

ZnO/Ag Composite Nanoparticles for Surface Plasmon Resonance Based Sensor Application in UV-Vis Region

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ABSTRACT

In this paper we have analyzed a composite nanoparticle (ZnO/Ag) to find out either it is compatible or not to use it as a surface plasmon resonance (SPR) based sensor. For this sensor we have considered the UV-Visible (UV-Vis) region. The surface plasmon resonance responses of the ZnO/Ag are found for sample-I at 363 nm and 453 nm and for sample-II at 355 nm and 455 nm. The surface plasmon resonance responses of other single nanoparticles are also discussed here for performance comparison in the UV-Vis region to distinguish a better SPR based sensor that works both in UV as well as in visible region.

Keywords: *Surface plasmon resonance, composite nanoparticles, UV-Visible region, sensor.*

1 INTRODUCTION

SURFACE plasmon resonance based sensors are optical sensors that exploit electromagnetic waves of special characteristics. Surface plasmon resonance occurs when there is an existence of a surface plasma wave [1]. A surface plasma wave (SPW) is an electromagnetic (EM) wave. This EM wave propagates along the boundary between a metal and a dielectric. At the interface of the metal and dielectric it behaves like quasi-free electron plasma. As the magnetic vector is parallel to the plane of interface, an SPW is a transverse-magnetic (TM) wave [2]. This type of wave is characterized by the propagation constant and electromagnetic field distribution. So when there is a perturbation in this SPW there will be a distinct resonance comparing with the reference SPR. By observing the shifted SPR with the reference SPR the detection can be done, which is the cause due to the surrounding medium. This is the way how a SPR based optical sensor works [3]. Different kind of metals can be used as the metal layer to make the dielectric-metal interface so that the SPW can exist. Mostly used metals are Silver (Ag) and Gold (Au) [4], [5]. But the problem with this Ag or Au is that they work either in UV region or in visible region. So in case of a sensor to sense something in UV-Vis region the sensor with only Au or Ag metal layer will not work. So we need a new type of metallic layer so that it can work both in UV as well as in visible regime. That's why a composite nano-particle ZnO/Ag is analyzed in this work to find out the working possibility of that sensor in UV-Vis regime.

A nanoparticle is a microscopic particle with at least one dimension less than 100 nm. Nanoparticles are of great scientific interest as they are effectively a bridge between bulk materials and atomic or molecular structures. A bulk material should have constant physical properties regardless of its size, but at the nano-scale this is often not the case. Size-dependent prop-

erties are observed such as quantum confinement in semiconductor particles, surface plasmon resonance in some metal particles and superparamagnetism in magnetic materials. Nanoparticles often have unexpected visible properties because they are small enough to confine their electrons and produce quantum effects.

The optical properties of a metallic nanoparticle depend mainly on its surface plasmon resonance, where the plasmon refers to the collective oscillation of the free electrons within the metallic nanoparticle. It is well known that the plasmon resonant peaks and line widths are sensitive to the size and shape of the nanoparticle, the metallic species and the surrounding medium. These phenomena, observed only in the nanometer regime, can be explained by both intrinsic and extrinsic size effects on the plasmon bandwidth in metallic nanoparticles.

When two nanoparticles are brought into proximity (within 2.5 times the particle short axis length), their plasmons couple in a distance-dependent manner. Therefore, the optical properties are determined by those of individual particles and by the electrostatic interaction between them. The resulting optical spectrum depends on interparticle separation, particle size and shape, and the dielectric environment [6], [7]. Here the ZnO/Ag, a composite nano-particle is prepared and the optical property of this nanoparticle is analyzed. The surface plasmon resonance (SPR) property is basically monitored and analyzed for sensor application in UV-Visible regime.

2 EXPERIMENTAL SETUP

Intensive investigations on semiconductor and metal nanoparticles suspended in solutions have been undertaken extensively because of their size dependent characteristic and properties. The ZnO/Ag composite or junctioned nanoparticles sam-

ples were prepared by electrochemical method. Measurements were carried out at room temperature. The optical absorption of different samples were measured by Shimadzu (UV-1601) double beam spectrophotometer, with a deuterium lamp for ultraviolet (UV) and a tungsten halogen lamp for visible region. The synthesis method used in the present study is a modified version of the one originally used by Reetz and Helbig for Pd particles.

