

Synthesis and X-ray Photoelectron Spectroscopy Studies of Poly(vinyl pyrrolidone) Capped Gold Nanoparticles in a Hybrid Nanocomposite

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ABSTRACT

A polymer composite of Au-metal reinforced N-polyvinyl pyrrolidone (PVP) is synthesized in a shape of thin laminates. The process involves a direct reduction of the $\text{Au}^{3+} \rightarrow \text{Au}^0$ in presence of active PVP molecules under hot conditions in water at 60-70°C. A stabilized Au-PVP surface interface of Au-nanoparticles capping in stable PVP polymer molecules is formed. The surface regulating PVP polymer insulates the particles from Au^{3+} and further aggregation. A viscous sample, after evaporating the water at 60-70°C, is casted as a film or in a shape of a thin laminate. Varying the Au-content 0.05 -1.0 wt% in Au-PVP, films are studied in terms of optical absorption, X-ray photoelectron spectroscopy (XPS), and X-ray diffraction. The Au-metal reflects in two characteristic $4f_{7/2}$ and $4f_{5/2}$ XPS bands of 83.1 and 86.8 eV respectively. The shifting of the binding energy E_b in the Au 4f peaks to a lower value relative to the bulk value confirms the microscopic interaction between the Au nanoparticles and the PVP polymer in the hybrid composites.

Keywords: Gold nanoparticles, Nanocomposites, PVP polymer, XPS.

1 INTRODUCTION

In the past decades, there has been a strong interest in the research and development of the Au-polymer nanocomposites for several applications. It has been shown that the optical and other properties of Au or Ag-metal nanoparticles in a hybrid nanocomposite highly depend on the size, shape and distribution in a matrix [1-4]. Dispersion, stabilization, and immobilization of metal particles are a big challenge. As filler small particles support a large interfacial area in composites. The interface controls the degree of interaction between two components and thus controls the final properties. Geometry of the sample as films, with a molecularly oriented structure of polymer, governs the microstructure and other properties of the composites. A suitable polymeric addition during the synthesis allows dispersion of the metal particles, prevents the oxidation and coalescence, and templates a long-time stability of dispersed particles [1, 4-7]. Commonly used additives for the purpose, especially in the case of Au-

nanoparticles, are poly(vinyl pyrrolidone) (PVP) [5-7], poly(ethylene glycol) [8], and poly(vinyl alcohol) (PVA) [9-13]. Particularly, pyrrolidone groups of PVP molecules of refreshed surfaces extend strong covalent bonding (through the donation of the N lone pair of electrons) to nascent Au-surfaces. As a result of the lowered effective surface energy, the concerned particles no longer tend to separate or aggregate so easily. Our group [9-13] developed Ag- and Au-reinforced PVA nanocomposite colloids and films. A single step in-situ process involved no additional stabilizer or immobilizer. Here, we report synthesis of the Au-PVP films (0-1 wt% Au) and their characterization in terms of optical absorption, X-ray photoelectron spectroscopy (XPS), and X-ray diffraction.

2 EXPERIMENTAL DETAILS

A highly pure PVP (weight average molecular weight ~ 40,000 and polymerization number = 360) from Aldrich chemicals was used to prepare an aqueous PVP solution (10 g/dl) by magnetic stirring in a 100 ml batch at 60-70°C temperatures. 10-20 min stirring ensures a colorless transparent solution. Then, an aqueous $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ (0.05 M) of an analytical grade (99.99%) (Merck chemicals) was added drop by drop to it during the stirring at this temperature. As we reported in reaction with PVA [9, 12], an instantaneous $\text{Au}^{3+} \rightarrow \text{Au}$ reaction follows via a displacive Au^{3+} ligand reaction with PVP in a polymer complex. The PVP molecules act as a reductant as well as a stabilizer to resulting Au of nanoparticles. Average color changes from a beautiful wine-red via a light blue to a brown, depending on the Au^{3+} -content (0.05-1.0 wt% Au). Thus obtained nanocolloid of Au-nanoparticles embedded in PVP molecules and of those dispersed in the aqueous PVP solution has been cooled down and aged for 24 h. The viscous Au-PVP sample obtained by evaporating part of water at 60-70°C temperature has been casted in form of thin laminates in a mould of glass or plastic.

