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Proposing a Feasible Mechanism to Support the Exhibition of Superb Colloidal Stability of Gold Nanoparticles with Poly Vinyl Pyrrolidone in the form of a Nanofluid in N, N'-Dimethyl Formamide

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ABSTRACT

In this article, proposed a probable mechanism to corroborate execution of excellent colloidal stability of gold (Au) nanoparticles (NPs) in presence poly (vinyl pyrrolidone) PVP polymer in N, N'-dimethyl formamide (DMF) solvent, as nanofluids (NFs) in support of experimental outcomes. Appearance of a surface plasmon resonance band near 525 nm in the absorption spectra suggests formation of gold NPs in presence of PVP in DMF. The emergence of X-ray diffraction peaks at 111, 200, 220 and 222 corresponds to diffraction angles 38, 45, 65 and 78, respectively, reveals that Au NPs have fcc crystal structure. Slight red-shift (i.e., from 525-530 nm) in the surface plasmon resonance band of the one year aged sample strongly suggests that Au-NPs are highly stable in presence of PVP, particularly in DMF. An enhancement in the some of the vibration bands of PVP in presence of Au-NPs suggests donor-acceptor type interaction between Au-NPs and PVP via O-atoms. In comparison to bare PVP, an increased zeta potential value with an enhanced surface conductivity in Au-PVP NF in DMF suggests that both PVP and DMF supplies electrons to the surface of Au-NP. In the aged sample, hardly any change in the zeta potential value supports the absorption analyses. Shear thinning characteristics in the Au-PVP NF in DMF suggests presence of cross-linked structure between PVP, DMF and Au-NP. Core-shell structure from the microstructures of the NF demonstrates that PVP and DMF molecules are encapsulating Au-NPs via O-atoms. Development of highly stable Au-NPs is useful for drug delivery applications.

Key words: Nanofluids, nanocomposites, surface plasmon resonance, zeta potential, bingham flow, colloidal stability, core-shell nanostructures

INTRODUCTION

Nanofluids (NFs) describe a homogeneous dispersion of nanoscale materials of 2-100 nm size in a liquid. NFs-a new class of functional materials have become the subject of intensive research in optoelectronics, catalysis, bio-medicals and sensors (Chen *et al.*, 2005; Kedia and Kumar, 2012, 2013; Moon *et al.*, 2013; Liu *et al.*, 2008; Lu *et al.*, 2012). Synthesis of metal-polymer nanocomposites/NFs with controlled microstructure and functional properties are an integral part of an emerging and rapidly growing nanotechnology. The widespread applications of such nanomaterials largely results from the unique size-and morphology dependent optical and electrical properties of inorganic nanoparticles (NPs) such as gold (Au), silver (Ag), platinum, TiO₂, etc. Owing to possession of vast surface area, the NPs possess a huge amount of excess Gibbs free-energy relative to the bulk value and thus are thermodynamically not so much stable (Kedia and Kumar, 2012, 2013; Moon *et al.*, 2013; Lu *et al.*, 2012). Hence, a major limitation of a NF is that they possess a short-term colloidal stability. Hence, special precautions have to be taken to

avoid unwanted aggregation and precipitation of such particles. The most common strategy is to use a suitable stabilizer during the reaction. It suppresses due particle aggregation and promotes the functionalized properties (Kedia and Kumar, 2012, 2013; Moon *et al.*, 2013; Sun *et al.*, 2009). Apart from the basic chemistry, the properties of nanocomposites/NFs depend not only on the properties of their individual parents but also on their morphology and interfacial characteristics.

In recent years, stabilization of colloidal NPs has been the subject of active study because the high surface energy resulted from the large surface area of NPs drastically decreases the thermodynamic stability and later alters the nucleation and growth kinetics in such a way that it is very difficult to control the size and shape of NPs with high homogeneity. To control the nucleation and growth kinetics of NPs, an organic surfactant or a polymer has been introduced as a structure-directing/surface capping agent so that NPs have been enclosed within an organic/inorganic material in the form of a core-shell nanostructure. A surfactant or a polymer layer which is adsorbed on the reactive nascent surfaces in the growing NPs serves as a diffusion barrier layer to the growing structure, resulting in a diffusion-limited growth process in the subsequent growth step of such particles. In this regards, various synthetic routes have been proposed and tested to synthesize mono-dispersed NPs (Kedia and Kumar, 2013; Sun *et al.*, 2009; He *et al.*, 2002; Prozorova *et al.*, 2014).

From a thorough literature study, I found that the chemical methods are widely used to synthesize NPs of different shapes and sizes with functionalized properties. The commonly used polymers for surface stabilizing noble metals like gold are Poly Vinylidene Fluoride (PVF₂) (Chae *et al.*, 2007; Miranda *et al.*, 2009), Poly Vinyl Pyrrolidone (PVP) (Behera and Ram, 2014; Chen *et al.*, 2005; Kedia and Kumar, 2012, 2013; Liu *et al.*, 2008; Ram and Fecht, 2011; Pastoriza-Santos and Liz-Marzan, 2002; Slistan-Grijalva *et al.*, 2008) and Poly Vinyl Alcohol (PVA) (Behera, 2015; Tripathy *et al.*, 2006, 2007). Amongst the various macroscopic surface encapsulating agents tested by researchers, PVP is one of the most frequently used polymer in the synthesis metal NPs. In many literatures it is mentioned that PVP not only acts as a reducing agent but also a size-regulating agent. It is reported that reducing power of PVP from Au³⁺ ions to Au atom in water and various organic solvents is mainly due to presence of lone-pair of electrons on the O-atom of the lactam ring (Behera and Ram, 2014; Pastoriza-Santos and Liz-Marzan, 2002; Ram and Fecht, 2011; Slistan-Grijalva *et al.*, 2008).

Even though abundant literatures are available on the synthesis, characterization and applications of Ag and Au colloids in presence of polymer in both aqueous and non-aqueous solvents, Till date even a single literature is not available to support the execution of excellent colloidal stability of Au-PVP NFs especially in DMF. It is already reported that DMF reduces Ag⁺/Au³⁺ ions to Ag/Au NPs of various shapes includes spheres, nanoprisms and nanowires usually at higher temperatures (60-150°C). Liu *et al.* (2008) have reported that DMF is acting as both stabilizing and reducing agent. They found that a dilute solution of HAuCl₄ in DMF can be progressively reduced to stable Au NPs, but at relatively higher temperature (~140°C). In an experiment, Pastoriza-Santos and Liz-Marzan (2002) reported formation of highly stable PVP-protected metal NPs in DMF, but at a temperature of 156°C. I had synthesized Au-PVP NFs in DMF that showed colloidal stability of more than a year. So, absence of any literature to support the excellent stability of metal NPs with PVP in DMF in particular makes me curious in finding the possible reason behind displaying the much needed attribute for heat transfer and drug delivery applications.

