Coulomb Blockade effect in Ag-PVA Nanocomposites

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Abstract—*Silver nanoparticles are synthesized via chemical route taking polyvinyl alcohol as matrix. Different samples are prepared by the variation of physical parameters, viz: stirring temperature, stirring time and time of heating. The as-synthesised samples are then characterized by UV-Visible (UV-Vis), High Resolution Transmission Electron Microscopy (HRTEM) and X-ray Diffraction (XRD). The characterization results confirm nano formation. Devices are then fabricated from the nanosamples. I-V characteristics are recorded by Keithley CV meter under dark and light environment. The result shows that the Coulomb Blockade effect is prominent in the device characteristics.*

Keywords*: Silver nanoparticles, Coulomb Blockade.*

1. INTRODUCTION

Materials reduced to the nanoscale can show different properties compared to what they exhibit on a macroscale. For instance, opaque substances can become transparent (copper); stable materials can turn combustible (aluminum); insoluble materials may become soluble (gold). A material such as gold, which is chemically inert at normal scales, can serve as a potent chemical catalyst at nanoscales. Much of the fascination with nanotechnology stems from these quantum and surface phenomena exhibited by matter at the nanoscale.

The metal nanoparticles (nps) due to their Localised Surface Plasmon Resonance (LSPR) phenomenon, they can be widely used in different fields, viz optical, optoelectronics and biotechnology. Numerous reports are there on enhancement of power conversion efficiency (PCE) of organic photovoltaic devices using metal nps. An international team of researchers led by Prof. Yang in 2011 at ULCA (University of California, Los Angeles) reported 20% efficiency of existing Optical Photo Voltaics using gold nps[1] .The incorporation of inorganic nps has been investigated in organic thin film transistor (OTFT). Significant steps towards the enhancement of non-volatile memory and ultimately the realization of np based electronic devices was made by Srinivasan and coworkers[2].They fabricated metal-insulator semiconductor (MIS) devices and enhanced stability of the immobilized nps was tested by sonication. The MIS devices showed well-defined cyclic voltammetry (CV) hysteresis curves which imply good memory effect[2]. In case of metal nanoparticles of size≥2nm, quantum confinement effects can be neglected. The charging energy, due to the transfer of individual electrons is the dominant single electron effect in case of metal tunnel junctions. In 1950, Gorter[3] and Darmois[4] recognized the effects of single electron charging in the conductance properties of very thin metallic films. The thin metal films tend to form plannar arrays of small islands due to the surface tension, and conduction occurs due to the tunneling between these islands.

In the present work, synthesis and characterization of the silver nanoparticles embedded in PVA has been carried out. Moreover, the I-V characteristics are studied by fabricating devices of Ag/PVA nanocomposites which exhbit Coulomb Blockade effects.

2. EXPERIMENTAL SECTION

2.1 Synthesis

$AgNO_3$ solution is prepared by dissolving $AgNO_3$ powder in distilled water. The mixture is stirred at room temperature. PVA solution is prepared.$AgNO_3$ solution and PVA solution is mixed in the ratio of 1:1 and then the reaction mixture is heated to 90˚C. Different samples (table 1) are prepared by keeping them in the oven for different time intervals.

Table 1: Physical parameters for Ag/PVA samples

Sample Code	Temp. of stirring of PVA(˚C)	Time of stirring of PVA(hr)	Time of heating (hr)
AgP_1	60-70	3	10
AgP_2	70-80	3½	20
AgP_3	80-90	4	30
AgP_4	90-100	4½	40

2.2 Characterisation

(a) UV-Vis Spectroscopy

The UV-Vis spectra for the samples AgP_1, AgP_2, AgP_3 and AgP_4 are given in Fig. 1.The data are taken with the help of HITACHI U-3210 double beam spectrophotometer. The wavelength corresponding to SPR peaks along with the size calculated[5] is given in table 2.The peaks at ~ 300nm is due to PVA.