The optical absorption of the Au-PVP films was studied by a uv-visible spectrometer (Ocean Optics, Inc. Model-SD 2000). A scanning electron microscope of Oxford model Leo1550 was used to study microstructure in these samples. The phase analysis of the samples was carried out with X-ray diffractograms, which were measured by PW 1710 X-ray diffractometer with 0.15405 nm $\text{CuK}\alpha$ radiation as the

X-ray source at a scanning rate $0.05^\circ/\text{s}$ over the diffraction angle 2θ in the $10\text{-}100^\circ$ range. A VG ESCALB MK-II X-ray photoelectron spectrophotometer was used to measure the typical XPS spectra from the Au-PVP polymer films. This involved exciting the sample, under a reduced pressure $\sim 10^{-8}$ Pa, with Mg $K\alpha_{1,2}$ radiation of $h\nu = 1253.6$ eV energy operating at 12 kV and 20 mA.

3 RESULTS AND DISCUSSION

3.1 UV-visible Spectra in Au-PVP Nanocomposites

The photographs in Fig. 1a compare the developments in the apparent visible colors in forming the Au-PVP nanocomposite films of 0, 0.05, 0.10, 0.20, and 1.00 wt% Au-contents. An intense pink color occurs in the 0.05 wt% Au-content film. The color turns into a blue when raising the Au-content to 0.1 wt%. A relatively faint and brown color follows in a 0.2 wt% Au-content. The color appears dark brown when the Au-content is raised as high as 1.0 wt% in the Au-PVP films. The observation demonstrates that the color is intrinsic of the optical properties of the Au-reinforced PVP molecules of hybrid nanocomposite particles. The volume fraction, shape, and size in the Au-PVP nanocomposite complex particles govern the optical properties. Occurring of selective intense colors of sample infers primarily a preponderance of the involvements of the electronic transitions in the visible region. Scattering from the composite particles is another source of their apparent colors. Zhou et al. [7] synthesized purple color films of icosahedral Au-nanocrystals on the glass slide by a dip-coating method.

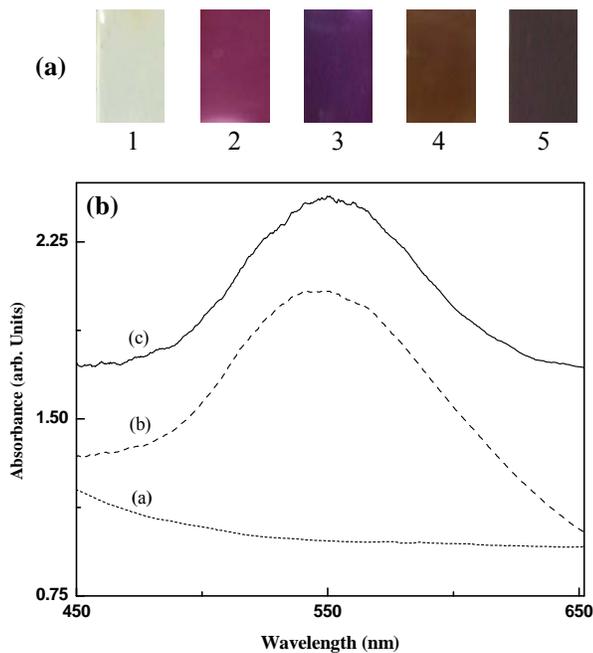


Fig. 1: (a) Apparent colors in Au-PVP nanocomposites films; 1 to 5 having 0, 0.05, 0.1, 0.2, and 1.0, wt% Au, respectively, and (b) optical absorption spectra in the Au-PVP films of (a) 0, (b) 0.05, and (c) 0.1, wt% Au-contents.