In this study, synthesis of highly stable Au-NPs in presence of PVP in DMF at relatively much lower reaction temperature (i.e., at 40°C) is discussed. In support of experimental outcomes of UV-visible, emission, Fourier transform infrared (FTIR) spectroscopy, X-Ray Diffraction (XRD), rheology, zeta potential and microstructures, I propose a plausible mechanism in explaining the exhibition of excellent colloidal stability of Au-PVP NFs in DMF.

MATERIALS AND METHODS

Materials: Gold hydroxide Au(OH)₃ powder containing 79% Au of reagent grade was purchased from Alfa Aesar. Analytical standard DMF of 99.9% purity was purchased from Sigma-Aldrich. Polyvinyl pyrrolidone (PVP) of average molecular weight ~40,000 was purchased from Sigma-Aldrich. Chemicals were used as received without further purification.

Synthesis of Au-PVA NFs in DMF: Two solutions, i.e., Solution 1 and 2 were prepared to synthesize Au-PVA NFs in DMF solvent. The Solution 1 (i.e., a PVP solution of strength 40 g L⁻¹) was obtained by dissolving requisite amount of PVP in DMF by hot magnetic stirring for 3 h at 60-70°C. The Solution 2 (i.e., 2 mM Au(NO₃)₃ solution) was prepared by dissolving a required amount of Au(OH)₃ powder in dilute HNO₃. Now, the Solution 2 was added dropwise to a 5 mL Solution 1, while stirring using a magnetic stirrer at 40°C. After hot stirring the solution for 5 min, a light purple colored NF was obtained thereof which was sonicated at 40°C in an ultrasonicator (OSCAR, 20 kHz frequency and 250 W power) for 5 min to prepare stable NF. The Au-PVP NFs thus prepared at relatively low reaction temperature (here 40°C) were kept in vacuum oven for experimental study using, various techniques, such as; UV-Visible, emission, Fourier transform infrared (FTIR) spectrometer, rheometer, zeta potential and High Resolution Transmission Electron Microscope (HRTEM).

Experimental techniques: A Perkin-Elmer double beam spectrophotometer (Model-LAMBDA 1050) was used to measure the optical absorption spectra of aqueous 40 g L⁻¹ PVP solution with and without Au-NPs. The spectrum was recorded against a reference (DMF or 40 g L⁻¹ PVP with DMF) in quartz cell of 10 mm optical path length. A Thermo Nicolet Corporation FTIR spectrometer (Model-NEXUS-870) was used to study the vibration spectra of the PVP and Au-PVP solution in DMF. The spectra have been recorded in an attenuated total reflectance mode using a ZnSe crystal, as a sample holder. The emission spectra were recorded with a computer-controlled Perkin-Elmer (Model-LS 55) luminescence spectrometer in conjugation with a red sensitive PMT detector (RS928). A high-energy pulsed xenon discharge lamp was used as an excitation source (average power 7.3 W at 50 Hz). Zeta potential (ζ) of diluted samples were measured using a Malvern Nano ZS instrument using phase analysis light scattering technique. A rotational rheometer (TA instruments, Model: AR-1000) of parallel plate geometry was used to measure the rheological properties of PVP and Au-PVP NFs in DMF. To measure the data, a few drops of the fluid were placed on the lower plate of the system. The shear rates $\dot{\gamma}$ was varied from 10-500 sec⁻¹ while recording the data. Also the shear viscosity (η) and shear stress were measured at selective $\dot{\gamma}$ -values in the 10-500 sec⁻¹ range. Microscopic images of the PVP-capped Au-NPs were studied using, a JEM-2100 (JEOL, Japan) instrument. The samples for taking HRTEM images were prepared by depositing one drop of diluted solution on a carbon coated 400-mesh copper grid and then kept the sample in a desiccators at room temperature.

RESULTS AND DISCUSSION

Absorption spectra and XRD pattern: Figure 1 shows the absorption spectra of (a) DMF, (b) 40.0 g L⁻¹ PVP in DMF and (c) 100 μM Au-NPs with 40.0 g L⁻¹ PVP in DMF. As evident from the Fig. 1, two distinct absorption bands are showing in the UV region for the DMF solvent; one at 241 nm and other at 291 nm. The first peak corresponds to $\pi\text{-}\pi^*$ and the later to $n\text{-}\pi^*$ transition of $>\text{C} = \text{O}$ group of the amide-based solvent (Hunt and Simpson, 1953). In Fig. 1, the absorption spectrum of 40.0 g L⁻¹ PVP in DMF is also exhibiting two bands, but differs in their intensities and peak position in the UV region. They comes from $\pi\text{-}\pi^*$ and $n\text{-}\pi^*$ transitions of $\text{C} = \text{O}$ moiety of the pyrrolidone group. The difference in the peak intensities and slight change in their positions hints some chemical interaction between PVP and DMF molecules. In an article, Kedia and Kumar (2012) have reported that dipole-dipole interaction exists between PVP and DMF molecule. For both samples in the visible region of the two spectra, no band was noticed. A broad band near 525 nm that was noticed for Au-PVP NF in the visible region shows formation of Au-NPs (Behera and Ram, 2014; Chen *et al.*, 2005; Kedia and Kumar, 2012, 2013; Pastoriza-Santos and Liz-Marzan, 2002; Ram and Fecht, 2011). It is a Surface Plasmon Resonance (SPR) band (a typical signature for the formation of metal NPs) that obtain due to collective oscillations of electrons of Au-NPs, when light of suitable wavelength falls on it (Kedia and Kumar, 2012, 2013).

