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A Nanoparticle and Au-PVA Nanocomposites: Synthesis and Characterization

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Abstract:

This research aims to prepare a nanocolloidal solution of gold and gold capped with PVA by chemical reduction method by sodium tri-citrate as a reducing agent and using gold chloride as a source of gold ions in aqueous solution at low temperatures (room temperature). The prepared solution was diagnosed by scanning electron microscope as well as the X-Ray-Diffraction. The results showed that the shape of the prepared particles is spherical with diameters close to 10 nanometers and with good scattering.

1. Introduction

noble metal nanoparticles have generated a great deal of interest Optical characteristics, magnetic properties, catalytic properties, and so on are also size-dependent[1]. The plasmon resonance absorption metal nanoparticles exhibit in the UV–visible band is an additional factor. Electrons located in the conduction band occur in an orderly manner because of the small particle size of the material. The particle size, chemical environment, adsorbed species on the surface, and dielectric constant [2-4] are all factors that influence the particle shift. Gold nanoparticles (Au NPs) and silver nanoparticles (Ag NPs) have distinct optical properties, notably with respect to color. Collective oscillations of conduction electrons paired with incident light make them useful for a range of applications[5,6].Gold is a noble and vital metal due to its resistance to chemical abrasion and oxidation as well as its resilience to high temperatures and temperature fluctuations, which can affect surrounding conditions such as metalworking[7]. AuNPs are readily functionalized, having a wide range of functionality Most appropriate for bioimaging applications are a variety of ligands ranging from polymers, DNA, peptides, RNA, and fluorescent compounds As well, numerous cytotoxicity investigations showed their low cytotoxicity[8]. Inertness due to the atomic weight of Au results in toxicity flexible chemistry, environmentally acceptable design, and versatility in numerous domains make polymeric matrices a good choice for hybrid nanocomposites synthesis [9-11].Noble metal nanoparticles such as Ag and Au NPs have been a source of great interest due to their novel electrical, optical, physical, chemical and magnetic properties [12]. They were very attractive for biophysical, biochemical, and biotechnological applications due to their unusual physical properties, especially due to their sharp plasmon absorption peak at the visible region. Another important advantage Ag and Au nanoparticles were stable for a period of months. Additionally, Gold and silver nanoparticles are chemically stable and typically exhibit surface enhanced Raman scattering SERS in the visible wavelength range, where they may cause a tremendous increase in various optical cross-sections. The resonance frequencies strongly depend on particle shape and size as well as on the optical properties of the material within the near-field of the particle [13]. Silver, for example, has been for thousands of years, used as a disinfectant; from the other side nobody can neglect its value as a catalyst [14]. On the other hand, Gold nanoparticles have gained considerable attention in recent years for potential applications in nanomedicine due to their interesting size dependent chemical, electronic and optical properties. Also, gold nanoparticles show promise in 4 enhancing the effectiveness of various targeted cancer treatments such as radiotherapy and photothermal therapy [15]. Nanoparticles are widely used in biosensor development. Gold nanoparticles (AuNPs), known as colloidal gold, are fluid suspensions of gold particles with diameters ranging from 1– 100-nm that have been protected with a capping reagent. AuNPs are one of the most studied nanomaterials due to their distinctive optical and electronic properties and good biocompatibility [16].The optical properties of AuNPs have been known since early in human history; perhaps the most well-known example is the Lycurgus Cup from the 4th century AD at the British Museum in London, whose glass appears red in transmitted light and green in reflected light. Detailed analysis revealed that the presence of nanometer-size metal crystals of Ag and Au gave the cup its unusual optical properties the first chemical synthesis of gold colloid was reported by Michael Faraday in 1857 [17]. The deep red solution of colloidal gold was obtained by the reduction of an aqueous chloroauric ($AuCl4^-$) solution by phosphorus in CS_2, a two- phase system [17]. In the modern era, AuNPs have become a hot topic, and more controllable synthesis methods and applications in diverse nanosystems had been developed.

