

“PVP-Solvent Interaction” Guided Shape Control Synthesis of Gold Nanoparticles and Their Application in Ultra Specific Dye Sensing

Shiva Upadhyay¹, Udit Pant¹, Piyush Sharma¹, Prashant Kumar Tyagi¹, Nikhil Bhati¹, Manoj Verma*²

¹SwamiShraddhanand College, University of Delhi, Delhi-110036, India

²Department of Physics & Astrophysics, University of Delhi, Delhi-110007, India

Abstract: A novel one step synthesis of gold nanoparticles has been reported at room temperature by utilizing mild yet effective reducing ability of polymer poly(N-vinyl-2-pyrrolidone) (PVP). Conformational changes in the intrinsic chemical structure of the PVP when dissolved in different solvents drastically changes its reducing/capping ability which results in synthesis of different anisotropic size/shaped gold nanoparticles with unique physico-chemical properties. However, sterically stabilized gold nanoparticles show excellent stability under ambient conditions but presence of dye molecules can induce slight aggregation in the colloids and hence gold nanoparticles can be potential candidates for such sensing applications. Moreover aggregation behavior of gold colloid in the presence of dye molecules highly depends on nanoparticles morphology, so by tuning the shape/size of gold nanoparticles detection level of analytes can decrease substantially which enhances the sensing limit. Herein, we have reported shape controlled synthesis of gold nanoparticles using polymer-solvent interaction; plasmonics signatures were well corroborated with XRD measurements and TEM observations. Sincere efforts were made to establish role of shape and size of metal nanoparticles on sensing capabilities.

Keywords: Gold Nanoparticles, XRD, Shape controlled Synthesis, Dye sensing, PVP.

I. Introduction

Sensing of chemical and biological molecules plays an important role in biomedical [1], chemistry [2], physics [3] as well as environmental studies [4]. Development of cost effective, highly sensitive sensors requires advanced technology coupled with fundamental knowledge of physics, chemistry and biology [5]. Nanostructures feature excellent physico-chemical properties [6] which can be utilized in development of highly specific and efficient sensors [7]. Among other metal nanoparticles, gold nanoparticles being inert and highly stable are considered to be excellent scaffolds for the fabrication of chemical and biological sensors [8]. More elaborative, gold nanoparticles can be synthesized in a simple manner via wet chemical synthesis route and can be made highly stable. They possess unique optoelectronic properties [9], which can be easily tuned by tuning their size/shape and surrounding chemical environment [10]. Thus, Au nanoparticles provide an excellent platform for sensing a wide range of biological or chemical ligands for the selective binding and detection of various analytes [11].

Even though there is huge literature present for the work of chemical sensing using gold nanoparticles as probes, but still there is lack of knowledge in dependence of sensing applications on shape and size of gold Nanoparticles [12]. Selective selection of dye molecules based on differential morphology not only increases the sensing capabilities but also opens up the gate for sensing a large number of analytes with a single system. It is well known that anisotropic gold nanoparticles show longitudinal LSPR peak in NIR region which is more concretely depends on surrounding medium than transversal LSPR peak in optical region. [13] So, using anisotropic particles sensing limit can increase drastically in some cases. However, in some systems using anisotropic particles may not be so beneficial because they tend to aggregate more often than isotropic ones in some special situations. [14] So, correct knowledge of utilizing different shape/size gold nanoparticles in sensing application is highly needed. In this work, we have systematically tuned the shape of gold nanoparticles, by using differential ability of PVP in reduction and stabilization when used in different solvents. More precisely, when HAuCl₄ is reduced by PVP in methanol, 2-propanol, DMF yields different shapes pseudo-spherical, anisotropic multibranching and star like morphology respectively. XRD calculations shows all the synthesized nanoparticles are well crystalline in nature. Crystallite size obtained with scherrer formula corresponds well with TEM micrographs. Change in optical spectra of nanocolloids in presence of trace amount of dye molecules shows the sensing capabilities of gold nanoparticles.

