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Green Synthesis of Metal Nanostructures

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ABSTRACT: In the present study, metal (Ag and Cu) nanostructures were prepared in presence of ethylene glycol using PVP with the aid of conventional household microwave. The microwave assisted methods enjoy the obvious advantages of symmetric and volumetric heating, ease of synthesis and decreased time of reaction. The choice of Ag and Cu is attributed to their large catalytic activity, high antibacterial capability, prominent Surface Enhanced Raman Scattering (SERS) etc. The characteristic Surface Plasmon Resonance (SPR) peak for these nanostructures confirms their formation. Further, shape and morphological studies were done through Transmission Electron Microscopy. The as prepared fast, rapid and green synthesis of Ag and Cu nanostructures may found applications in SERS, electrochemical and biological sensors etc.

Keywords: Green synthesis; microwave irradiation; metal nanostructures; UV-visible absorption; transmission electron microscopy.

INTRODUCTION: The field of nanoscale materials and structures is an emerging area of active research and development in modern world of science and technology [1]. In recent years, metal nanoparticles like gold, silver and copper have attained a considerable interest due to their unique properties, small size and surface plasmon behavior [2-3]. Out of these silver and copper find the highest level of applications in the diverse fields of science and technology due to their large catalytic activity, high antibacterial capability and high thermal and electrical conductivity. Their fair abundance and low cost also make them much more easily available and applicable [4-5].

Various methods are available for the synthesis of silver and copper nanoparticles, for example reduction in solutions, thermal decomposition of their respective compounds, radiation assisted, electrochemical, metal vapours, micro-emulsion techniques, microwave assisted process etc. [6]. Among all these, microwave assisted method is a promising route for the rapid preparation of metal Nanomaterials and comes under the green chemistry synthesis methods [7]. This method has the obvious advantages of symmetric and volumetric heating, ease of synthesis and decreased time of reaction. The microwave irradiations method with frequency of 2.456 GHz is applied to reaction mixture which results the formation of small size nanostructures.

In the present study, we have prepared silver (Ag) and copper (Cu) nanostructures in presence of ethylene glycol using Poly (Vinylpyrrolidone) (PVP) with the aid of conventional household microwave. The advancement of reaction is further monitored via studying the corresponding SPR peak with increase in time of reaction. The shape and morphology of as synthesized nanostructures were determined using Transmission Electron Microscopy (TEM) images.

EXPERIMENTAL:

Materials: Chemicals like Silver nitrate ($AgNO_3$), Copper nitrate trihydrate ($Cu(NO_3).3H_2O$), Ethylene Glycol (EG), sodium borohydride ($NaBH_4$) and Poly(vinyl pyrrolidone) (PVP) were used as it is as procured.

Synthesis of Silver nanostructures: The schematic representation of the method used for the synthesis for Ag nanostructures is presented in Figure 1