Many different techniques have been developed for the synthesis of AuNPs through the chemical reduction of $HAuCl_4$ in the presence of capping reagents. The most frequently utilized technique is the citrate method reported by Turkevitch et al. in 1951 [18] for synthesizing AuNPs of up to 150-nm in diameter.In this approach, Au (III) salt is first reduced to Au(I) ions, after which Au (0) species are formed through a disproportionation reaction. These activated Au (0) species are thermodynamicallyunstable and act as the center of nucleation for the further reduction of Au^+ ions. This growth process gives rise to well- dispersed AuNPs. In this method, citrate molecules act as both a reducing and capping reagent. The size of the AuNPs can be finely and easily tuned by adjusting the $HAuCl_4$:citrate ratio, temperature, or solution pH. The exclusive optical properties of AuNPs arise from localized surface plasmon resonance (SPR) [19]. When light irradiates a solution of dispersed metal nanoparticles, the electromagnetic frequency induces resonant coherent oscillation of the free electrons. When the frequency of the 9 incident light matches the frequency of electron oscillation, specific wavelengths of light are absorbed [20]. The oscillation frequency of AuNPs is usually in the visible region, giving rise to a strong color associated specifically with SPR-related absorption Optical absorption and emission depend on transition between conduction and valence band. like other metals, Noble metals, don't have their electrons on bounded". There is a cloud around the atomic core and thus they become good conductors. "When a photon with certain wavelength comes onto this cloud, photon can be absorbed and oscillations in the electron cloud are produced". "This phenomenon is formed on the surface of metals thereby it is called

"Surface Plasmon Resonance"". Otherphotons with various wavelengths can be reflected and may not get in oscillation[21]. "The penetration depth of Electromagnetic(EM) waves in metal is at the order of 30 nm , Providing that the diameter of a N,P is smaller than 30 nm, the EM waves can propagate ,the particle". Eventually, a net charge difference occurs on the surface of nanoparticle .These charges form an oscillating dipole and radiate EM waves. The radiated EM waves are known as" Localized Surface Plasmon Resonance (LSPR)"." If some of the photons are released with the same frequency in all directions, this process is called "scattering"". "If some of the photons are converted into phonons or vibrations of the lattice, this process is referred to as absorption. If the diameter of a particle gets smaller, the energy required to collectively excite motion of the surface Plasmon electrons increases [22]. If the shape of the particles changes, same conditions occur. Thus, we observe changes in Plasmon resonances causing a difference in absorption peaks." Moreover, on the condition that a surrounding medium changes, the surface Plasmon resonance band changes as well due to the dielectric properties of the surrounding medium"[22]. Magnetic NPs are of great curiosity for investigators from a eclectic range of disciplines, which include heterogenous and homogenous catalysis, biomedicine, magnetic fluids, data storage magnetic resonance imaging (MRI), and environmental remediation like water decontamination etc. Literature revealed that NPs perform best when the size is < critical value i.e. 10-20 nm. At such low scale the magnetic properties of NPs dominated effectively, which make these particle priceless and can be used indifferent applications. The uneven electronic distribution in NPs leads to magnetic property. These propertiesare also dependent on the synthetic protocol and various synthetic method like solvothermal , co-precipitation, micro- emulsion, thermal decomposition, flame spray synthesis etc. canbe used for their preparation [23]. It is well-known fact that metals NPs have thermal conductivities higher than those of fluids in solid form. For example, the thermal conductivity of copper at room temperature is about 700 times greater than water and about 3000 times greater than that of engine oil. Even oxides such as alumina (Al2O3) have thermal conductivity higher than that of water. Therefore, the fluids containing suspended solid particlesare expected to display significantly enhanced thermal conductivities relative to those of conventional heat transfer fluids. Nanofluids are produced by dispersing the nanometric scales solid particles into liquid such as water, ethylene glycol or oils. Nanofluids are expected to exhibit superior properties relative to those of conventional heat transfer fluids and fluids containing microscopic sized particles. Because the heat transfertake place at the surface of the particles, it is desirable to use theparticles with large total surface area. The large total surface area also increases the stability suspension. Recently it has beendemonstrated that the nanofluids consisting of CuO or Al2O3 NPs in water or ethylene exhibit advance thermal conductivity [23]. In the above parts, the characterization of AuNPs based on optical and physicochemical properties have been introduced. Although nearly all studies are in the experimental stages, it is clear that AuNPs have potential applications in different fields. Based on their characteristics, applications have been explored, particularly in medical field, including deliver carriers (drug, gene and protein deliver), therapeutics (PTT, PDT and RT), diagnostics, imaging, and other biological activities. In the following sections, these applications will be discussed in detail. In recent years, the idea of using AuNPs as delivery carriers hasattracted the wide attention of researchers. AuNPs can be used for the delivery of drug, gene, and protein. Chemotherapy is the most common method of cancer therapy but its potential is limited in many cases. Traditional drug delivery (oral or intravenous administration) for chemotherapeutic drugs, results in the dissemination of the drug throughout the whole body, with only a fraction of the dose reaching the tumor site.