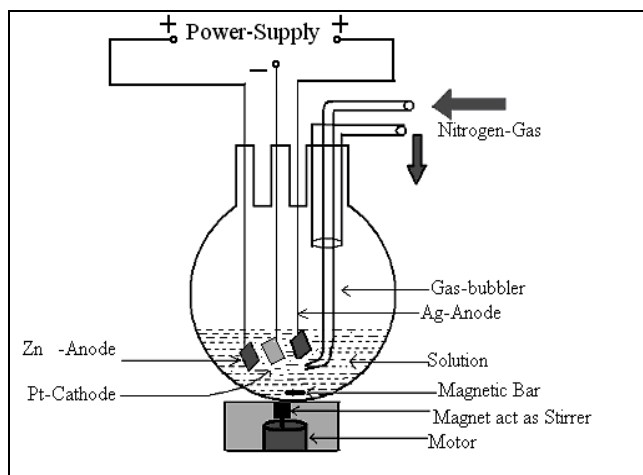


Fig. 1. Electrochemical cell for synthesis of ZnO/Ag nanoparticles.

This method is suitable for the synthesis of semiconductor as well as metal nanoparticles. Here we have synthesized one of the exclusive purposes for both metal and semiconductor simultaneously in a single experiment. An inexpensive three electrodes electrochemical cell was used in which the two anodes are of bulk metal and semiconductor. Platinum in the form of a foil served as a cathode. The distance between the two consecutive electrodes were 2 cm. An electrolyte, containing a mixture of 40 ml of Acetonitrile (CH_3CN) and 10 ml of Tetrahydrofuran ($\text{THF}(\text{CH}_2)_4\text{O}$) (ratio 4:1), along with 0.275g of capping agent viz. Tetradecyltrimethyl Ammonium Bromide (TTAB), was used. The experimental set-up is shown in Fig. 1. Electrolysis was carried out at room temperature, under nitrogen atmosphere for few hours in constant current mode.

In the overall process the bulk metal and semiconductor are oxidized at the anode, the metal and semiconductor cations migrate to the cathode, and reduction takes place with formation of Zinc Oxide/Silver (ZnO/Ag) junctioned nanoparticles with the presence of Oxygen. The nanoparticles were separated by centrifugation and washed at least three times with Acetonitrile. They were dried at room temperature.

3 EXPERIMENTAL RESULTS

Here we used two samples of ZnO/Ag so that we can have the difference between two results. For the first sample (ZnO/Ag-I) we supplied a constant current of 15 mA about 10 minutes. For the second sample (ZnO/Ag-II) we supplied a constant current of 10 mA about 10 minutes.

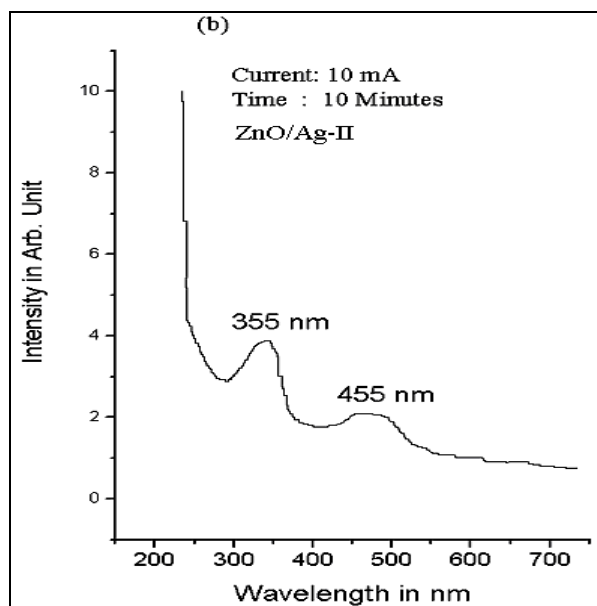
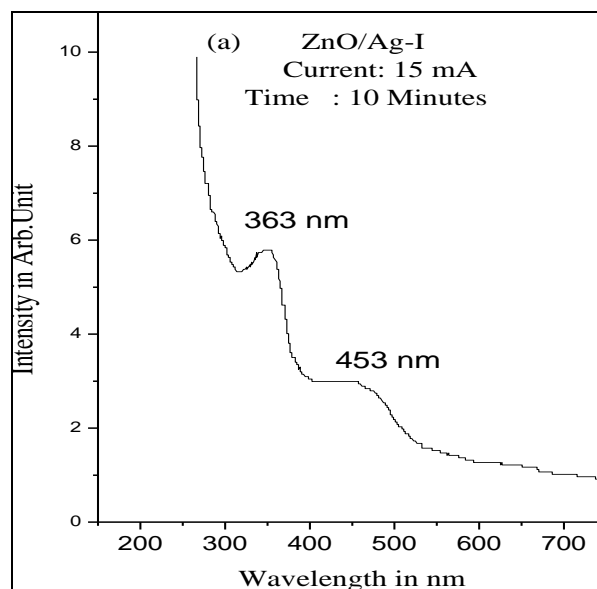