Fig. 1b shows the absorption spectra in the 450-650 nm range for three selective samples of Au-PVP nanocomposite films of (a) 0, (b) 0.05, and (c) 0.1 wt% Au-content, respectively. This specific region of the spectrum is characteristic of the surface plasmon resonance (SPR) absorption in Au-nanoparticles. No absorption occurs over this region in a pure PVP film. The 0.05 wt% Au-PVP film, which reflects in a bright pink characteristic color in Fig. 1a, exhibits a strong absorption band, with maximum absorption wavelength $\lambda_{\text{max}} = 545$ nm. It shifts to red at 550 nm upon increasing the Au-content to 0.1 wt% in the sample. Two bands at about 570 and 640 nm in a purple color film of icosahedral Au-nanocrystals were reported by Zhou et al. [7] Enhanced particle-particle interactions in larger Au-contents in such Au-PVP nanocomposite share the energy loss at the expense of the SPR absorption process, i.e., a red-shift of the λ_{max} value in one kind of the particles. The final shape and size, which determine the interfacing in Au-PVP composite particles, more effectively tune the SPR band in terms of both the λ_{max} value.

3.2 Microstructure and X-Ray Diffraction in Au-PVP Nanocomposites

The crystalline nature of Au-PVP films are analyzed with X-ray diffractograms. Fig. 2 shows X-ray diffractogram in a typical 1.0 wt% Au-PVP film, ~ 3 mm thickness. Such a thick sample of sufficiently large Au-content is chosen in order to meet a reasonably resolved diffractogram of lattice reflections from small Au-particles, which are covered in a thin PVP surface layer. Six peaks of diffractogram (from the Au-crystal lattice) occur, in the $10\text{-}100^\circ$ range of the diffraction angle 2θ , in superposition of a broad scattering background in part of the noncrystalline PVP polymer matrix. As marked therein, it involves a broad diffraction halo of wavevector $q = 15.9 \text{ nm}^{-1}$. The Au-metal surface supports occurrence of the polymer counterpart surface layer of this structure. This is feasible if the polymer deposits in thin layers, especially over the Au-particles, in a hybrid Au-PVP composite structure.

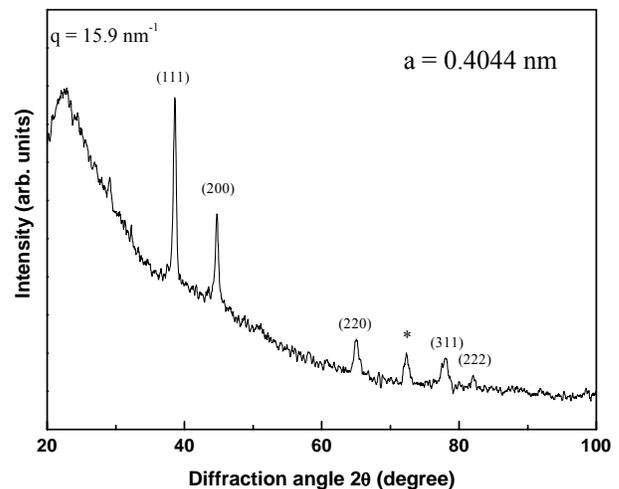


Fig. 2: X-ray diffractogram in 1.0 wt% Au-PVP nanocomposite films.

As in bulk Au-metal [14], the sharp diffraction peaks in Fig. 2 are assigned to (111), (200), (220), (311), and (222) lattice reflections in an Fm3m fcc crystal structure. The intensities (I_p) as well as the interplanar spacings (d_{hkl}) in these peaks differ from the values in bulk Au-metal. The d_{hkl} values determine a lattice parameter $a = 0.4044$ nm (density $\rho = 19.77$ g/cm³) against the bulk value $a = 0.4079$ nm ($\rho = 19.28$ g/cm³) [14]. Using the fwhm-values (fwhm: full width at half-maximum I_p -value) in these peaks in the Debye-Scherrer formula [15] yields ~ 30 nm Au-crystallite size.

Fig. 3 portrays SEM images from the surfaces in (a) 0.1 and (b) 0.5 wt% Au-PVP films. The whitish contrasts of sharp images ascribe the Au-particles. Such Au-particles, which, in fact, are capping in thin PVP polymer films, are dispersed in a polymer matrix of less whitish (diffuse) contrasts in a cloud type of the features. Occurrence of the polymer in the Au-surface layers and the matrix obscures virginal shapes in the Au-particles.