Targeting of specific cells, organs, and tissues, in a controlledmanner, has become a key issue and challenge. Drug delivery systems (DDSs) is a promising approach to general anticancer therapy, which may provide efficient targeted transport and overcome the limitation of biochemical barriers in the body, e.g., the brain blood barrier. Moreover, DDSs can enable controlled function in delivering drugs for early detection of the diseases and damaged sites [24]. Gold nanoparticles are used as contrast agents in the diagnosis of heart diseases, cancers, and infectious agents. For example, X-ray computer tomography (CT) is a common diagnostic imaging tool for gold nanoparticles *in vivo* detection, which is used to visualize tissue density differences that provide image contrast by X-ray attenuation between soft tissues and electron- dense bone. Gold nanoparticles also exhibit good signal

intensity and stability when acting as the promising materials forNIR imaging. Gold nanoparticles are the most commonly used nanoparticles for lateral flow assays. Due to the optical properties of gold nanoparticles, detection with the naked eye can be achieved with excellent sensitivity. The assay can also beadapted to run both in non-competitive and competitive mode [25].

Gold nanoparticles can strongly absorb light as the result of the SPR. The absorbed light can efficiently be converted to heat by the fast electron–phonon and phonon–phonon processes, which makes gold nanoparticle a useful tool for photothermal therapy of cancers or other diseases. For example, when excited by light at wavelengths from 700 to 800 nm, near-IR absorbing gold nanoparticles can produce heat and eradicate tumors. Based on the enhanced permeability and retention effect and the explosionto the appropriate laser light, gold nanoparticles can be precisely accumulated in tumor cells and targeted treat tumor, which contribute much to the "see and treat" approach. This study is aims to preparing Au NPs. and study the physical properties. alsoPreparing Au-PVA nanocomposites and study the physicalproperties.

2. Methodology

2.1 Au colloid synthesis

Gold nanoparticles were prepared by chemical reduction methodusing materials Gold chloride as a source for gold ions and tri sodium citrate as a reduction agents. Where The gold chloride solution was diluted to reach a concentration of 0.005 M by dissolving it in non-ionic water. an amount of (5 milliliters) from 0.005 gold source mixed with (35 milliliters) deionized water on a magnetic apparatus and heated until it reaches a boiling point and leaves it to boil for (15-20) seconds. one mL from Sodium citrate (prepared from disolving 1 g form TSC pwoder im 100 mL DI water) added to the mixture in paragraph above then the heat is turned off and left on the magnetic mixing device. the solution turns colorless and then turns dark red (violet and then to bright red, which is a guide to reaching gold nanoparticles of size Smaller (less than 20 nm) .

Au-PVA

Au-PVA composites were prepared by chemical reduction method using materials Gold chloride as a source for gold ions and tri sodium citrate as a reduction agents and PVA as a capping agent. Where The gold chloride solution was diluted to reach a concentration of 0.005 M by dissolving it in non-ionic water. an amount of (5 milliliters) from 0.005 gold source mixedwith (35 milliliters) deionized water on a magnetic apparatus and heated until it reaches a boiling point and leaves it to boil for (15-20) seconds. 10 mL of 1% PVA solution was mixed with solution above. one mL from Sodium citrate (prepared from disolving 1 g form TSC powder in 100 mL DI water) added to the mixture in paragraph above then the heat is turned off and left on the magnetic mixing device. the solution turns colorless and then turns dark red (violet and then to bright red, which is a guide to reaching gold nanoparticles.

Characterization techniques

There is a variety of diagnostic methods that can be used to test some important properties of materials such as crystalline structures, surface morphologies, chemical compositions, optical properties. "X-ray diffractions (XRD), fields emissions scanning electrons microscopy (FESEM), transmissions electrons microscopy (TEM), Fourier transformation infrared spectroscopy (FTIR), UV-Visible spectroscopy (UV-Vis) .