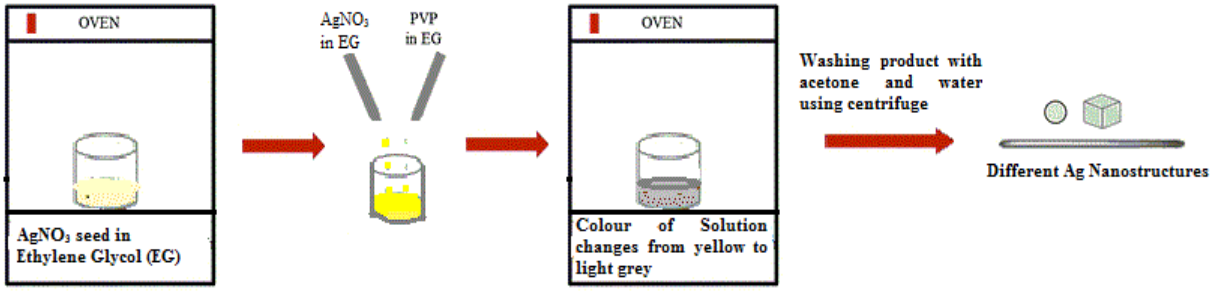

Figure 1: Scheme of synthesis of silver nanostructures

The synthesis of Ag nanostructures is outlined in scheme 1. Here we have used seed solution method to synthesize silver nanostructures. For this, first of all we prepared a seed solution by dissolving 3.5 mg $AgNO_3$ in 5 ml EG using magnetic stirring abbreviated as solution A. Another solution was prepared by dissolving 0.25 gm $AgNO_3$ in 7.5 ml of EG, with magnetic stirring named as solution B. Meanwhile 0.1 gm of PVP was dissolved in 25 ml EG with constant magnetic stirring. Firstly 25 ml of EG was heated in microwave at 170^0 for 2 minutes. Then the seed solution, solution A was added to EG and the solution was again heated at 170^0 for 2 minutes. At this time, the colour of solution was changed to pale yellow indicating the onset of formation of Ag nanoparticles or seeds. After that solution B and PVP solution were added to the reaction mixture simultaneously. This solution was again heated for 3 minutes under the same reaction conditions. After that samples were taken after every minute and named as Ag-1, Ag-2 and Ag-3. The colour of sample firstly changes to dark yellow indicating the formation of large nanoparticles and then started changing to greyish showing the formation of different Ag nanostructures. All the samples were washed firstly with acetone and then with De-ionized water (DI) to remove EG and excessive surfactant PVP.

Synthesis of Copper Nanostructures: The synthesis of Cu nanostructures is outlined in Figure 2. First of all, PVP solution was prepared by dissolving 0.2664 gm PVP in 20 ml EG with the help of magnetic stirring. The solution of Cu was prepared by dissolving 0.5798 gm $Cu(NO_3).3H_2O$ in 20 ml EG with magnetic stirring. After that 10 ml EG was heated in microwave at temperature 140^0 C for 2 minutes followed by simultaneous addition of PVP solution and Copper solution. Then the reaction mixture was microwaved for next 4 minutes under same conditions. After that a pinch of solid $NaBH_4$ was added to the mixture and the colour was changed to reddish brown and the resulting solution was further microwaved for one more minute in order to obtain desired copper nanostructures. Again the samples were washed with acetone and DI to remove EG and excessive surfactant PVP.

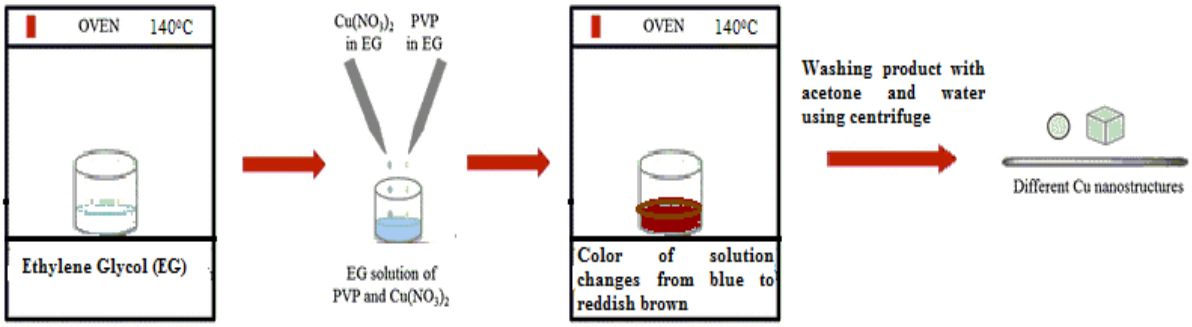

Figure 2: Scheme of synthesis of copper nanostructures

Characterization: The UV-Visible absorption measurements were performed on single beam systronics UV-Vis spectrometer 117 within the range 250nm to 800nm, at Department of Physics, Kurukshetra University, Kurukshetra. The Transmission Electron Microscopy (TEM) images were recorded using the TECNAI (Fei, Electron Optics) Transmission Electron Microscope operated at 200 kV, available at AIIMS, New Delhi on 14/10/2016.

RESULTS AND DISCUSSION:

Silver Nanostructures:

UV-Visible Absorption Spectra: The occurrence of Ag nanostructures (Ag-1, Ag-2 and Ag-3) was first confirmed by their characteristic Surface Plasmon Resonance (SPR) peak observed in UV-Visible absorption spectroscopy (Figure 3). The UV-Visible absorption spectrum of Ag-1 contains a sharp peak at 430 nm, confirming the presence of spherical Ag nanoparticles [8]. Further with increase in microwave irradiation time (sample

Ag-2), the SPR peak shifted to 434 nm and also gets broadened thereby providing evidence for increased average particle size and widening of particle size distribution.

