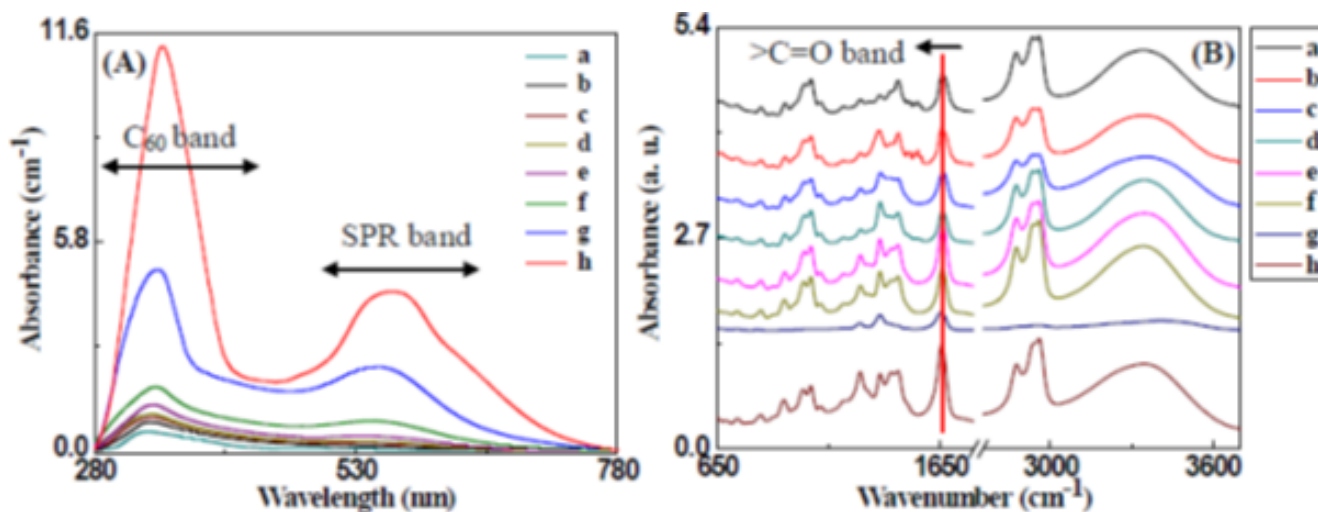


Fig 1. (A) Absorption spectra of Au: C_{60} -PVP NFs consisting of (a) 0, (b) 1, (c) 2, (d) 3, (e) 5, (f) 10.0, (g) 30.0, and (h) 50.0 μ M Au along with 10.0 μ M C_{60} in the presence of 40.0 g/L PVP in butanol and (B) Infrared spectra of Au: C_{60} -PVP NFs consisting of (a) 0, (b) 1, (c) 2, (d) 3, (e) 5, (f) 10.0, (g) 30.0, and (h) 50.0 μ M Au along with 10.0 μ M C_{60} in the presence of 40.0 g/L PVP in butanol.

3.2 Emission spectra and rheology in Au: C_{60} -PVP NFs

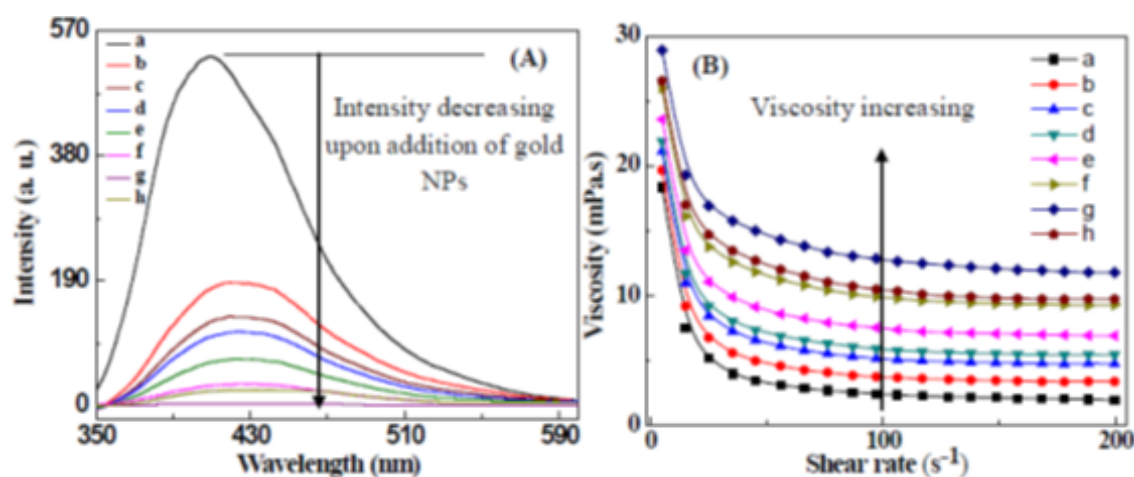


Fig 2. (A) Emission spectra of Au: C_{60} -PVP NFs consisting of (a) 0, (b) 1, (c) 2, (d) 3, (e) 5, (f) 10.0, (g) 30.0, and (h) 50.0 μ M Au along with 10.0 μ M C_{60} in the presence of 40.0 g/L PVP in butanol and (B) Rheogram of Au:PVP- C_{60} NFs consisting of (a) 0, (b) 1, (c) 2, (d) 3, (e) 5, (f) 10.0, (g) 30.0, and (h) 50.0 μ M Au along with 10.0 μ M C_{60} in the presence of 40.0 g/L PVP in butanol.