In order to study the execution of superb colloidal stability of Au nanocolloid with PVP in DMF, we compare the absorption spectra of freshly prepared sample and a sample aged for a period of 1 year. Figure 2 shows the absorption spectra recorded of Au-PVP NFs in DMF, (a) Freshly prepared and (b) After 1 year of synthesis. For sample (a) which shows a peak centered at 525 nm, absorbance maximum (A_{max}) of 0.3 cm^{-1} and Full Width at Half Maximum (FWHM) of 90 nm was calculated from the spectrum. For the aged sample, we noticed a red-shifted SPR band that centered at 530 nm, with A_{max} of 0.32 cm^{-1} and FWHM of 88 nm. A slight red-shift in the SPR band suggests that Au-NPs are not agglomerating in presence of PVP in DMF and will hardly change their cluster size. We calculated the size of PVP-capped Au-NPs using the well-known Kreibig and Frangstein relation (Slistan-Grijalva *et al.*, 2008):

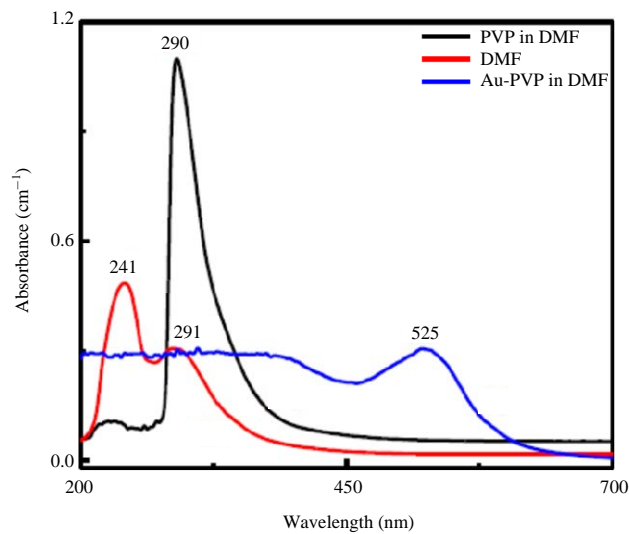


Fig. 1: Absorption spectra of DMF PVP in DMF and Au-PVP nanofluid in DMF

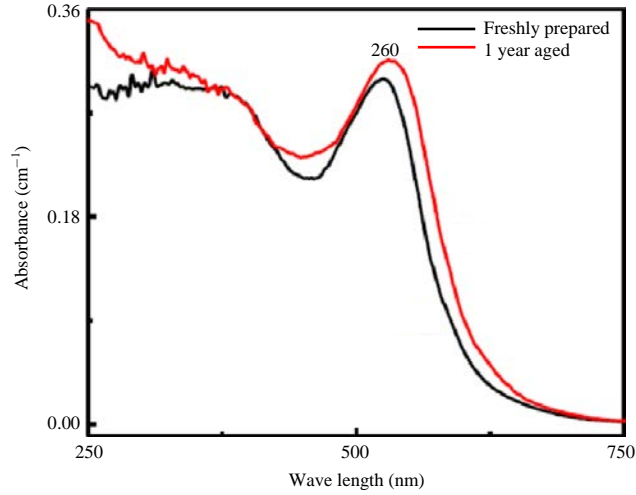


Fig. 2: Absorption spectra of Au-PVP nanofluid sample

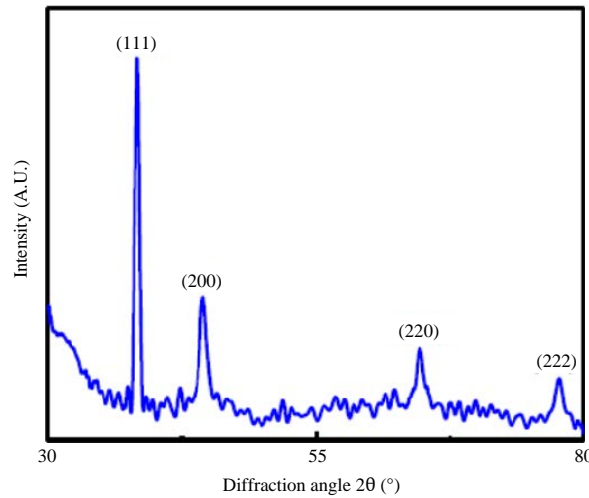


Fig. 3: X-ray diffraction pattern of Au-PVP nanocomposite film

$$R_{n+1} = R_n \left(\frac{(A_{\max} \delta)_{n+1}}{(A_{\max} \delta)_n} \right)^{1/3} \quad (1)$$

where, δ is the FWHM and R_n stand for size of PVP-capped Au-NPs in sample (a). It is found from the TEM image as 25 nm. Here, $n+1$ denotes for after 1 year and A_{\max} expressed in nm^{-1} . So, by substituting respective values in eq. 1, the R_{n+1} is found to be 28.2 nm. The obtained results indicate an increase of only 3.2 nm diameters in particle size after 1 year. Such a small increase in the cluster size hints that PVP is acting as a good stabilizing agent for Au-NPs.

The XRD pattern of a spin-coated Au-PVP film was studied in order to know about the crystal structure of the Au-NPs formed in the nanofluid. Figure 3 shows the XRD pattern measured from the Au-PVP films consisting of 100 μM Au. Four distinct peaks 111, 200, 220 and 222 that corresponds to diffraction angles (2 theta) of 38, 45, 65 and 78, respectively were reveals that Au has fcc crystal structure (Chen *et al.*, 2005; Tripathy *et al.*, 2006, 2007).

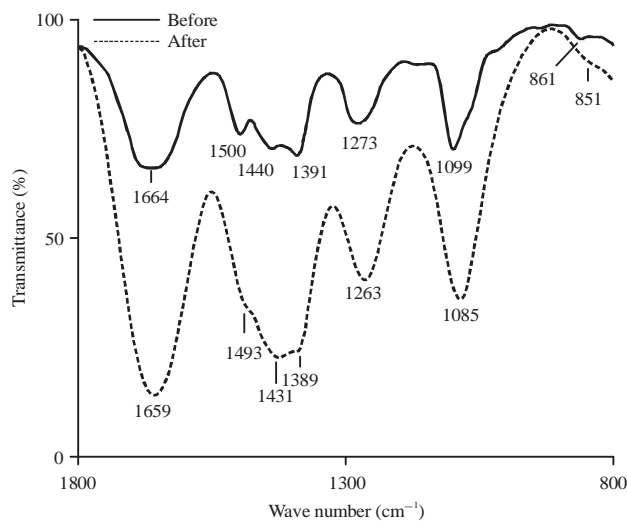


Fig. 4: Fourier transform infrared spectra of PVP containing 100 μM Au-NPs in DMF