II. Experimental And Characterizations

PVP, HAuCl_4 , Crystal violet dye and bromo-phenol dye were obtained from Aldrich chemicals and were used as received. Solvent methanol, 2-Propanol and DMF were purchased from Merck and used as received without further purification. All the glass wares were cleaned with soap solution followed by aqua-regia and rinsed with triple distilled water prior to the actual experiments. In a typical synthesis of gold nanoparticles, 0.27 mM aqueous solution of hydrochloroauric acid ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$) was mixed with 15 mL of 10 mM polyvinylpyrrolidone (PVP average MW = 10,000) solution in methanol, 2-propanol and DMF and kept undisturbed at room temperature. The transformation from pale yellow solution to different vibrant colors within few hours of reaction signifies the formation of gold spherical nanoparticles. Optical absorption measurements were carried out in the wavelength range of 200–1100 nm using Thermo Scientific absorption spectrophotometer. TEM samples were prepared by drying the 5-fold centrifuged samples in ethanol at around 6500 rpm (to remove excess PVP) on carbon Formvar coated copper grids and the images were acquired using the FE-Technai G2 system operated at an accelerating voltage of 300 kV. The crystal structure parameters were evaluated by analysing the X-ray diffraction (XRD) spectra collected with Cu-K α radiation using a Bruker D-8 Advance X-ray diffractometer using the five-fold centrifuged nanoparticle samples drop casted on a glass substrate.

III. Results And Discussion

The optical absorption spectra (as shown in figure 1(a)) delineate the formation of gold nanoparticles at a PVP to metal ion ratio of ~ 3333 in various solvents. The addition of metal ions in PVP-methanol complex results in the change in solution color from pale yellow to ruby red within 3 hrs readily indicating the formation of spherical gold nanoparticles. Absorption spectra of spherical shape shows a single surface plasmon resonance (SPR) peak at 532 nm (Fig. 1 (a)) due to isotropic nature of spherical shape of ca 40 nm as confirmed from the TEM images (Fig. 1 (b)). While in case of 2-propanol solvent, we get anisotropic multibranched nanostructures as shown in TEM micrographs (Fig. 1 (c)). Absorption spectra of multibranched nanoparticles shows two peaks, one around 550 nm while other around 600 nm corresponding to symmetrical and asymmetrical oscillations of surface plasmons around anisotropic morphology of gold nanostructures. On the other hand in case of DMF, we get 3-dimensional hyper branched exotic star shaped gold nanoparticles (Fig. 1(d) which show two surface plasmons resonances respectively at 550 nm and 900 nm (Fig. 1(a)). In this case, transverse plasmon band at lower wavelength (higher energy) arises due to the core of metal nanoparticles, whereas the longitudinal band at higher wavelength (lower energy) occurs due to surface tips/edges.

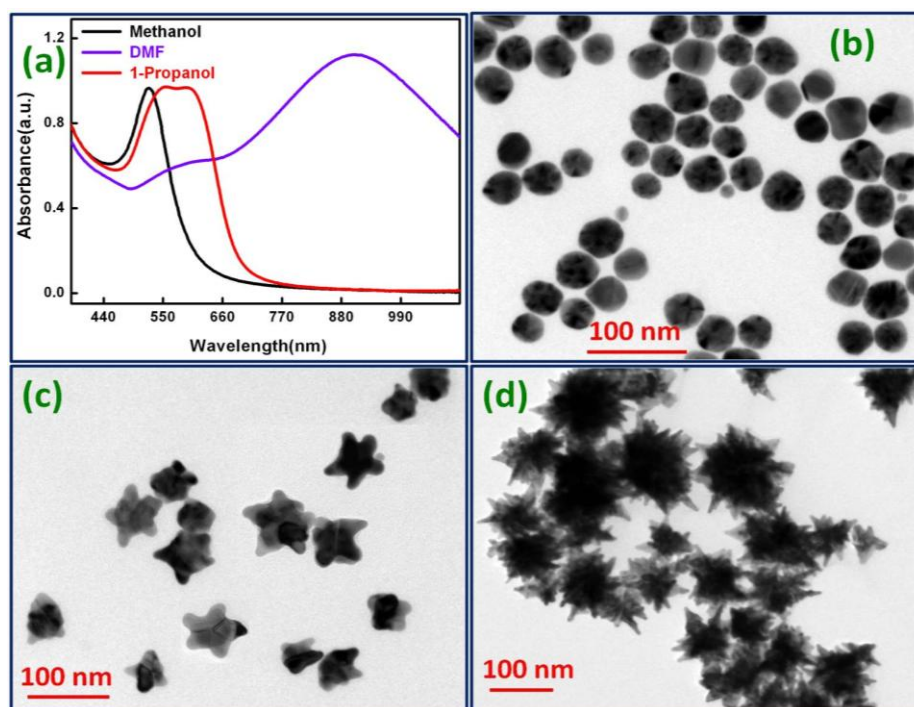


Fig. 1(a) shows optical absorption spectra of gold nanostructures synthesized in different solvents. Fig. 1(b), 1(c) and 1(e) shows the morphology of gold nanostructures synthesized in methanol, 2-propanol and DMF respectively.