Fig. 2. Optical absorption spectra of (a) ZnO/Ag sample-I (b) ZnO/Ag sample-II [8].

The ZnO/Ag nanoparticles were characterized using UV-VIS spectroscopy. From the Fig. 2(a) we can see that there are two resonance peaks one at 363 nm and another at 453 nm. At 363 nm this peak is the excitonic absorption peak of ZnO and the surface plasmon resonance peak is 453 nm for Ag. Next we use second sample with different concentration of Ag and we get the result as shown in Fig. 2(b). Similarly here the surface plasmon resonance peak is at 455 nm.

4 ANALYSIS & COMPARISON

If we consider the EM spectrum it is clearly seen that the visi-

ble (Vis) range is from 400 to 700 nm approximately and the UV region is below 400 nm.

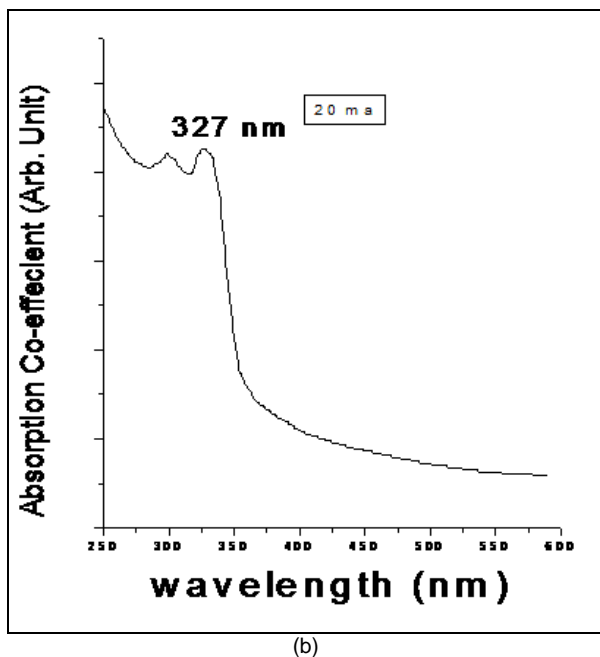
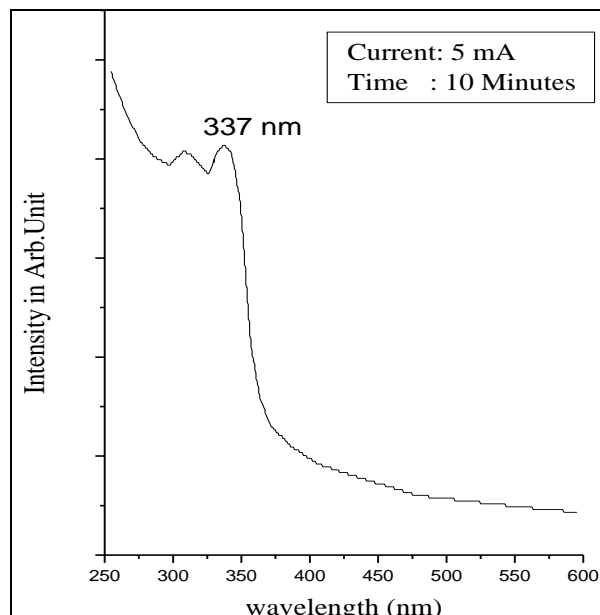
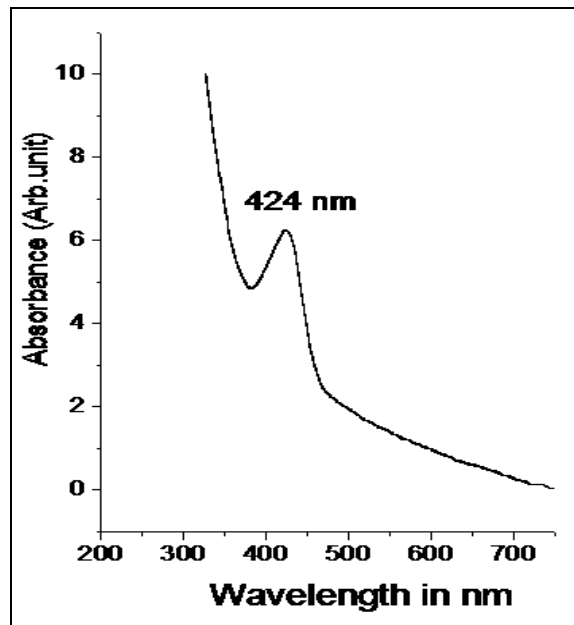