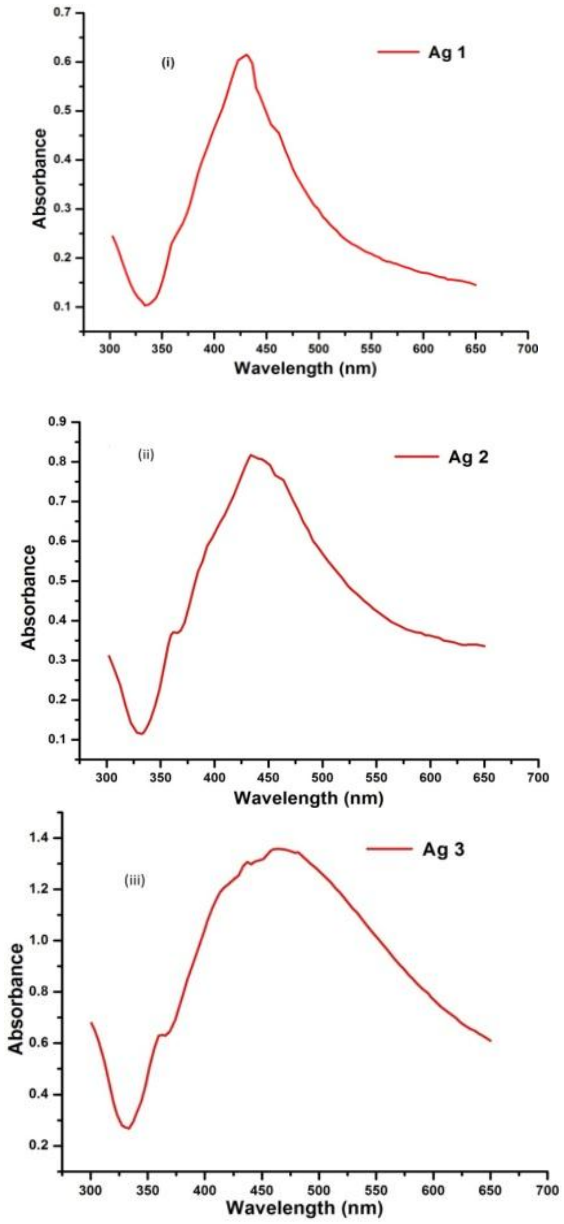

Figure 3: UV-Vis. absorption spectra for (i) Ag-1, (ii) Ag-2 and (iii) Ag-3

Also an edge is appeared at 363 nm in the spectrum showing the presence of non-spherical Ag nanostructures [9]. With further increase in microwave irradiation time (sample Ag-3), the SPR peak further shifted to 464 nm and also further broadened which again shows increased particle size and broad size distribution. The occurrence of other peak (367 nm) in the spectrum is attributed to change of shape of Silver Nanostructures from spherical to Non-spherical (cubical, triangular and polygon).

TEM Images: The TEM images of sample Ag-3 are shown (along with histograms showing particle size distribution) at two different positions (Figure 4). In TEM images, the particles of various shapes are formed (spheres, rods, cubes, triangles etc.), thus supporting the results of UV-Visible spectroscopy. The average particle size lies between 70-80 nm.

The synthesis mechanism for Ag nanostructures is proposed as follows [10]: The formation of Ag nanostructures in seed solution method generally involves two steps. In the first step Ag nanoparticles were formed by reducing $AgNO_3$ with Ethylene Glycol. In the second step $AgNO_3$ and PVP were added simultaneously to the reaction system, allowing the nucleation and growth of Ag nanostructures. Silver atoms formed through the reduction of $AgNO_3$ with EG nucleate through the homogenous nucleation. These Ag nanoparticles are well dispersed because of the presence of PVP, a polymeric surfactant that could chemically adsorb onto the surface of Ag nanoparticles through O-Ag bonding. It is well known that the surface energies of larger particles are lower than the smaller ones. When this dispersion of Ag nanoparticles is continuously heated at high temperature, the small nanoparticles progressively disappeared to benefit of the larger ones via a process known as Ostwald ripening. With the assistance of PVP, some of large nanoparticles may be able to grow in rod shaped structures. But in the present study this case doesn't arise to considerable extent due to a heavy coverage of PVP on the surfaces of larger nanoparticles, hence it resulted in the isotropic growth for all the faces.