FTIR and emission spectra: The vibrational bands of PVP in DMF (a) Before and (b) After adding a specific amount of Au-NPs are shown in Fig. 4. In comparison to the FTIR spectra of PVP in DMF, a marked enhancement in the band intensity of C = O stretching band (1664 cm^{-1}), C-N (1463 cm^{-1}) stretching band and CH_2 (1381 cm^{-1}) bending vibrations in the pyrrolidone ring of PVP polymer was observed specifically in presence of Au-NPs. Earlier reports suggest that such augmentation in the band intensity could occur only when PVP polymer gets adsorbed on the surface of Au-NP via non bonding electrons of O-atoms of pyrrolidone ring (Behera and Ram, 2013a; Hunt and Simpson, 1953; Kedia and Kumar, 2012; Prozorova *et al.*, 2014; Slistan-Grijalva *et al.*, 2008). In PVP, it is reported that the direct participation of N-atom is less favored due to steric hindrance effect (Behera and Ram, 2013b; Kedia and Kumar, 2012; Prozorova *et al.*, 2014; Slistan-Grijalva *et al.*, 2008; Borodko *et al.*, 2006). In the Au-PVP sample, a profound enhancement in the band intensity of C = O stretching band strongly suggests a surface enhanced IR absorption of PVP molecules in presence NPs. It suggests a donor-acceptor type interaction between Au NP and C = O group of PVP and DMF molecule. Such interaction is essential to stabilize NPs via steric shielding. In an article, Borodko *et al.* (2006) have reported a marked improvement in intensities of $>\text{C} = \text{O}$ bands in PVP polymer in presence of Pt-NPs. A red-shift of 5 cm^{-1} i.e., from $1,664\text{--}1,659\text{ cm}^{-1}$ was noticed in the C = O stretching vibration in presence of Au-NPs. Such a small band shift implies a weak interaction between PVP molecules and Au surface via O-atom of C = O group due to steric effect. From FTIR spectra, Kedia and Kumar (2013) have reported that PVP interacts via O-atom with Au^{3+} ions and reduces the later to yield Au^0 species in DMF. In another report, Prozorova *et al.* (2014) have accounted from FTIR the spectra that an interaction occurs between Ag-NPs and poly vinyl triazole matrix. Slistan-Grijalva *et al.* (2008) have ascribed a band shift of C = O band of PVP polymer to a lower frequency in presence of Ag-NPs to donor-acceptor interaction between the two moieties.

Figure 5 depicts the emission spectra of PVP (a) Without Au-NPs, (b) PVP with $100\text{ }\mu\text{M}$ Au-NPs and (c) PVP with $100\text{ }\mu\text{M}$ Au-NPs after 1 year (all are excited at 300 nm). It is reported that PVP exhibits an intense emission at 392 nm due to $\pi\text{--}\pi^*$ transition in the C = O group (Behera and Ram, 2013c; Miranda *et al.*, 2009). It is also reported that, PVP hardly loses its intensity in

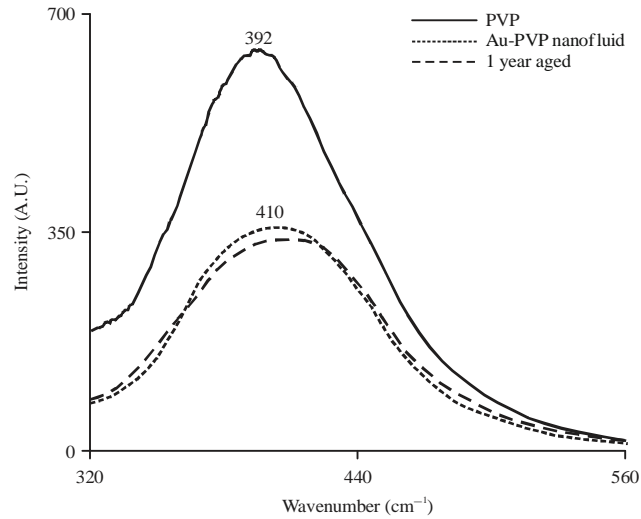


Fig. 5: Emission spectra of PVP, Au-PVP nanofluid and 1 year aged Au-PVP nanofluid in DMF. Samples were excited at 300 nm

presence of a solvent (Ram and Fecht, 2011; Behera and Ram, 2013a). So, in my case, a red-shift in $\pi-\pi^*$ band of PVP has occurred from 392-410 nm in presence of Au-NPs. Red-shift will occur as some amount of energy of PVP will be lost by the process of electron transfer from the C = O group (i.e., electron donor) to the electron deficient Au-NP (i.e., electron acceptor) in a donor-acceptor complex (Behera and Ram, 2013b). Further, a strong quenching in the emission intensity (i.e., as much as 50%) of PVP was noticed in presence of Au-NPs with 40 g L⁻¹ PVP in DMF. It also suggests an existence of a donor-acceptor type interaction between the PVP, DMF and Au-NP which is required to encapsulate and stabilize Au NPs (Behera and Ram, 2013c; Dulkeith *et al.*, 2002; Ghosh *et al.*, 2004; Karthikeyan, 2010). In a report, Liu *et al.* (2008) have stated that red-shift of excitation wavelength results from agglomeration of Au-NPs via PVP cross-linking process in a donor-acceptor complex. They also concluded that Au-NPs profoundly quench the emission intensity of PVP. In comparison to the spectra b and c, a small decrease in the emission intensity in the sample-c reveals that this sample is highly stable.

Zeta potential: To further validate the existence of interaction between PVP and Au-NP, the zeta potential (ζ) of PVP in DMF with and without Au-NPs was studied after three time dilution in DMF. As shown in Fig. 6a, sample (a) of 40 g L⁻¹ PVP in DMF displays an average ζ -value of (-) 7.0 mV with surface conductivity (s_{sc}) = 0.019 mSec cm⁻¹ at pH 7.5. Whereas, an Au colloid (b) consisting of 100 μ M Au-NPs with 40 g L⁻¹ PVP in DMF results in a larger ζ -value of (-) 27.0 mV, with an enhanced s_{sc} = 0.25 mSec cm⁻¹ at pH 7.4. A larger ζ -value with an enhanced s_{sc} -value in Au-PVP nanofluid in DMF suggests a large electron charge density that has resulted from accumulation of a large number of nonbonding electrons of C = O groups of both PVP and DMF molecules around the Au-NP. Similar effect has already been reported in PVP-capped fullerene (C₆₀) and Au NFs in both aqueous and non-aqueous medium where PVP acts as an active electron donor (Behera and Ram, 2012a, 2013a, 2014). In a report, Ahlberg *et al.* (2014) have reported a negative ζ -value of (-) 20.0 mV for PVP-coated Ag-NPs owing to aggregation of electrons on the