Figure 2A shows the emission spectra in the 350-600 nm region in the NFs, which consists of (a) 0, (b) 1, (c) 2, (d) 3, (e) 5, (f) 10.0, (g) 30.0, and (h) 50.0 μM Au along with 10.0 μM C₆₀ in the presence of 40.0 g/L PVP in butanol. Spectra shows that a small doping of 1 μM Au decreases the light intensity of PVP band by nearly $\sim 30\%$ as a consequence of energy transfer from PVP to Au-surface⁽²⁻⁸⁾. Doping of 50 μM Au almost vanish ($\sim 0\%$) the light emission from PVP.

Figure 2B shows the rheograms i.e., variation of viscosity measured as a function of shear rate (γ -value) in Au:C₆₀-PVP NFs consisting of (a) 0, (b) 1, (c) 2, (d) 3, (e) 5, (f) 10.0, (g) 30.0, and (h) 50.0 μM NG with 10.0 μM C₆₀ with 40.0 g/L PVP molecules in butanol. From the Figure 2B it is observed that the initially shear viscosity drops rapidly over initial $\gamma \leq 50\text{s}^{-1}$ values before achieving a stable η -value over the larger γ -values ($\sim 200\text{s}^{-1}$). All the eight plots exhibit typical non-Newtonian behavior of viscosity. From the rheograms it is further observed that the base h-value in a base C₆₀:PVP NF has been increased (shown in the Figure 2B as an upward arrow). It is due to formation of cross-linked network structures between NG and PVP-capped C₆₀ particles⁽⁵⁾.

3.3 Microstructures in Au:C60-PVP NFs

Transmission electron microscopic image in Figure 3 taken from a sample of 1 μM Au in 10.0 μM C₆₀ with 40.0 g/L PVP displays core-shell structures of hexagonal platelets of sizes varies between 5–25 nm. A lattice image in Figure 3B suggests that crystalline Au atom are present in the complex with a 0.235 nm interplanar spacing, which results from the (111) planes of an fcc Au⁽⁵⁾.

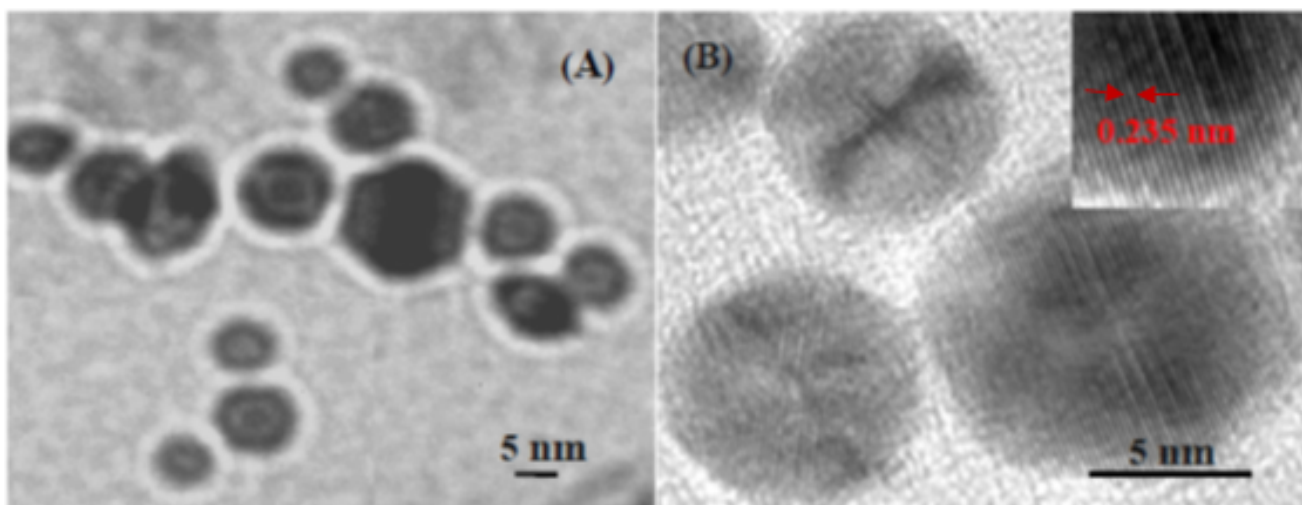


Fig 3. Micrographs of 1 μM Au in 10.0 μM C₆₀ with 40.0 g/LPVP.

4 Conclusion

UV-Vis spectra confirm the formation of NG and attachment of NPs to PVP-C₆₀ NPs. IR spectra confirm interaction between Au and $>\text{C}=\text{O}$ group of PVP. Rheological study reveals that all the NFs follow non-Newtonian flow characteristics. Morphological study reveals that NFs consists of hexagonal platelets of Au-PVP-C₆₀ NPs. Decrease in the light emission of PVP-molecules in presence of NG suggests that Au-PVP-C₆₀ NFs could find applications in bio-sensing.

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