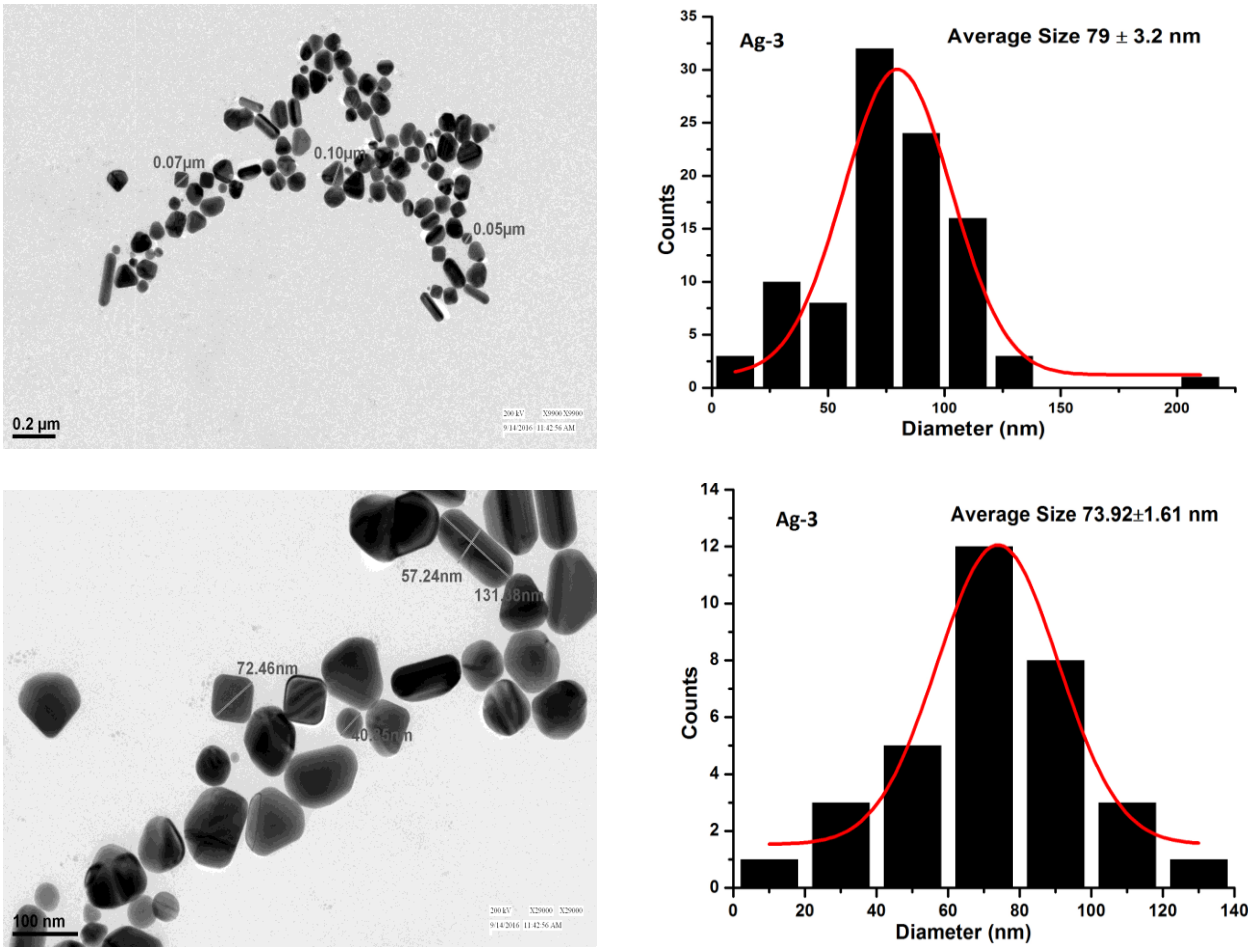

Figure 4: TEM images of sample Ag-3 along and corresponding histogram

Cu Nanostructures:

UV-Visible Spectra: The presence of copper nanostructure was firstly confirmed by the position of their characteristic SPR peak at around 604 nm in the UV-Visible absorption spectrum (Figure 5) [11]. The spread in the SPR peak confirms the diversion of nanostructures from spherical to the non-spherical (triangular, cubical and other non-spherical) [12]. But as is shown in UV-Visible absorption spectrum this spread is very narrow, hence a small distribution in the shape of Cu nanostructures took place as is confirmed by the TEM image.

TEM Images: TEM image of copper nanostructures along with corresponding histogram is shown in Figure 6. This TEM image confirms the presence of some spherical nanoparticles along with some non-spherical nanostructures of Cu in the given sample which is in agreement with the results obtained from UV-Visible spectroscopy. The average particle size of Cu nanostructures obtained from histogram is 94.81±1.01 nm.