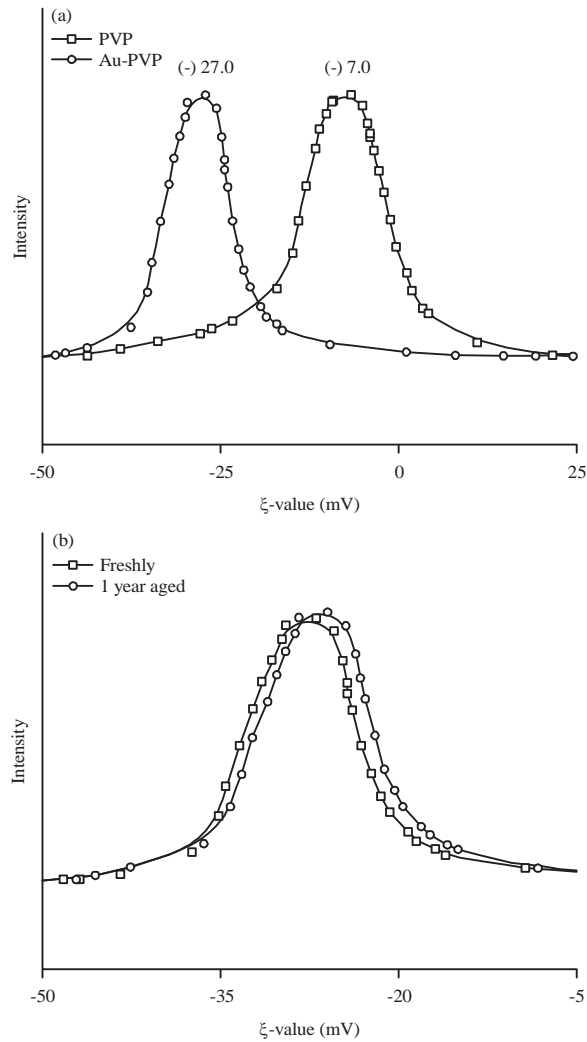


Fig. 6(a-b): (a) Zeta potential band of PVP and Au-PVP nanofluid in DMF and (b) Zeta potential band for freshly prepared Au-PVP nanofluid and 1 year aged sample in DMF

surface of Ag-NP. In our earlier experiment on Au-PVP nanofluid in 1-butanol and water, we have reported a ξ -value of (-) 20.0 mV. In this experiment, a relatively larger ξ -value of (-) 27.0 mV clearly hints contribution of the DMF solvent in addition to the role of PVP in achieving such longer colloidal stability. Studart *et al.* (2007) have reported a ξ -value of (-) 25 mV at 8.0 pH for copolymer-capped alumina NPs and argued that such a low zeta potential level is not enough to provide an electric double layer so that, the NPs can prevent particle agglomeration. Therefore, an electro-steric stabilization is responsible for the colloidal stability of surface coated NPs.

In finding the possible cause of presentation of extremely high colloidal stability of Au-PVP NFs in DMF, we further study the ξ -band distributions of (a) Freshly prepared and (b) Aged 100 μ M Au-PVP nanofluid in DMF. As shown in Fig. 6b, even after 1 year of aging, the ξ -value has hardly change i.e., it has changed only from (-) 27.0 to (-) 26.0 mV. It implies that the sample has not undergone any agglomeration process in presence of both encapsulants (i.e., PVP and DMF). Hence, the NPs have exhibited excellent colloidal stability even after such a long time period.

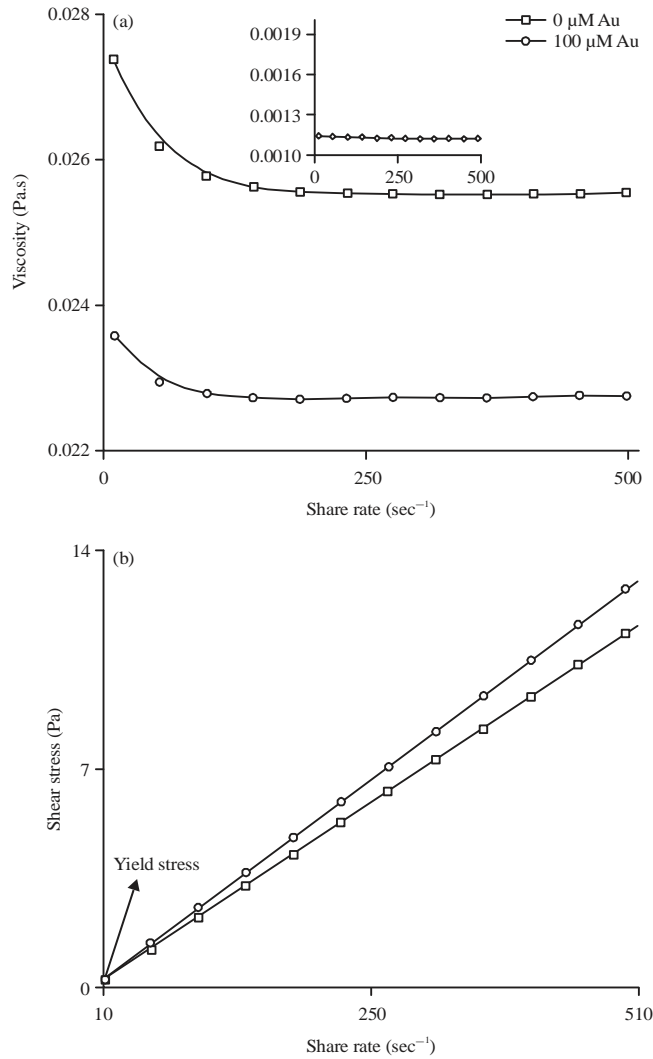


Fig. 7(a-b): Variation of (a) Shear viscosity as a function of shear rate and (b) Shear stress as a function of shear rate in Au-PVA NFs with 40.0 g L⁻¹ PVP in DMF 0 and 100 μM Au. Inset shows the rheogram for the DMF solvent