Transmissions Electrons Microscopy (TEM) (TEM) is procedure can be used to imaging the nanoscalematerials, by means of electrons beam that was focused on top of a sampleproducing an enlarged version to seem on a luminous monitor or aphotographic film, or to be sensed via a CCD camera. In this study, the transmission Electron Microscopy model a JEOL JEM. 2010 electron microscopy . This device is conducted at the Tehran University.

Energy Dispersive X-ray Spectroscopy

For a semi-quantitable analyzation of components, EDX hasbecome one of the essential methods that determines as both a mass orweight fraction percentage of sample components. Some of the EDXdetectors are SEM radiation, SEM field and microscope radiationtransmission. It delivers data from the incident beam of electrons on the fixatedpoint by a raster scanning of sample superficial. Furthermore, a map of theproducts to be tested can be supplied. Analysis atomic composition of the sample occurs while the electron-beam energy is enough to remove the electron from the internal orbit of the atoms when the interaction ofelectrons with the material. The vacuum resulting from the expulsion of the electron from the internal orbit was occupied by means of an electron from the outside orbit of the same atom

In this study, the Field Emissions Scanning Electrons Microscopy FESEM model MlRA3 from TE SCAN Company.

This device is conducted at Tehran University.

The FTIR Measurement

It was considered one of the important techniques fordistinguishing the bonding between atoms and molecules of organic matter anddetermining the presence of effective groups and it also

3. Results and discussions

Powder X-ray diffraction pattern in Fig. 3.1 demonstrations that the Au nanocolloidal . The band gives an intense peak at 2θ = 38.47∘ , 44.84∘ which correspond to the (111), (200) plane proving the structure of Au-NPs to be face center cubic (fcc).

The crystallinity of Au-NPs is pure by comparing its XRD pattern with the database; JCPDS file number 00-004-0784. Incase of Au-PVA same peaks appeared at same corresponding planes with small shift towered higher angles.