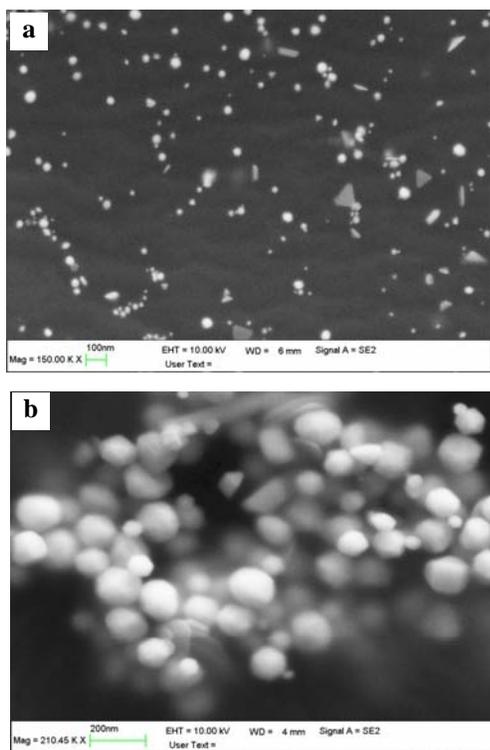


Fig. 3: SEM images in (a) 0.1 and (b) 0.5 Au-PVP films.

At low magnification, the particles appear in nearly spherical shapes, 40-50 nm diameters, distributing uniformly on a polymer surface. Few are triangular prisms. The polymer supported Au-particles have a narrow size distribution, with 70-80 % particles of the average value. Average width (D) in such images is 40-50 nm while the height varies from 40 to 100 nm. The D-value ascribes the size in such Au-crystallites along with the polymer surface layer (5 -10 nm in the thickness) in correlation to the 30 nm value derived by the fwhm values. Bigger particles are clusters of such crystallites. This is feasible in an early

stage of the growth process by a recombination reaction of the crystallites.

3.2 XPS in Au-PVP nanocomposite films

The Au-metal nanoparticles are embedded in the PVP polymer matrix via chemical linkage with PVP molecules. Studies on the nature of the microscopic interaction between Au particles and PVP polymer chains are important in understanding the Au-PVP hybrid composite system. The XPS studies are performed for the free-standing films of pure and reinforced PVP polymer molecules in form of Au-PVP nanocomposites. Fig. 4a shows a typical XPS spectrum measured from the pure PVP films. A prominent C1s band with normalized intensity value $I_p = 100$ occurs of binding energy E_b -value of 281.6 eV confirming the carbon occurring in the PVP molecular in layers. Furthermore, the O1s peak (Fig. 4b) appears as the second most intense peak with a value $I_p = 40$ at the average peak value at ~ 530.7 eV. As shown this band has a doublet structure. A deconvoluted spectrum consists of two band components of 529.9 and 531.6 eV of the E_b -values. The O1s band component of 531.6 eV is assigned to the O²⁻ bonded to the C atom (in form of the C=O group) in the PVP molecules.

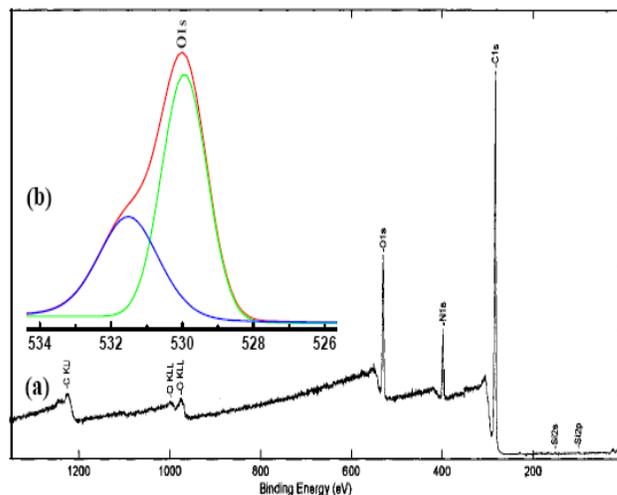


Fig. 4: (a) XPS spectrum in the virgin PVP films, with (b) a close-up of the O 1s band.