Rheology in Au-PVP nanofluid in DMF: Figure 7a depicts a variation of shear viscosity (η) as a function of shear rate ($\dot{\gamma}$) in 40 g L⁻¹ PVP in DMF (a) Before and (b) After addition of 100 μM Au-NPs. Inset in Fig. 7 shows the rheogram for the DMF. As can be seen from the graphs, the two rheograms exhibit a non-Newtonian behavior of viscosity whereas DMF exhibiting a Newtonian behavior. A non-Newtonian behavior reveals that some interaction occurs between PVP and DMF in Sample-a and in Sample-b, it exists between PVP, Au and DMF. It is also seen that the base η -value has increased reasonably when Au-NPs were added so that it can form a network structure with PVP in DMF. In Fig. 7b, a linear shear stress (τ) against $\dot{\gamma}$ -value plot prevails over 10-500 sec⁻¹ $\dot{\gamma}$ -values on Sample-a and Sample-b. The data points in Fig. 7b fit very well in a characteristic relation of a Bingham plastic with a residual yield stress (t_y) (Behera, 2015; Barnes and Walters, 1985; Phule *et al.*, 2013). It is obtained from the linear fit of Fig. 7b that a t_y -value of 88.0 mPa, which is found in a basic PVP solution has increased to a value 145.0 mPa

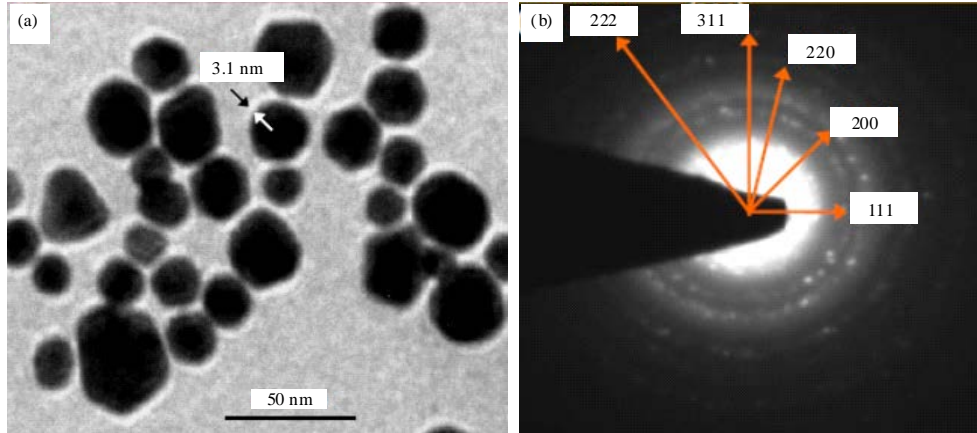


Fig. 8(a-b): (a) TEM images taken of $100.0 \mu\text{M}$ Au-NPs with 40 g L^{-1} PVP in DMF showing core-shell nanostructures and (b) Rings of an electron diffraction pattern of Au-NPs corresponds to 111, 200, 220 and 311 planes of fcc Au atom

when it is grafted with $100.0 \mu\text{M}$ Au. It suggests that Au-NPs are helping in formation cross-linked network structure with PVP in Au-PVP nanofluid in DMF. Liu *et al.* (2008) reported that PVP polymer provides a cross-linking environment so that Au-NPs can forms clusters easily.

Microstructure in Au-PVP NFs in DMF: The TEM images obtained from Au-PVP NFs is shown in Fig. 8a. As seen from the image, PVP-capped Au NPs of 10-35 nm size were obtained with PVP polymer. It is also found that the size distributions of PVP-encaged Au-NPs are not uniform. The polydispersity may be ascribed to low content (i.e., 40 g L^{-1}) of surface encapsulating agent (i.e., here PVP) in the medium (Kedia and Kumar, 2012, 2013; Moon *et al.*, 2013). In an article, Studart *et al.* (2007) have reported that high content of encapsulant is important for developing NPs of uniform size distributions and providing optimal colloidal stability. A typical PVP-encapsulated Au-NP in Fig. 8a demonstrates a distinct amorphous surface layer made of PVP that is encaging Au-NP. The surface layer of 3.1 nm thickness appears as a whitish contrast because electrons can easily pass through it. The PVP-layer adheres firmly to the dark region of the Au-NP. Similar core-shell nanostructures have already reported by many researchers. For example, Rahme *et al.* (2008) have accounted core-shell structures in tri-block copolymer-capped Au-NPs. In another experiment on organic-inorganic hybrid nanostructure, a similar kind core-shell structure is reported in Ag-NPs coated with polystyrene/methyl methacrylate matrix (Quaroni and Chumanov, 1999). It is also reported that Au-NPs were coated with polyelectrolyte exhibits core-shell NPs stabilized in a nanofluid (Schneider and Decher, 2004; Pereira *et al.*, 2014). Our groups have already reported on the formation of Au-PVP core-shell structures in both aqueous and non-aqueous solvents (Ram and Fecht, 2011; Behera and Ram, 2012b, 2013a-c, 2014). Figure 8b shows the selected area electron diffraction pattern taken from the bulk of Au-NP and are assigned as, 111, 200, 220, 311 and 222 planes of face centered cubic Au (Behera and Ram, 2013a, 2014; Kemal *et al.*, 2008).

Stabilization mechanism: Let us illustrate the stabilization mechanism proposed in this study to support the exhibition of a long term colloidal stability of Au-NFs in presence of PVP in DMF. Figure 9 explains the step-wise path followed in the formation and encapsulation of NG in presence