XRD patterns of synthesized nanostructures reveal their high crystalline nature (Fig. 2). In case of spherical particles, diffraction peaks at 38.40° , 44.65° , 64.79° and 77.99° arises due to $\langle 111 \rangle$, $\langle 200 \rangle$, $\langle 220 \rangle$ and $\langle 311 \rangle$ reflections of fcc crystal structure of gold which matches with JCPDS card number-04-0784. For other shapes of nanostructures XRD peaks minutely shifts and broadened or sharpened depending on the crystal overall strain and average crystallite size. Instrumental corrected broadening β_{hkl} corresponding to each diffraction peak has component of both size broadening as well as strain induced broadening. The Debye-Scherrer equation shows the size induced broadening by relation

$$D = \frac{K\lambda}{\beta_{hkl} \cos \theta} \quad (1)$$

Where β_{hkl} is integral half width, K is constant equal to 0.90, λ is wavelength of incident X-ray ($\lambda=0.154$ nm), D is average crystallite size, and θ is the Bragg angle. Crystallite size were calculated using scherrer equation using “ β ” and “ θ ” of dominant plane $\langle 111 \rangle$ for all the particles and shown in the Fig. 3. Average crystallite sizes calculated from the XRD were found to be in well agreement with TEM micrographs (See Fig.1 and Fig. 3).

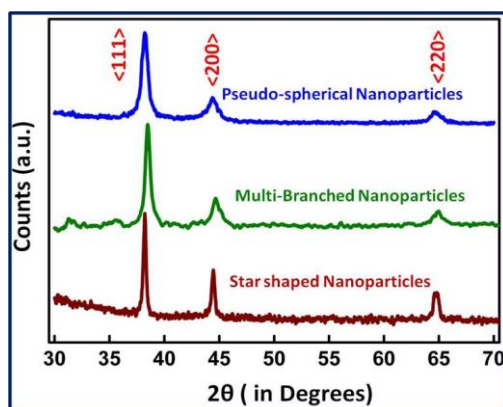


Fig.2 shows the XRD patterns of different shaped gold nanoparticles synthesized in methanol, 2-propanol and DMF respectively.

Shapes	2θ (in Degrees)	θ (in Radians)	Cosθ	β (in Degrees)	β (in radians)	Average Crystallite Size
Spherical Nanoparticles	38.4025	0.33486	0.94447	0.2165	0.003775	38.8
Multi-Branched Nanoparticles	38.3071	0.33403	0.94472	0.1832	0.003195	45.9
Star Shaped Nanoaprticles	38.2516	0.33355	0.94488	0.1174	0.002047	71.6

Fig. 3 shows XRD parameters of synthesized gold nanostructures and calculated average crystallite size in each case.

For examining chemical sensing of synthesized gold nanostructures, we selected two types of dye (Bromophenol and crystal violet) as analyte. It is well known that plasmonic behavior of gold particles in the presence of dye molecules can change considerably. When (0.3 mM) of gold nanoparticles were mixed with different concentration of dyes (20 μ M and 50 μ M), a change in color of nanoparticles was observed which was due to the change in absorption spectra (See Fig. 4) of gold nanoparticles which in other words can be said as chemical sensing. All the spectra were taken after 4 hours of dye-nanoparticle conjugation to ensure all possible outcomes of dye-nanoparticles interaction on absorption spectra of gold nanoparticles. For the case of bromophenol, Pseudo-spherical particles show a red-shift of 6 nm and 14 nm (Fig. 4(a)) in presence of 20 μ M and 50 μ M of bromophenol respectively without changing the shape of LSPR peak which indicate that shape and dispersity of nanocolloids was maintained during sensing process. Maintaining size/shape and dispersity of nanoparticles during sensing process is extremely important because these factors dictate the reusability and stability of chemical sensors. On the other hand, when multi-branched and star shaped nanoparticles mixed with 20 μ M and 50 μ M of bromophenol; their absorption spectra red shifts and broadens (Fig. 4(c) and Fig. 4(e)) which can be attributed to the aggregation of gold nanoparticles in presence of dye molecules. So, from all these observations we can say that for detection/sensing of bromophenol with gold nanoparticles, spherical shape nanoparticles are more sensitive, reusable and effective than multi-branched and star shaped nanoparticles.