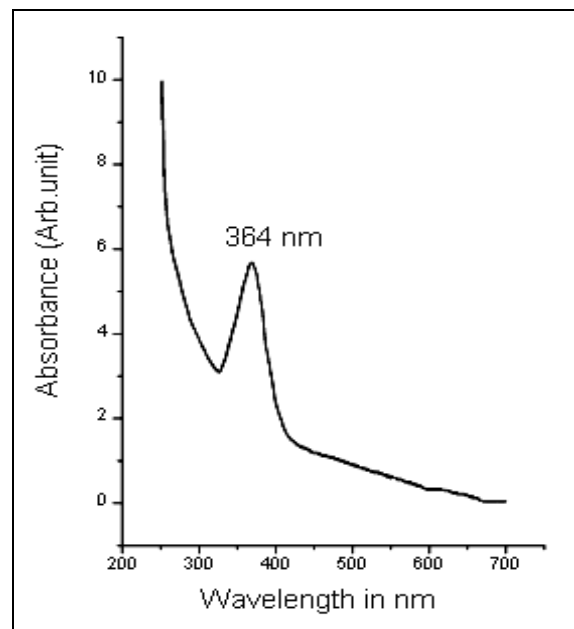
Fig. 3. Optical absorption spectra of TTAB capped ZnO nanoparticles (a) having an average diameter of 10 nm showing absorption feature at about 337 nm and 308 nm [8] (b) having an average diameter of 12 nm showing absorption feature at 327 nm and 299 nm.

In case of ZnO nanoparticle the resonance peak is at 337 nm and 308 nm (Fig. 3(a)) which is in the region of UV in EM spectrum. For a second sample with different nanoparticle diameter we get the result as shown in Fig. 3(b), where the resonance peaks are at 327 nm and at 299 nm, which are also in UV region.

In case of Ag nanoparticle characteristics, consider the Fig. 4(a) and Fig. 4(b) which show optical absorption spectra of Ag nanoparticles. The absorption feature clearly shows at 424 nm, while for another sample, it appears at 364nm. It is clear from that for Ag the resonance peaks are at visible region for one sample and another is in UV region. But the main difference between these two is that for the visible region case the nanoparticle size is higher than the nanoparticle size in the sample corresponds to UV region. It is important to note that in case of SPR based sensor the metallic layer should be thin in size to get the effect of SPR.

