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Synthesis and Characterization of Pectin Functionalized Bimetallic Silver/Gold Nanoparticles for Photodynamic Applications

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Abstract

Over the last decade, nanotechnology has become one of the most energetic evolving areas in research field. The astonishing properties of nanostructured materials are utilized in many field of research like energy, electronics and medicines. In this work, Functionalized silver, gold and Bimetallic Silver/Gold nanoparticles were prepared through chemical reduction in aqueous solution, following a method that was affable to the environment; this work will be stretching for photodynamic activities. $AgNO_3$ and $HAuCl_4$ were reduced using in-situ techniques in the presence of pectin and folic acid. Using the optical properties of metallic nanoparticles, surface plasmon resonance was determined from UV-Vis spectroscopy analysis, and the values obtained for silver and gold were approximately 350 nm and 543 nm in wavelength respectively. The absorption peaks of the surface plasmon band show a shift due to the size effect of the nanoparticles. The average hydrodynamic size and the size distribution of the synthesized nanoparticles were obtained through dynamic light scattering. To obtain a better understanding of the functionalization and conjugation conditions, High-resolution transmission electron microscopy has been used. The development of this process, which is compassionate for the environment, opens the possibility for many applications in the field of photodynamic applications.

Keywords: Silver; Gold; Nanoparticle; Surface plasmon resonance

Introduction

Nanotechnology is the emerging field, which has been used not only for the specific field but also has been used in the areas of physics, chemistry, biological applications. Nanotechnology is not human made word, it is intrinsically present in natural things, now human beings use this technology for Electrical, Electronics, Medical, computing, Space engineering, storage device, energy converting system because of it supreme properties. Nanotechnology comes from nanosized materials which has been making extraordinary applications in various field. Nanomaterials not only fabricated by single material but also by making composites using organic and inorganic materials. While comparing the bare and composites nano particle always composites possess amazing efficiency and stability. Especially polymers like natural and synthetic are used for making composition of nanomaterials. Here pectin used as stabilizing agent which has been used to avoid the agglomeration of metal nano particles, generally unfunctionalized metal nano particles easily get aggregated and this process is avoided by further polymer functionalization. Pectin is a natural anionic polymer that has been taken for diverse applications. It is non-toxic, bio-degradable, easily available, low cost. Pectin is used for biomedical applications. Silver and gold are used as precursor due to the special optical properties, which have been used for lot of applications like imaging, drug delivery, diagnostic and sensor, especially used for photodynamic applications. Herein we report the synthesis of pectin functionalized Ag, Au and Ag/Au nano particles with a facile solution approach at room temperature. This proposed work will extend for the photodynamic applications.

Materials and Methods

All experimental substance utilized were of analytical grade and were used without further refining. In a typical procedure, 0.008 gm of $HAuCl_4$ and $AgNO_3$ were added into a 0.2 gm pectin/0.003 gram of folic acid (24 hrs). After full dissolution, 40 mL of 1.2 mM $NaBH_4$ solution was added drop wise under constant stirring. The chemical reaction was allowed to proceed at room temperature for 5 h under ice bath. Then, the obtained precipitate was centrifuged at 10,000 rpm for 10 min and collected and cleaned with distilled water several times to dispose the byproducts. After Freeze-drying in lyophilizer, the final product was received as violet and brown powders.

Methods

Fourier transform infrared (FTIR) spectra of the prepared nanoparticles were obtained with a Shimadzu IR-400 spectrometer with the KBr pressed disks. Detailed nanostructure analysis was carried out using a Transmission electron microscope (TEM). The UV-Vis spectrum of the product dispersed in distilled water was obtained using in a UV-Vis spectrophotometer (UV-1601PC, Shimadzu Corporation). A particle size analyzer (90Plus, Brookhaven Instruments) was used to measured the average hydrodynamic size distribution of Pectin-Folic acid/Ag NP and pectin- Folic acid-Ag/Au nanocomposite [1-12].