The synthesis mechanism of Cu nanostructures, ethylene glycol is employed as reducing agent and the proposed mechanism is as follows: [13]

$$2HOCH_2\text{-}CH_2OH \longrightarrow 2CH_3CHO + 2H_2O \quad (1)$$

$$2CH_3CHO + Cu^{2+} \longrightarrow CH_3COOCCH_3 + 2H^+ + Cu \quad (2)$$

In the first step, EG changes to aldehyde on heating at temperature 145^0 C which further act as reducing agent and produces copper micro particles with no specific faces. With the addition of $NaBH_4$, and subsequent heating, reduction of micro particles to nano particles takes place which is also indicated by colour change from light blue to reddish brown. Further addition of PVP not only stabilizes the produced nanostructure by acting as

surfactant but also promotes the anisotropic growth of Cu nanostructures [14].

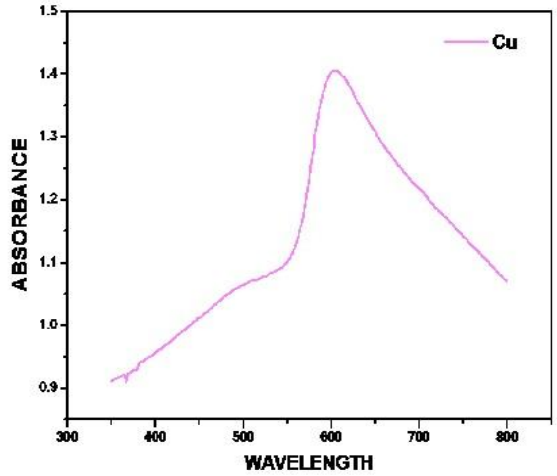

Figure 5: UV-Vis absorption spectra for Cu nanostructures

CONCLUSIONS: A solution-phase route to the large scale synthesis of Silver and Copper nanostructures using microwave irradiation has been demonstrated which also follows the rule of green chemistry. The formation of Ag and Cu nanostructures was confirmed by their characteristic SPR spectra observed in UV-Visible absorption analysis. TEM analysis shows that Ag and Cu nanoparticles of various shapes are formed with average sizes 76 and 94 nm respectively. Also an attempt has been done to correlate the observed structures in TEM with corresponding SPR peak in UV-Visible spectrum.

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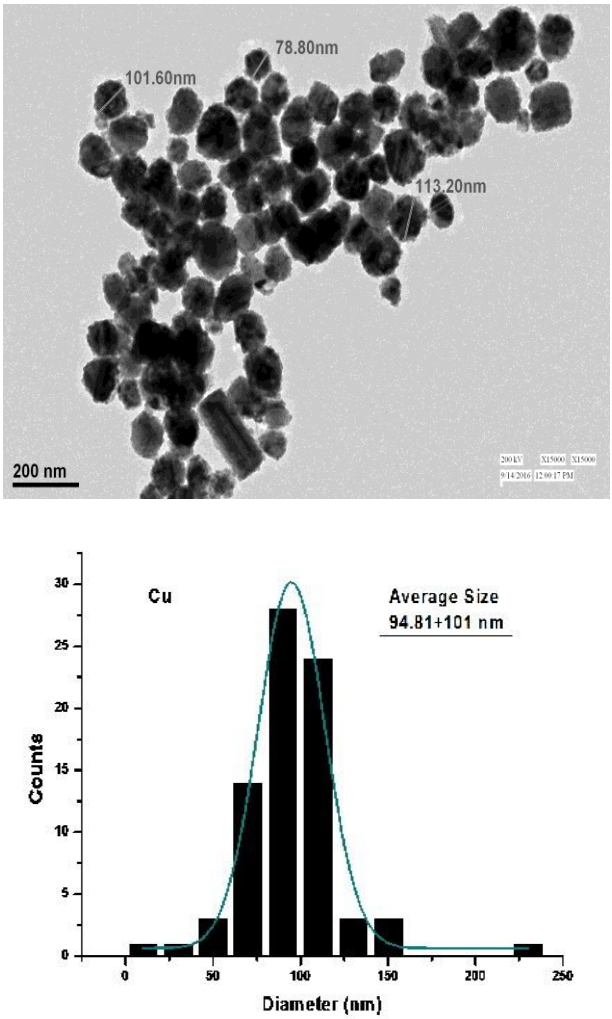

Figure 6: TEM image and histogram of Cu nanostructures

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