In order to study the valence state of gold and its interaction with matrix, in 0.1 wt% Au-PVP nanocomposite films, we analyzed the characteristic Au 4f_{7/2} and 4f_{5/2} XPS bands. As portrayed in Fig. 5, a well-resolved double structure of the concerned XPS signal occurs with the two components of 83.1 and 86.8 eV E_b -values, respectively, with a separation ΔE_d between the two bands of 3.7 eV. The bands are assigned to the spin-orbit spitted components of the Au-4f level in the pure Au-metal [16]. In comparison to the bulk, the Au nanoparticles have relatively lower E_b -values in the 4f_{7/2} and 4f_{5/2} Au-bands in the Au-PVP nanocomposites. The shifting in E_b -values confirms the microscopic interaction between the Au nanoparticles and the PVP polymer in the hybrid composites. A surface polymer coating of Au-

particles, or a reinforcing of Au-particles in a polymer matrix in a composite structure, causes a modification in E_b values according to interactions between the two phases. The shift in the E_b -value can be attributed to chemical bonding with the surroundings and interparticle interactions. In general, a coating of the Au nanoparticle by a thin surface layer PVP in nanocomposite structure is of interest in this work causes a shift in E_b -values in the characteristic bands according to the prominent interactions between the two phases.

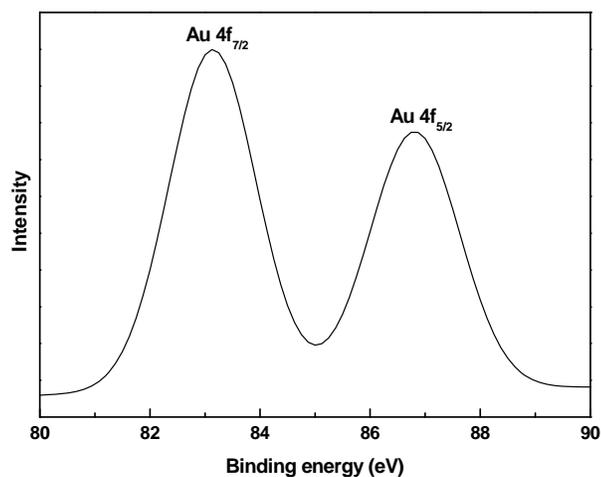


Fig. 5: The Au 4f_{7/2} and 4f_{5/2} XPS bands in the 0.05 wt % Au-PVP nanocomposites film.

The XPS confirms that PVP molecules exist on the surface of the Au cores, which play a very important role in the formation and evolution of the different shape and size of the of the Au nanoparticles, e. g. twinned Au plates, polyhedral plates, truncated triangular shaped particles as observed in the SEM (Fig. 3).

4 CONCLUSIONS

The colored Au-PVP nanocomposite films are synthesized by a simple in-situ $Au^{3+} \rightarrow Au$ conversion reaction in an aqueous medium of PVP molecules followed by casting of the Au-PVP nanocolloids. The Au-SPR absorption band, which occurs over 450-650 nm, varies sensitively in its position as well as the intensity when varying the Au-content 0-1 wt%. An intense bluish-pink color of a nanocomposite occurs in the 0.05 wt% Au, with the absorption maximum λ_{max} at 545 nm which shifts to 550 nm upon raising the Au-content to 0.1 wt%. The XRD peaks in Au-PVP nanocomposite confirm the lattice reflections in an Fm3m fcc crystal structure. The polymer supported Au-particles have a narrow size distribution, with 70-80 % particles of the average size value 40-50 nm. The shifting in E_b -values in XPS bands confirms the microscopic interaction between the Au nanoparticles and the PVP polymer in the hybrid composites. The results are useful for designing and fabricating novel metal-polymer nanocomposites in specific shapes of thin films, sheets, plates, wires, or cylinders useful for electronic and optical devices.

ACKNOWLEDGEMENTS

University Grant Commission (UGC), Government of India, is acknowledged for providing the research fellowship.

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