Results and Discussion

Fourier transform infrared spectroscopy

Pectin-folic acid/Ag, Pectin-Folic acid/Au, Pectin-Folic acid-Ag/Au spectrum shown in Figure 1. An observable absorption peak at about 1617 cm^{-1} can be establish for the Pectin-Folic acid-Ag/Au sample; this is a typical IR absorption peak of folic acid, generating from stretching mode of the bending mode of N-H bond. The remaining peaks in Pectin-Folic acid-Ag/Au composite are stimulated by pectin, which

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is confirmed by comparing of the IR spectrum of the composite with that of the pectin. The peak at 1724 cm^{-1} is assigned to C=O or C=C double bond of pectin [11,12]. The absorption peaks at 1637 and 3394 cm^{-1} are similar to stretching bands of COO- and OH groups of pectin respectively. It is found that the intensities of two peaks at 1724 and 2923 cm^{-1} (induced by carboxyl and CH_2 groups of pectin, respectively) for pectin-composite. This peaks from the participation of COO- and CH_2 groups in a hydrogen bond system, which stabilizes the pectin conformation in solid state. The above results specify that the final product is a true composite of pectin and Folic acid. The pectin peaks were not disconnected by washing the sample continuously, signifying that there are molecular interactions between pectin and folic acid. When compared these three synthesized system functional groups of pectin and folic acid were interacted and formed the conjugated system.

UV-Visible spectroscopy

Figure 2 shows the room temperature UV-Vis absorbance spectrum for the as prepared sample Pectin-Folic acid/Ag, Pectin-Folic acid/Au and Pectin-Folic acid-Ag/Au. A broad absorbance peak centered at 543 nm was found this was due to surface plasmon resonance of Ag/Au nanoparticles. The peak between 350-500 nm due to the presence of gold nanoparticles in the Pectin-Folic acid-Ag/Au composite. The absorption peak between the region of 300-400 nm by silver nanoparticles present in the Pectin-Folic acid/Ag composites. When compared with bare silver nanoparticles and gold nanoparticle and Pectin-Folic acid-Ag/Au NP absorption peak shifted towards higher wavelength and peak intensity are increased which indicates folic conjugation makes opensites around noble metal nanoparticles, which also augmented the oscillation of surface electrons on Ag/Au nano particles.

DLS and zeta potential

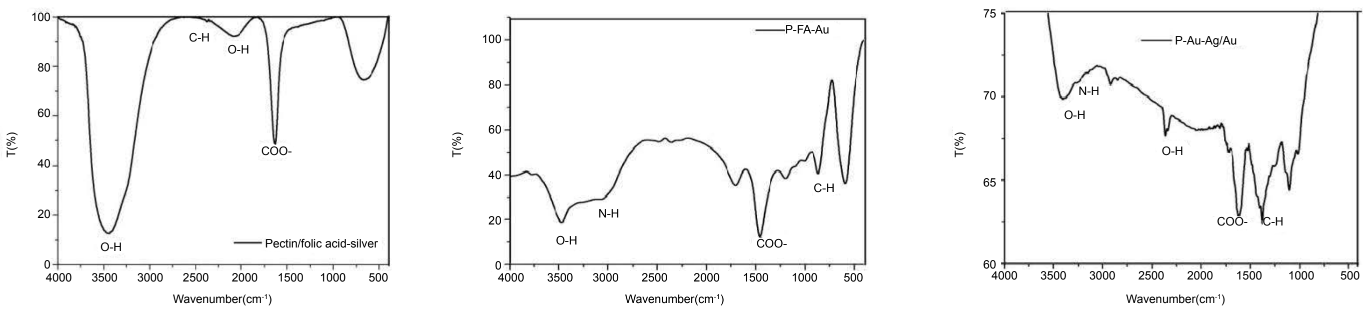
The zeta potential was equal to -27.9 mV and its corresponding hydrodynamic diameter is 220.2 nm. We can suggest that the silver nanoparticles getting a negative zeta potential due to the capping of pectin layer around nanoparticle which indicates particles are fairly stable due to the electrostatic repulsion. Zeta potential of Pectin-Folic acid/Ag NP is -46 mV and corresponding hydrodynamic diameter is 117.8 nm. Pectin-Folic acid/Ag when compared with Pectin-Folic acid-Ag/Au is having larger diameter and less zeta potential which indicates repulsion between the nano particle which starts to decrease the stability of the particles due to the presence of ions by precursors.

Morphologies of pectin-folic acid/Ag, pectin-folic acid/Ag and pectin-folic acid-Ag/Au

The structural properties of Pectin-Folic acid/Ag Pectin-Folic acid/Au and Pectin-Folic acid-Ag/Au were probed by HRTEM. Figures 3a, 3b and 3c shows the image of Ag, Au and Ag/Au alloyed nanoparticles functionalized by pectin. Both samples consist of particles with a similar spherical shape. HRTEM gave further close into the ultra assembly of atoms. All particles were polycrystalline. In Figure 3c, different contrast is the result of different Bragg conditions, reflecting the different crystallite orientation.