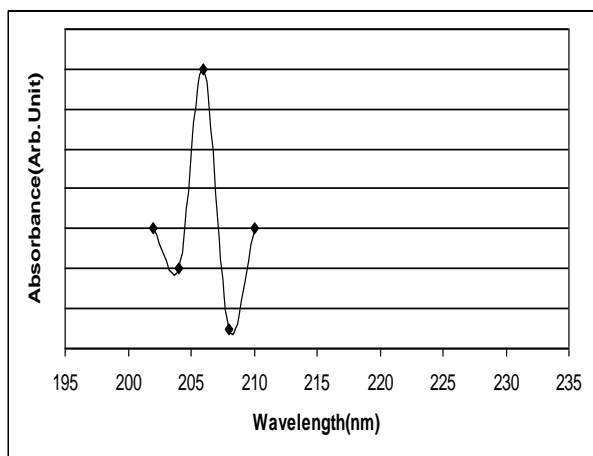


(a)

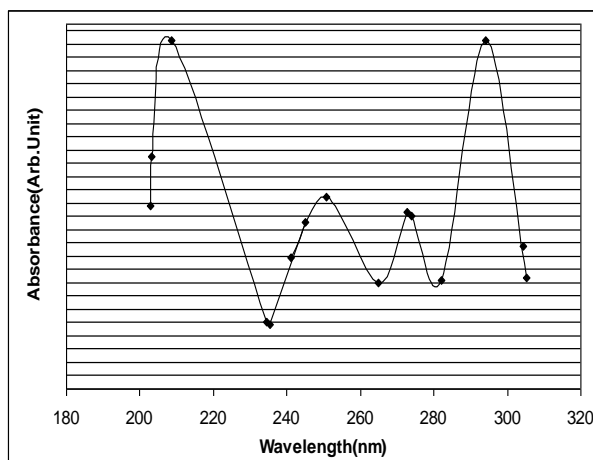


(b)

Fig. 4. Optical absorption spectra of TTAB capped Ag nanoparticles showing absorption feature at about (a) 424 nm and (b) 364 nm respectively [9].



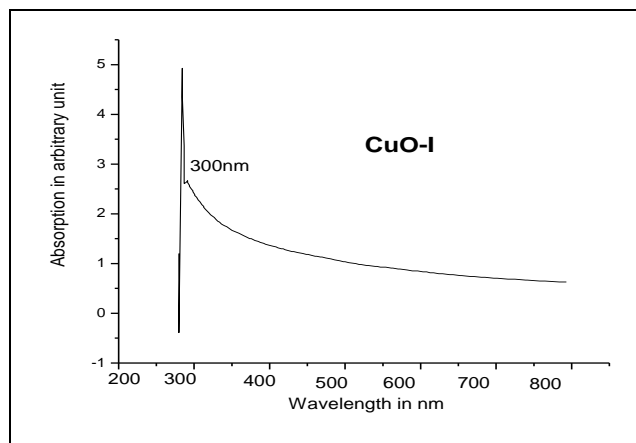
(a)



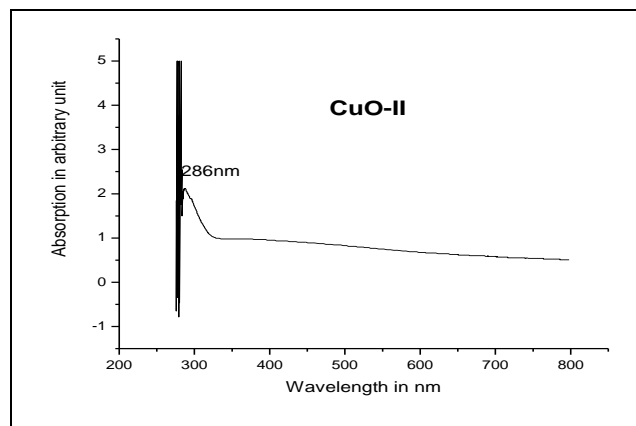
(b)

Fig. 5. Absorbance spectra for Au nanoparticles (a) sample-I, Plasmon resonance at 206nm (b) sample-II, Plasmon resonance at 294nm [10].

Same sized Gold (Au) nanoparticle was also used to find out the resonance peak in [10] and it is found that the resonance peaks are within 200 nm to 300 nm which are completely in UV region. As shown in Fig. 5(a) and in 5(b).