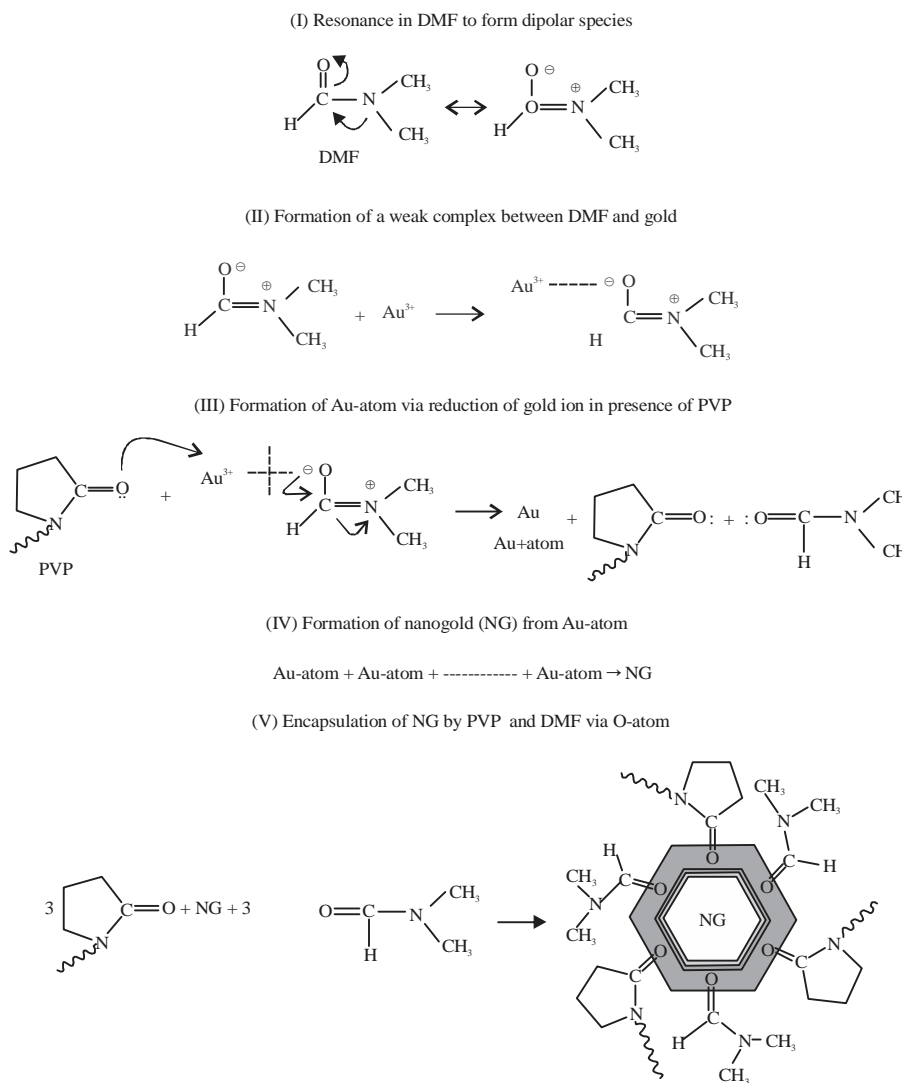


Fig. 9: Scheme for explaining formation of highly stable proficiently capped Au-NPs in presence of PVP in DMF

of PVP and DMF molecules. As per the proposed mechanism, in the first step, a DMF molecule via a resonance process forms a dipolar ionic species. When gold salt is dissolved in DMF, this reactive species forms a weak complex with the gold ion as per the step-ii. In an experiment, Kedia and Kumar (2013) have proposed a Fig. 9 on the synthesis of Au-NPs which showing interaction of metal ions with PVP-DMF-NaOH system. When, PVP is added to the DMF-gold salt solution, PVP polymer donates its non-bonding electrons which present on the O-atom so that gold ion reduces to Au-atom as per the step III. As the obtained Au-atoms are reactive owing to high surface-to-volume ratio, they immediately coalesce to Au-nanocluster (i.e., called here as nanogold NG) in the organic medium (step IV). As the NG is electron deficient, the electron rich PVP and DMF molecules quickly encage the nanoparticle via the O-atoms, so that, it forms a stable and rigid nanostructure in the liquid medium (step V) of exceptional colloidal stability.

CONCLUSION

A highly stable Au-PVP NF was prepared using a wet chemical method in DMF. In aid of experimental outcomes, a plausible mechanism was proposed towards the exhibition of outstanding colloidal stability of Au-PVP NFs in DMF. A slight red-shift in the SPR band from 525-530 nm in the aged sample suggests that Au-NPs are highly stable in presence of PVP in DMF. Hardly any change in the zeta potential value in the aged sample further implies that it possess an excellent colloidal stability in presence of PVP particularly in DMF solvent. Shear thinning characteristics as revealed from the rheology study in the Au-PVP nanofluid in DMF suggests formation of cross-linking structure between PVP, DMF and Au-NP. Formation of core-shell structure in the nanofluid is possibly the main reason behind the demonstration of such superb colloidal stability of Au-NPs with PVP in DMF.

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REFERENCES

- Ahlberg, S., A. Antonopoulos, J. Diendorf, R. Dringen, M. Epple, R. Flock and R. Zellner, 2014. PVP-coated, negatively charged silver nanoparticles: A multi-center study of their physicochemical characteristics, cell culture and *in vivo* experiments. *Beilstein J. Nanotech.*, 5: 1944-1965.
- Barnes, H.A. and K. Walters, 1985. The yield stress myth? *Rheol. Acta*, 24: 323-326.
- Behera, M. and S. Ram, 2012a. Solubilization and stabilization of fullerene C₆₀ in presence of poly(vinyl pyrrolidone) molecules in water. *J. Incl. Phenom. Macrocycl. Chem.*, 72: 233-239.
- Behera, M. and S. Ram, 2012b. Synthesis of gold nanoparticles in presence of poly(vinyl pyrrolidone) from gold hydroxide precursor salt. *Adv. Mater. Res.*, 585: 115-119.
- Behera, M. and S. Ram, 2013a. Intense quenching of fluorescence intensity of poly(vinyl pyrrolidone) molecules in presence of gold nanoparticles. *Applied Nanosci.*, 3: 543-548.
- Behera, M. and S. Ram, 2013b. Spectroscopy-based study on the interaction between gold nanoparticle and poly(vinylpyrrolidone) molecules in a non-hydrocolloid. *Int. Nano Lett.*, Vol. 3. 10.1186/2228-5326-3-17
- Behera, M. and S. Ram, 2013c. Synthesis and characterization of core-shell gold nanoparticles with poly(vinyl pyrrolidone) from a new precursor salt. *Applied Nanosc.*, 3: 83-87.
- Behera, M. and S. Ram, 2014. Inquiring the mechanism of formation, encapsulation and stabilization of gold nanoparticles by poly(vinyl pyrrolidone) molecules in 1-butanol. *Applied Nanosc.*, 4: 247-254.
- Behera, M., 2015. An intensive study on the optical, rheological and electrokinetic properties of polyvinyl alcohol-capped nanogold. *Int. Nano Lett.*, 5: 161-169.
- Borodko, Y., S.E. Habas, M. Koebel, P. Yang, H. Frei and G.A. Somorjai, 2006. Probing the interaction of poly(vinylpyrrolidone) with platinum nanocrystals by UV-Raman and FTIR. *J. Phys. Chem. B*, 110: 23052-23059.
- Chae, D.W., S.S. Hwang, S.M. Hong, S.P. Hong, B.G. Cho and B.C. Kim, 2007. Influence of high contents of silver nanoparticles on the physical properties of poly(vinylidene fluoride). *Mol. Cryst. Liquid Cryst.*, 464: 233-241.
- Chen, Y., X. Gu, C.G. Nie, Z.Y. Jiang, Z.X. Xie and C.J. Lin, 2005. Shape controlled growth of gold nanoparticles by a solution synthesis. *Chem. Commun.*, 33: 4181-4183.