Using Crystal violet as sensing analyte, pseudo spherical particles (0.3 mM) when mixed with 20 μM shows a hump in absorption spectra at around 620 nm which could be due 2 dimensional aggregation(Fig. 4(b)). Moreover when we use 50 μM of crystal violet dye then eventually a second absorption peak was observed at 650 nm which confirms the aggregation of spherical gold nanoparticles in presence of crystal violet dye. Secondly, when we use multibranched nanoparticles for detection of crystal violet, absorption spectra shows that dispersity is quite maintained and a noticeable red shift is observed with increasing concentration of crystal violet dye (Fig. 4(e)). So, we can say that these multibranched nanoparticles act as better sensor for crystal violet than bromophenol. Interestingly, in case of star shaped nanoparticles, absorption spectra shows excellent shape and colloids stability and also shows a remarkable red shift of 40 nm and 78 nm when mixed with crystal violet 20 μM and 50 μM respectively (Fig. 4(f)). It was interesting to see that although spherical nanoparticles were best suitable for sensing bromophenol but in case of crystal violet they fail to maintain their dispersity. On the other hand, star shaped nanoparticles shows excellent reproducible sensing capabilities with analyte crystal violet but fails to yield good results in sensing bromophenol dye. So, we can conclude that shape/size of gold nanoparticles is an important factor which decides chemical sensing abilities and we should utilize varying optical and chemical or bio-conjugation properties of different size/shape nanoparticles to synthesize specific and enhanced chemical or biological sensors.

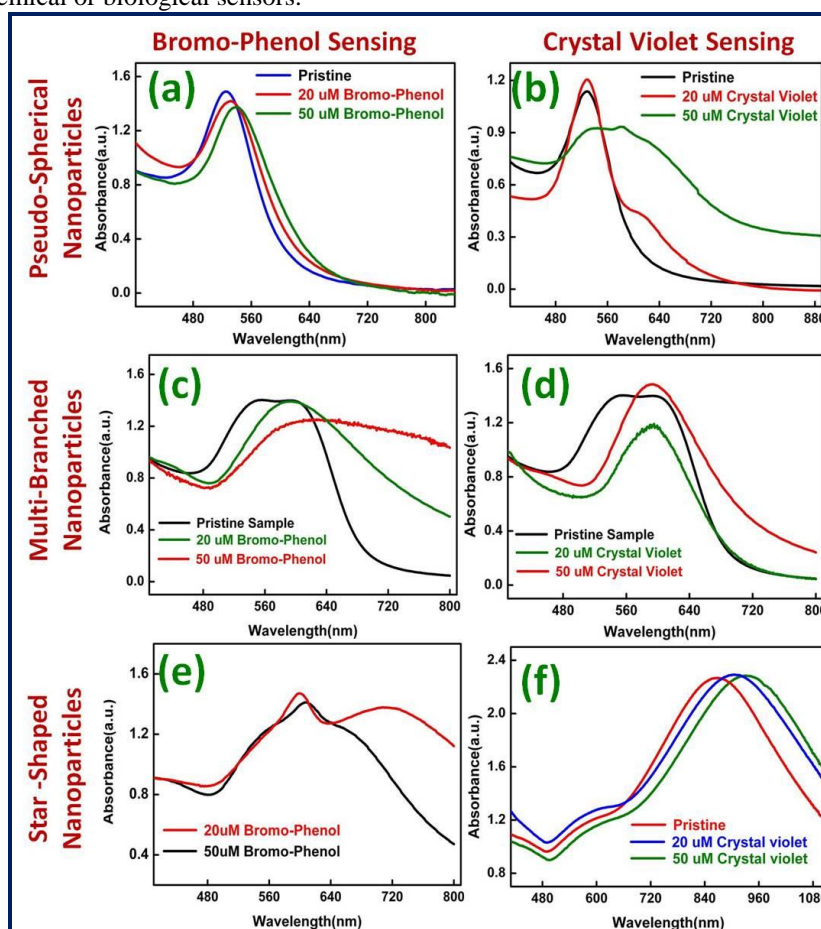


Fig. 4(a), 4(c) and 4(e) shows the absorption spectra of Pseudo-spherical, multi branched and star shaped nanoparticles respectively mixed with different concentrations of bromophenol dye. Similarly, Fig. 4(b), 4(d) and 4(f) shows the absorption spectra of Pseudo-spherical, multi branched and star shaped nanoparticles respectively mixed with different concentrations of crystal violet dye.

IV. Conclusion

In brief, we have used polymer-solvent interaction to synthesize different shape nanoparticles by using versatile nature of polymer PVP in reducing and stabilizing of gold nanoparticles. XRD calculations show the well crystalline nature of synthesized nanoparticles. We have systematically shown the importance of size/shape of gold nanostructures synthesized/stabilized by the polymer, PVP and its strategic effect on their abilities to sense two different dyes namely bromophenol and crystal violet. The central role of shape and size of as-prepared gold nanoparticle is not only giving distinct plasmonic signatures, but also in dictating their ability to interact with adsorbed analytes in a meticulous manner has been well-established analytically in a clear cut

manner beyond doubt.

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