(a)



(b)

Fig. 6. Optical absorption spectra of (a) CuO-I (b) CuO-II nanoparticles showing absorption feature at 300 nm and 286 nm respectively [11].

Next we considered another Oxide which is CuO to investigate the absorption spectra. Here we also used two samples of CuO so that we can have two types of diameter of the nanoparticles. From Fig. 6(a) & 6(b) we can see that for the CuO the resonance peaks are at 300 nm and at 286 nm which are definitely in UV region.

So it is clear from the above discussion that if we want to have the resonance peak in UV-Vis region, composite or junctioned nanoparticles are good solution to make a SPR based sensor.

5 CONCLUSION

The possibility to have a SPR based sensor based on composite or junctioned nanoparticle is discussed. It is found that for single nanoparticle ZnO, Au, CuO the SPR responses are at 337 nm, 206 nm and at 300 nm respectively. These are completely in UV regime. But for Ag we got one SPR response at 424 nm which is in visible region. For this single Ag nanoparticle the size is an important thing to consider. Now if we observe the ZnO/Ag composite nanoparticle we can see it works both in UV and visible regime. It is observed from the analysis that it is possible to make the SPR based sensor using single metal layer but in that case the sensing region will be fixed

either in UV or in visible regime. To make a sensor based on SPR which will also cover UV-Vis region composite nanoparticle is a good choice. The range of sensing can be increased or decreased by a small change in composite nanoparticle diameter.

REFERENCES

- [1] Anuj K. Sharma, Rajan Jha and B.D. Gupta, "Fiber-optic sensors based on surface plasmon resonance: A comprehensive review", *IEEE Sensor Journal*, Vol. 7, No. 8, August 2007.
- [2] J.Homola, "Present and future of surface plasmon resonance biosensors", *Anal Bioanal Chem* (2003), 377:528-539.
- [3] M. Piliarik, J. Homola, Z. Manikova, J. Ctyroky, "Surface plasmon resonance sensor based on a single mode polarization maintaining optical fiber", *Sens. Actuators, B* 90 (2003) pp.236-242.
- [4] M. Iga, A. Sekib, K. Watanabe, "Gold thickness dependence of SPR-based hetero-core structured optical fiber sensor," *Sensors and Actuators, B* 106 (2005) 363-368.
- [5] Anuj K Sharma and B D Gupta, "Fibre-optic sensor based on surface plasmon resonance with Ag-Au alloy nanoparticle films," *Nanotechnology* 17 (2006) 124-131.
- [6] J.M. Murday, "The coming Revolution.Science and Technology of Nanoscale Structures", *The AMPTIAC, Newsletter*, 6, 6(2002).
- [7] S. Chen and D.L. Carroll, "Synthesis and Characterization of Truncated Triangular Silver nanoplates", *Nanoletters*, 2, No.9, 1003-1007(2002).
- [8] M. A. Momin, M. A. Islam, M.M. Alam, T. Parvin and M. Islam, "Synthesis and photoluminescence evaluation of tetradecyltrimethyl ammonium bromide (TTAB) capped ZnO/Ag nanoparticles", *Journal of the Bangladesh Electronics Society*.Vol. 9, No. 1-2, June-December 2009.
- [9] M.M. Alam, M. Harun and M. Islam, "Synthesis and characterization of TTAB coated silver (Ag) nanoparticles", *Advanced Materials Research Vols 264-265 (2011)*, pp. 530-534.
- [10] S. Hossain , M. B. Hossain, M. A. Islam and Z. H. Mahmood, "Characterization of Au Nano Particles Synthesized by Electrochemical Process at Room Temperature", *XVI International Workshop on the Physics of Semiconductor Devices December 19-22, 2011, IIT Kanpur, India*, pp.88.
- [11] M. A.Momin, R. Pervin, M. J. Uddin, G.M. A. Khan, and M.Islam, "One Step Synthesis and Optical Evaluation of Copper Oxide (CuO) Nanoparticles", *Journal of the Bangladesh Electronics Society*.Vol. 10, No. 1-2, June-December 2010.