- Dulkeith, E., A.C. Morteani, T. Niedereichholz, T.A. Klar and J. Feldmann *et al.*, 2002. Fluorescence quenching of dye molecules near gold nanoparticles: Radiative and nonradiative effect. *Phys. Rev. Lett.*, Vol. 89. 10.1103/PhysRevLett.89.203002
- Ghosh, S.K., A. Pal, S. Kundu, S. Nath and T. Pal, 2004. Fluorescence quenching of 1-methylaminopyrene near gold nanoparticles: Size regime dependence of the small metallic particles. *Chem. Phys. Lett.*, 395: 366-372.
- He, R., X. Qian, J. Yin and Z. Zhu, 2002. Preparation of polychrome silver nanoparticles in different solvents. *J. Mater. Chem.*, 12: 3783-3786.
- Hunt, H.D. and W.T. Simpson, 1953. Spectra of simple amides in the vacuum ultraviolet. *J. Am. Chem. Soc.*, 75: 4540-4543.
- Karthikeyan, B., 2010. Fluorescence quenching of rhodamine-6G in au nanocomposite polymers. *J. Applied Phys.*, Vol. 108. 10.1063/1.3496668
- Kedia, A. and P.S. Kumar, 2012. Solvent-adaptable poly(vinylpyrrolidone) binding induced anisotropic shape control of gold nanostructures. *J. Phys. Chem. C*, 116: 23721-23728.
- Kedia, A. and P.S. Kumar, 2013. Controlled reshaping and plasmon tuning mechanism of gold nanostars. *J. Mater. Chem. C*, 1: 4540-4549.
- Kemal, L., X.C. Jiang, K. Wong and A.B. Yu, 2008. Experiment and theoretical study of poly(vinyl pyrrolidone)-controlled gold nanoparticles. *J. Phys. Chem. C*, 112: 15656-15664.
- Liu, X., C. Li, J. Xu, J. Lv and M. Zhu *et al.*, 2008. Surfactant-free synthesis and functionalization of highly fluorescent gold quantum dots. *J. Phys. Chem. C*, 112: 10778-10783.
- Lu, G., S. Li, Z. Guo, O.K. Farha and B.G. Hauser *et al.*, 2012. Imparting functionality to a metal-organic framework material by controlled nanoparticle encapsulation. *Nat. Chem.*, 4: 310-316.
- Miranda, D., V. Sencadas, A. Sanchez-Iglesias, I. Pastoriza-Santos, L.M. Liz-Marzan, J.L. Gomez Ribelles and S. Lanceros-Mendez, 2009. Influence of silver nanoparticles concentration on the alpha- to beta-phase transformation and the physical properties of silver nanoparticles doped poly(vinylidene fluoride) nanocomposites. *J. Nanosci. Nanotechnol.*, 9: 2910-2916.
- Moon, H.R., D.W. Lim and M.P. Suh, 2013. Fabrication of metal nanoparticles in metal-organic frameworks. *Chem. Soc. Rev.*, 42: 1807-1824.
- Pastoriza-Santos, I. and L.M. Liz-Marzan, 2002. Formation of PVP-protected metal nanoparticles in DMF. *Langmuir*, 18: 2888-2894.
- Pereira, S.O., A. Barros-Timmons and T. Trindade, 2014. Biofunctionalisation of colloidal gold nanoparticles via polyelectrolytes assemblies. *Colloid. Polym. Sci.*, 292: 33-50.
- Phule, A.D., S. Ram and A.K. Tyagi, 2013. Anchoring silver with poly(vinylidene fluoride) molecules in model flocculates and its effects on rheology in stable nanofluids. *J. Nanofluids*, 2: 249-260.
- Prozorova, G.F., A.S. Pozdnyakov, N.P. Kuznetsova, S.A. Korzhova and A.I. Emel'yanov *et al.*, 2014. Green synthesis of water-soluble nontoxic polymeric nanocomposites containing silver nanoparticles. *Int. J. Nanomed.*, 9: 1883-1889.
- Quaroni, L. and G. Chumanov, 1999. Preparation of polymer-coated functionalized silver nanoparticles. *J. Am. Chem. Soc.*, 121: 10642-10643.
- Rahme, K., J. Oberdisse, R. Schweins, C. Gaillard, J.D. Marty, C. Mingotaud and F. Gauffre, 2008. Pluronic-stabilized gold nanoparticles: Investigation of the structure of the polymer-particle hybrid. *Chem. Phys. Chem.*, 9: 2230-2236.

- Ram, S. and H.J. Fecht, 2011. Modulating up-energy transfer and violet-blue light emission in gold nanoparticles with surface adsorption of poly(vinyl pyrrolidone) molecules. *J. Phys. Chem. C*, 115: 7817-7828.
- Schneider, G. and G. Decher, 2004. From functional core/shell nanoparticles prepared via layer-by-layer deposition to empty nanospheres. *Nano Lett.*, 4: 1833-1839.
- Slistan-Grijalva, A., R. Herrera-Urbina, J.F. Rivas-Silva, M. Avalos-Borja, F.F. Castillon-Barraza and A. Posada-Amarillas, 2008. Synthesis of silver nanoparticles in a polyvinylpyrrolidone (PVP) paste and their optical properties in a film and in ethylene glycol. *Mater. Res. Bull.*, 43: 90-96.
- Studart, A.R., E. Amstad and L.J. Gauckler, 2007. Colloidal stabilization of nanoparticles in concentrated suspensions. *Langmuir*, 23: 1081-1090.
- Sun, C.Y., S.X. Liu, D.D. Liang, K.Z. Shao, Y.H. Ren and Z.M. Su, 2009. Highly stable crystalline catalysts based on a microporous metal-organic framework and polyoxometalates. *J. Am. Chem. Soc.*, 131: 1883-1888.
- Tripathy, P., S. Ram and H.J. Fecht, 2006. Gold nanoparticles from induced $\text{Au}^{3+} \rightarrow \text{Au}^0$ reaction in polyvinyl alcohol molecules in presence of sucrose in hot water. *Plasmonics*, 1: 121-127.
- Tripathy, P., A. Mishra and S. Ram, 2007. Immobilizing au-nanocolloids in co-branched polymer molecules in presence of gluconic acid in poly(vinyl alcohol) in hot water. *Mater. Chem. Phys.*, 106: 379-386.