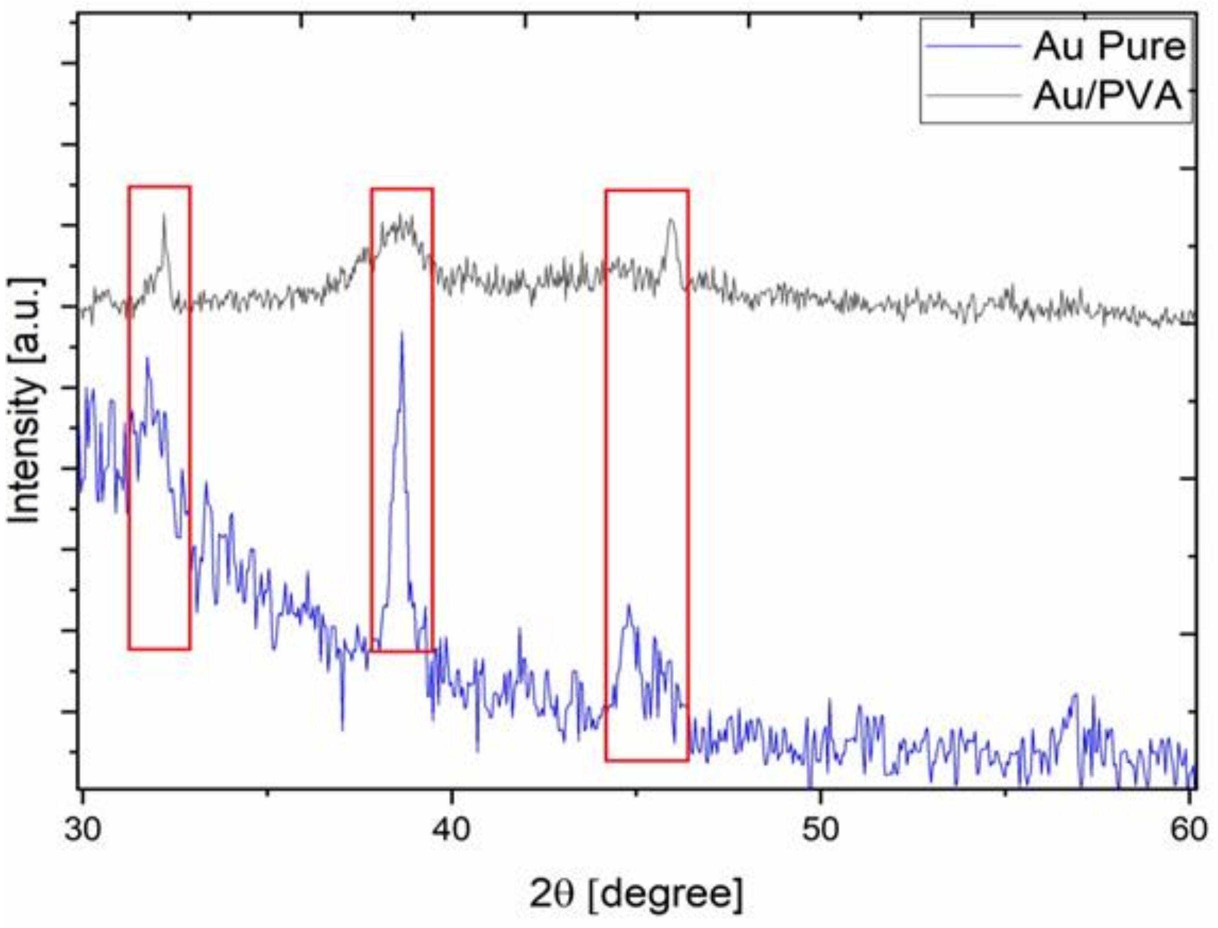

Figure 3.1 XRD patterns of Au NPs.

Fig. 3.2 illustrates the (SEM) images which indicate the meansize of the synthesized nanoparticles. The particles are spherical in shape with good homogeneity for both Au and Au-PVA. The average dimeter is about 15 nm for both samples.

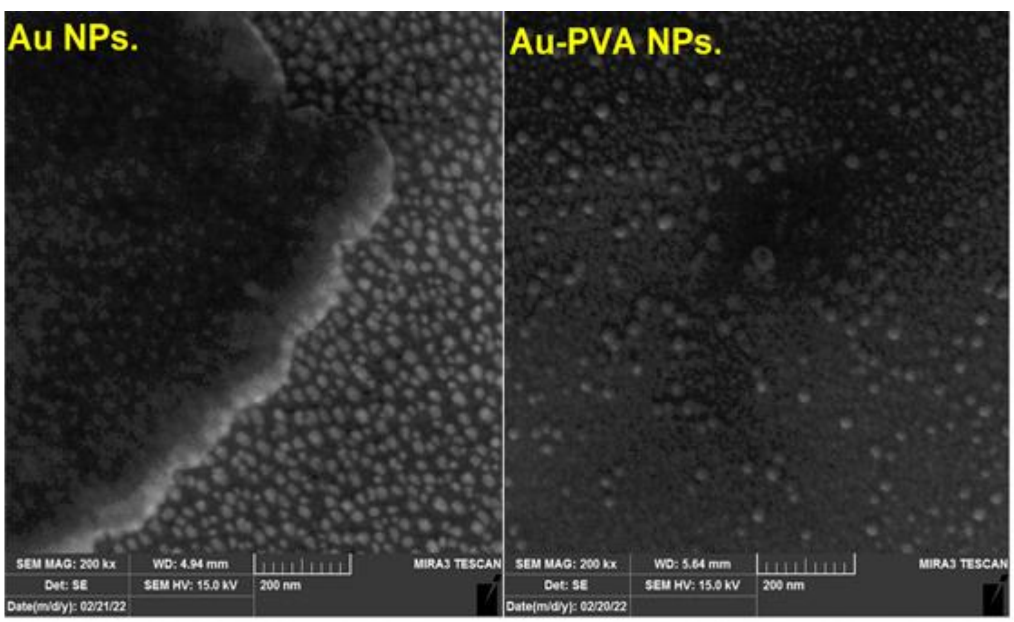

Figure 3.2. FESEM images of Au NPs.