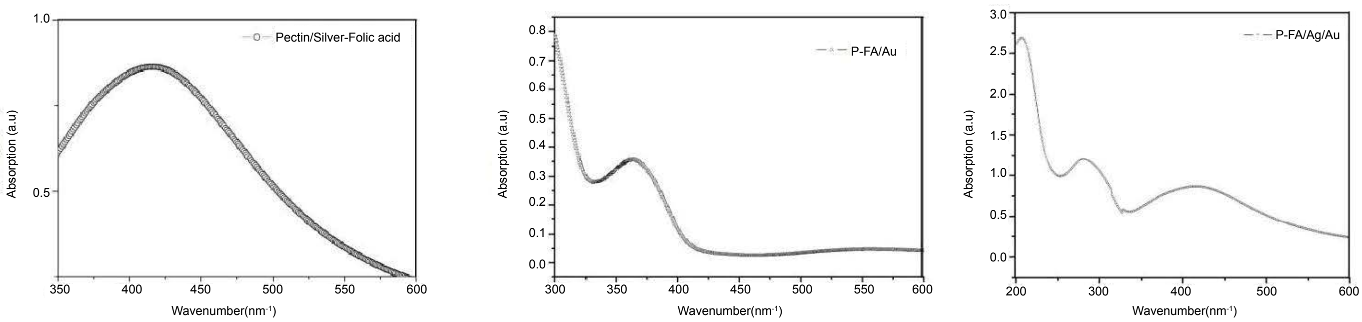
Conclusion

Pectin-Folic acid/Ag and pectin- Folic acid-Ag/Au nanocomposites were synthesized in aqueous solution at room temperature. The morphology, Hydrodynamic diameter and zetapotential, and optical absorption of the nanocomposites were studied. The experimental results confirm the pectin- Folic Acid-Ag/Au composite structure and



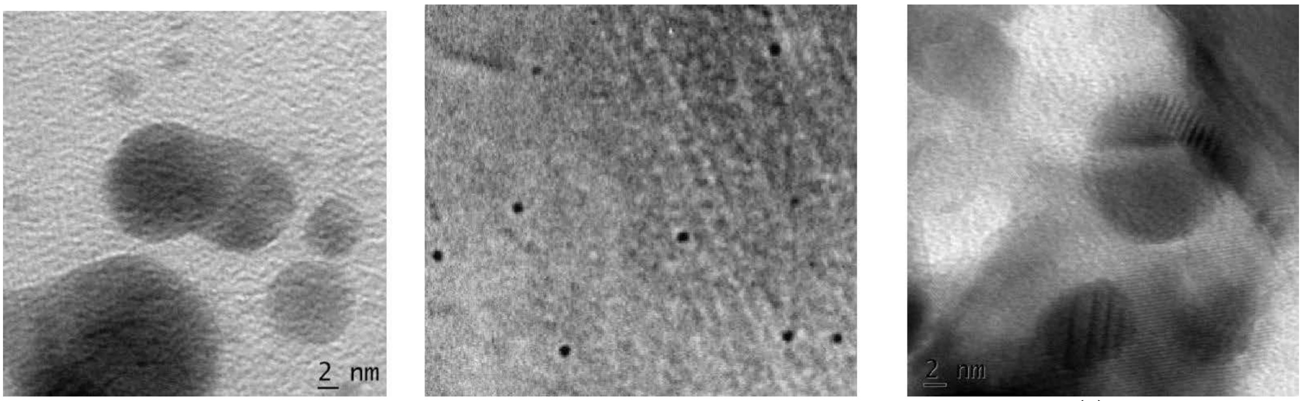
(a) (b) (c)

Figure 1: FTIR Spectra (a) Pectin-Folic acid/Ag; (b) Pectin-Folic acid/Ag (c) Pectin-Folic acid-Ag/Au.



(a) (b) (c)

Figure 2: UV Spectra Pectin-Folic acid/Ag;(b) Pectin-Folic acid/Au (c) Pectin-Folic acid-Ag/Au.



(a) (b) (c)

Figure 3: TEM Pictures of (a) Pectin-Folic acid/Ag; (b) Pectin-Folic acid/Ag (c) Pectin-Folic acid-Ag/Au.

the existence of strong interaction between pectin molecules- Folic acid with metal nano particles. This synthesized system will be stretching for cancer theranostics and photodynamic applications.

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