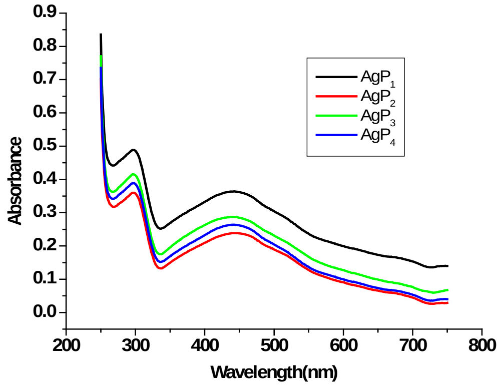


Fig. 1: UV-vis spectra of the samples AgP_1, AgP_2, AgP_3 and AgP_4

Table 2: Surface Plasmon resonance peak and the size estimated for the as–fabricated Ag/PVA samples

Sample Code	Wavelength corresponding to the SPR peak(nm)	Size(nm)
AgP_1	440	34
AgP_2	442.02	23
AgP_3	443.09	18
AgP_4	437.22	25

(b) X-ray diffraction

The XRD patterns of the sample AgP_4 is shown in figure2.The instrument used is BRUKER D8ADVANCE using CuK_α radiation(λ=0.15406nm). It is seen that three peaks are pronounced. The pattern shows broadening of peaks, indicating that there is formation of nano-sized particles. The other smaller peaks are due to the matrix taken or impurities present. For each of the peak positions, in an XRD pattern, the FWHM are determined and the sizes of the Ag nps are calculated by Debye Scherrer formula[6] and then the mean sizes are obtained. Size estimation from XRD results support nano formation.

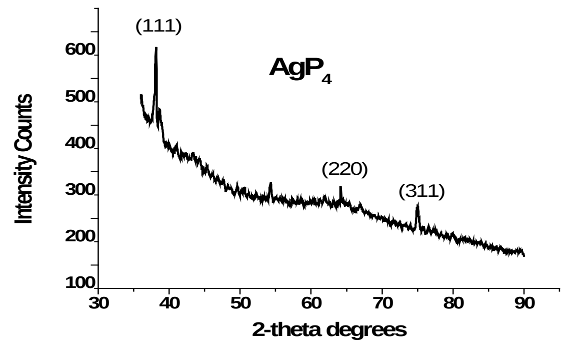


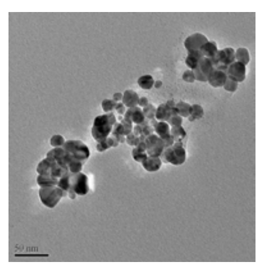
Fig. 2: XRD pattern of the samples AgP_4

Table 3: Shows the results obtained from XRD analysis

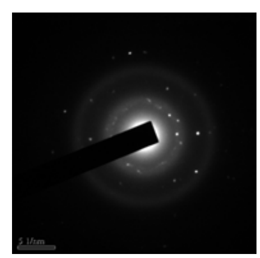
Sample code	2θ Degree	FWHM(β) (radian)	Dspacing (Å) from (XRD)	(hkl)	Size(nm)	Mean size(nm)
AgP_4	38.11	6.82	2.2	111	25	24.33
	64.16	6.84	1.4	200	23	
	75.01	6.82	1.2	311	25	

(c) High Resolution Transmission Electron Microscopy (HRTEM) and Selected Area Electron Diffraction (SAED)

Fig. 3 depicts the HRTEM images of the sample AgP_2 taken with JEOLJEM2100 microscope (at 200 KV with point resolution of 1.44Å, line resolution of 2.32Å and having super twin lenses). It is seen from the pictures that most of the particles are almost spherical in shape with size from ~20-40 nm. No agglomeration can be seen from these pictures. Fig. 5.12 c shows that the size of the np is ~20nm and the lattice d-spacing is 0.21nm. Similar results are obtained for other samples also.