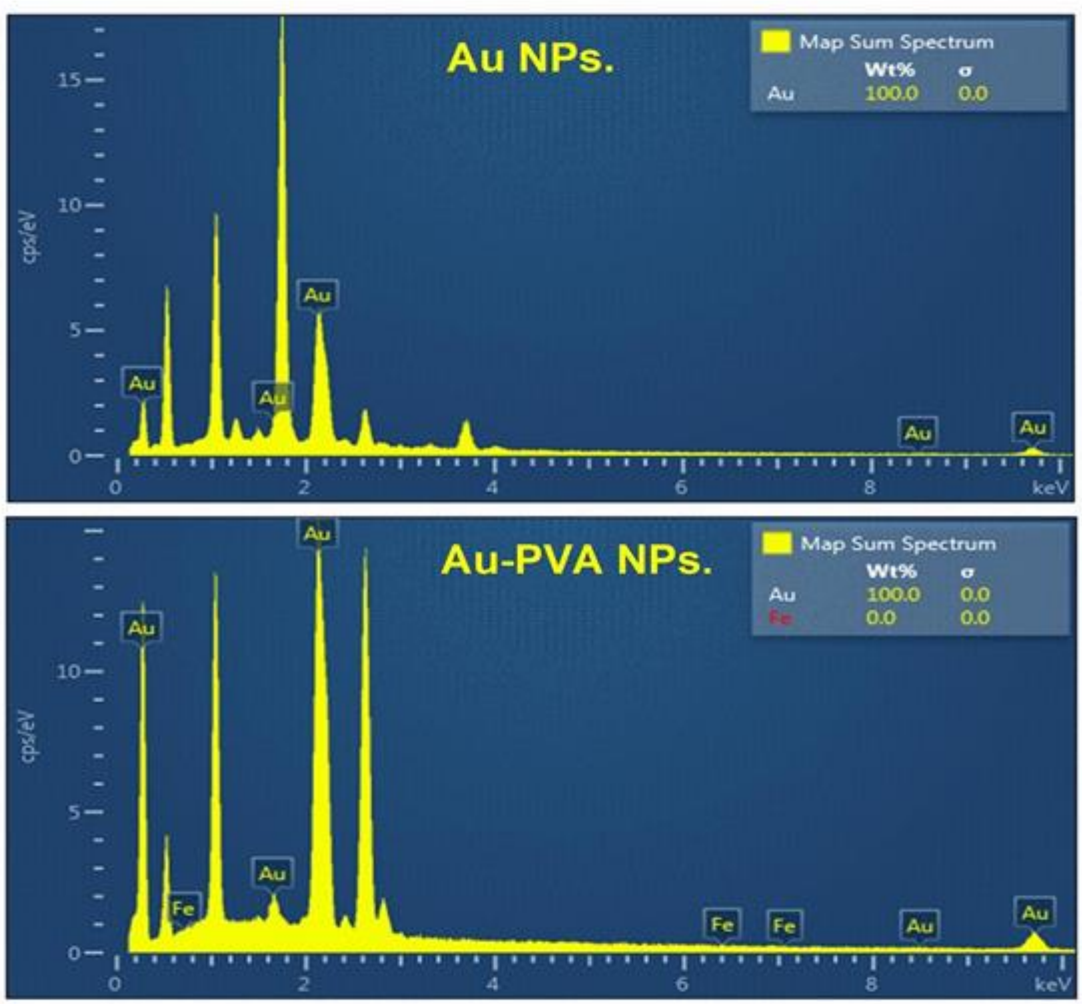

Figure 3.3. EDX spectra of Au NPs.

UV-Vis spectroscopy is used to study the absorption spectra ofgold nanoparticles. Figure 3.4 shows the UV–Vis absorption spectrum of Au NPs. the figure display the surface plasmon resonance position at 527 nm.

The absorption spectra of Au-PVA nanocomposite colloid solution shown in Figure 3.5. Absorption spectrum of Au-PVA colloid has surface plasmon absorption band 520 nm is the maximum wavelength. This result demonstrates the creation ofAu-NPs within the PVA matrix, as well as the presence of the quantum size effect. Crosslinking polymer molecules increasestheir molecular mass significantly, which increases the amountof polymer chains surrounding the Au-NPs. The location and form of the plasmon absorption are determined by the particle size and the surrounding medium's dielectric constant.

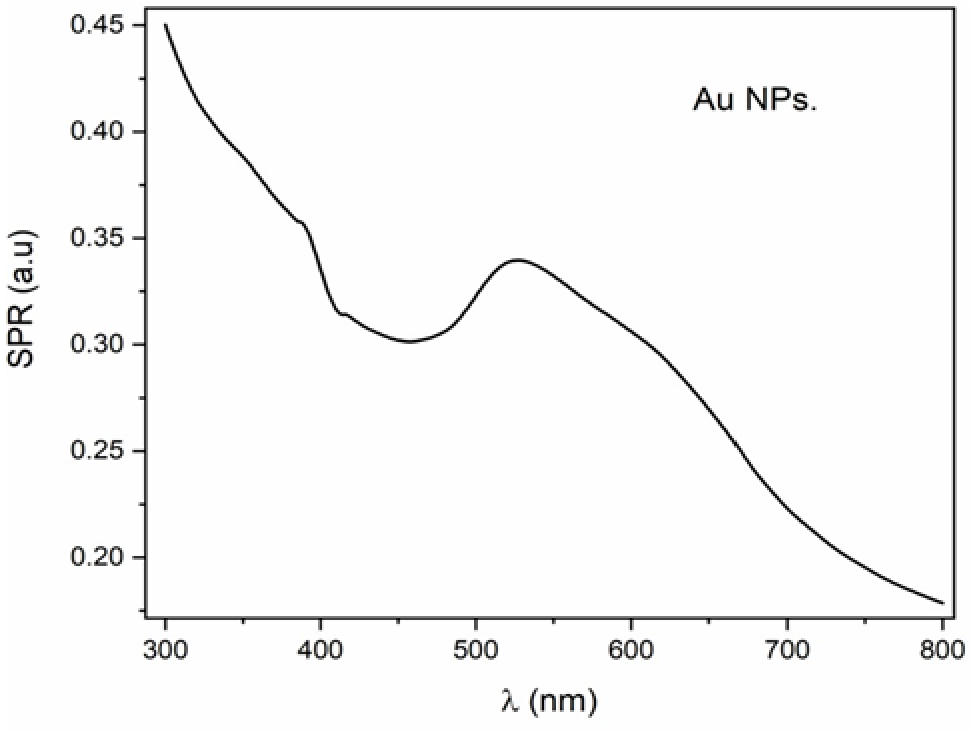

Figure 3.4. Absorption spectrum of Au Nps.

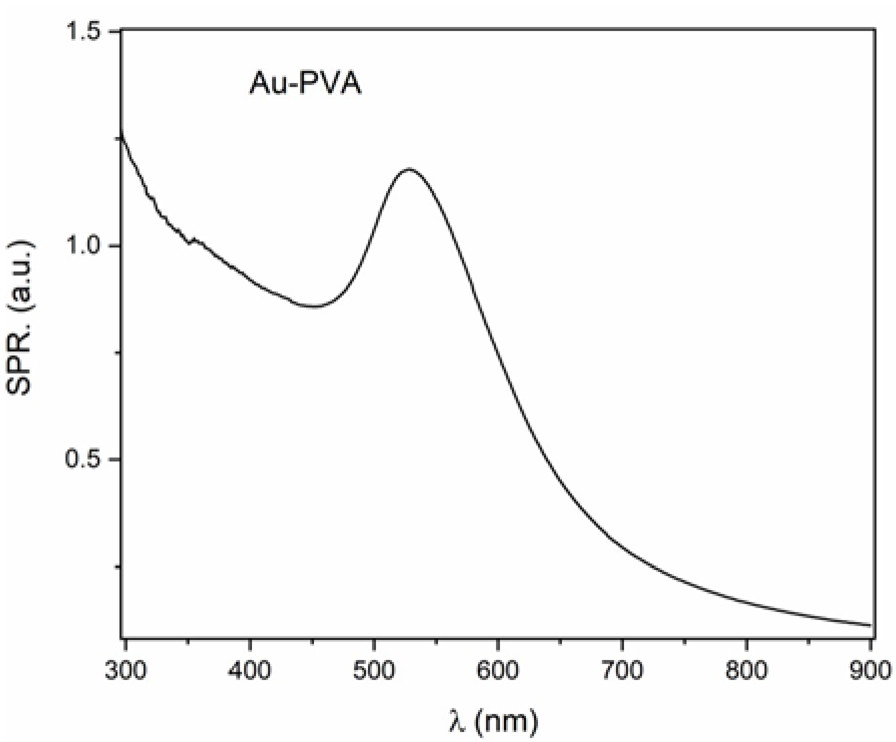

Figure 3.5. Absorption spectrum of Au-PVA.

4. CONCLUSION

gold nanoparticle and gold capped with nanocomposites PVA were synthesized using Tri-sodium citrate as a reducing agent. The gold nanoparticles were characterized by XRD, FESEM, UV/Vis and FTIR. UV/Vis spectra show the characteristic Plasmon absorption peak for the Au ranging from 520 to 530 nm. There was obviouschange observed in peak position.

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