(a)



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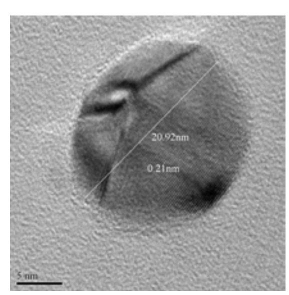
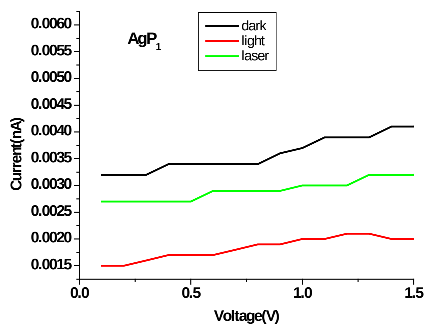


(c)

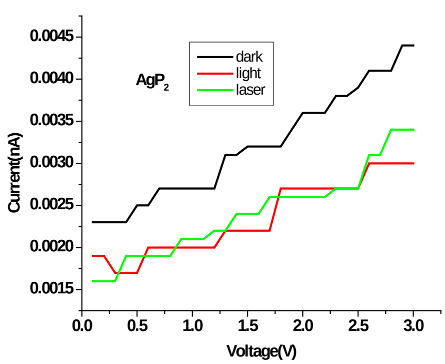
Fig. 3: HRTEM images of sample AgP_2 (a) collection of nps (b) SAED picture (c) image showing the size along with d-spacing.

2.2 I-V characteristics of the Ag/PVA nanocomposites:

The devices are fabricated taking copper wires as the electrodes. The silver nano sample is placed between the electrodes attached over a glass slide.The I-V characteristic of the as-fabricated Ag /PVA devices are recorded under dark, room light and laser light environment by CV meter (Keithley 2612A).The characteristics are given in Fig. 4 (a to d) which exhibit Coulomb staircase feature.



(a)



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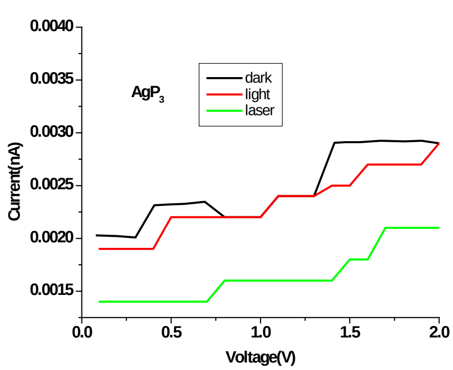

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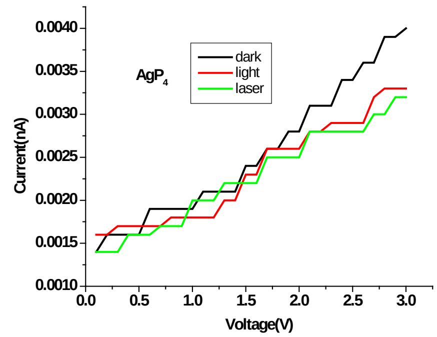

(d)

Fig. 4: I-V characteristics of the as-fabricated Ag/PVA devices under dark, room light and laser

It is seen from Fig. 4 that Coulomb staircase behavior is prominent in the characteristics under dark as well as light environment. I.A. Gladskikh et.al[7] in 2013 studied the hysteresis of conductivity in the granular silver films. They observed that the current-voltage characteristic has an ohmic behavior for Ag films of thickness 50Å. But for thicker films (85Å & 115Å), a non-linear increase of current was observed but no step nature was reported. Their conclusion is that electrical conductivity exhibited by the Ag np films follows the classical theory of percolation. Kakati[8] in 2013 while studying I-V characteristics of nano-schottky device comprising of Au nps & Cu doped CdS QDs observed Coulomb staircase feature under dark environment. This feature may be due to presence of the Au nps.

3. DISCUSSION AND CONCLUSION

The various characterisation results (UV-Vis, XRD, HRTEM, SAED) reveal that Ag/PVA nanocomposites, are successfully fabricated. The observed I-V characteristics of Ag/PVA nps exhibit Coulomb Blockade but not Resonant Tunneling features. This finding is in support of the fact that quantum confinement is not effective in metal nps of size $\geq$ 2nm.

4. ACKNOWLEDGEMENT

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