

## Eco-friendly electrochemical synthesis of rod shaped Ag nanostructures for battery application

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**Abstract:** An effective electrochemical method was applied for synthesis of macroporous granular silver by oxidation of  $\text{AgNO}_3$  using water as an eco-friendly solvent. The electrochemical synthesis of silver nanorods (nano-Ag) has been successfully carried out by using Pt (Platinum) / Ag (Silver) as anode and cathode. This synthesis rate is much faster than other methods and this approach is suitable for large scale production and hence to industrial usage. By changing the current density, it is possible to obtain different silver nanoparticle sizes. The influence of the different electrochemical parameters on the final size was studied by using different kinds of counter electrodes. The resulting Ag nanorods were characterized by Field-Emission Scanning Electron Microscope (FESEM), X-Ray Diffraction (XRD), cyclic voltammetry (CV), UV-Vis spectroscopy and FTIR analysis. Cyclic voltammogram was recorded to understand the electro catalytic behaviors of the rod shaped silver sample prepared.

**Keywords:** Platinum Electrode, Agnanorods, Electrolysis, Cyclic Voltammetry, UV-Vis absorption spectrum.

### I. Introduction

Nanotechnology is an important field of modern research dealing with design, synthesis, and manipulation of particles structure ranging from approximately 1-100 nm. Tremendous growth in this emerging technology has opened novel, fundamental and applied frontiers, including the synthesis of nanoscale materials.

Silver nanorods emerged as a boon product from the field of nanotechnology due to its electronic, optic, catalysis, good conductivity, biological & satirical properties, chemical stability, and antibacterial activity<sup>1-3</sup>.

Several methods have been reported for Ag nanorods synthesis, including Ag ions chemical reduction in aqueous solutions with or without stabilizing agents<sup>4-7</sup>, thermal decomposition in organic solvents<sup>8,9</sup>, biochemical reduction<sup>10,11</sup>, chemical and photo reduction in reverse micelles<sup>12-14</sup>, nano sphere lithography<sup>15</sup>, electrochemical reduction<sup>16</sup>, irradiation reduction<sup>17</sup>, microwave assisted and ultrasound reduction<sup>18,19</sup> in nanoqueous solvents with surface modifiers. Each method has typical advantages and disadvantages. Particularly, the electrochemical techniques are quite interesting because they allow obtaining particles with a high purity using fast and simple procedures and controlling the particle size easily by adjusting the current density. Through these techniques particles have been obtained with determined size and shape of several compositions. Also, this method is eco-friendly because it avoids the use of reducer agents that are usually toxic.

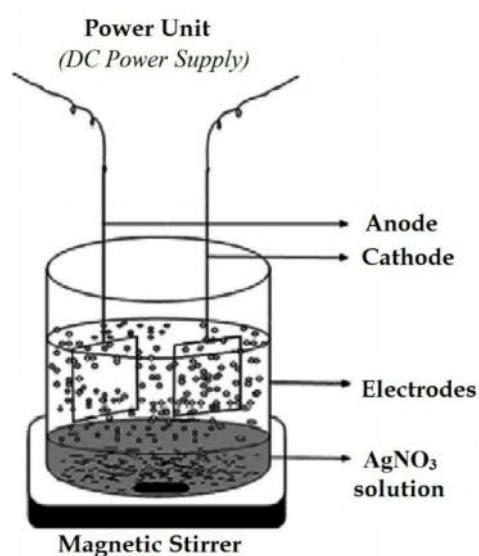
In this work we present an electrochemical method to prepare silver nanorods using Pt(Platinum) / Ag (Silver) as anode and cathode. Electrolysis synthesis of silver nanorods and its characterizations (XRD, FESEM, UV, CV and FT-IR) are studied in this research paper. This method can be used to prepare wide range of materials.

## 2. Experimental

### 2.1. Materials

All chemicals were of analytical grade and used without further purification. Double-distilled water was used throughout. Platinum and Silver electrodes (15 cm<sup>2</sup> each) are purchased from Sigma Aldrich (Germany). Silver Nitrate (AgNO<sub>3</sub>) was purchased from Merck Company.

### 2.2 Instrumental setup for Biphas Electrolysis method



**Fig. 1 Instrumental setup for Biphas Electrolysis method**

Fig. 1 shows preparative electrochemical oxidation was carried out galvanostatically using a 0-60 V and 0-3 A regulated DC power supply (Electrophoresis). Specially designed high voltage shrouded terminal socket is provided for 5 KV or 6 KV output.

Before electrochemical process the electrodes were kept in concentrated hydrochloric acid for about 3 hours. It was then washed with plenty of distilled water and was dried. It was degreased with trichloroethylene and kept immersed in a platinizing solution containing chloroplatinic acid in water with lead acetate being added in traces. This electrode was connected to the terminal of a DC power supply.

### 2.3. Preparation of Ag nanorods

We adopted electrolysis method for the synthesis of silver nanorods. Three gram of silver nitrate (AgNO<sub>3</sub>) salt was taken in a cleaned glass vessel, 100 ml of double-distilled water was poured, stirred well and a homogenous aqueous silver nitrate solution was prepared. The experiments were carried out in a standard electrolysis beaker having a sacrificial Platinum sheet as anode (counter electrode), and the same size Silver sheet as cathode (working electrode). These two electrodes were vertically placed face-to-face inside the cell. Platinum and Silver electrode were polished manually with 1 μm alumina powder to a mirror-like finish. Platinum electrode is connected with anode and Silver electrode with cathode of a D.C power supply unit and immersed in silver nitrate solution. The solution was stirred with a magnetic stirrer for 10 minutes to ensure that the AgNO<sub>3</sub> completely dissolved; the black silver nano rods were soon formed. Electrolysis of this solution was carried out by passing constant current inside solution through anode and cathode. At the end of electrolyzing process, Silver nanorods deposition on the cathode surface was observed, they were taken out carefully from the cathode surface and Silver nanorods were collected, washed with absolute alcohol and dried

in oven at 50 °C for 2 hours. The size of the nanorods was found to be strongly depending on the concentration of solution and current. Its structural characterizations were studied and the results confirmed the formation of Silver nanorods.

## 2.4. Characterization

The morphology of the products was investigated by Field-Emission Scanning Electron Microscope (FESEM) using (JEOL, JEM-2100F) at an accelerating voltage of 200 kV, powder XRD using Cu-K $\alpha$  radiation ( $\lambda=1.5438 \text{ \AA}$ ) in a Philips XRD 'X' PERT PRO diffractometer. IR absorption spectra was recorded in a FTIR Spectrum 1000 Perkin Elmer spectrometer on thoroughly dried samples using KBr as dilutant, UV-Vis spectra was obtained using Perkin Elmer UV-Vis Spectrophotometer and the Cyclic Voltammetric measurements (CV) were performed with an EG&G potentiostat/galvanostat in a conventional two-electrode cell at room temperature.. All the electrochemical experiments were carried out in a two-electrode cell (Pt/Ag) with using an electrochemical work station Model 660c (CH Instruments).

## 3. Results and Discussion

### 3.1 UV-Vis Spectrum of Ag nanorods

The optical behavior of Ag nanorods was studied by UV-vis spectroscopy. This shows a clearly resolved surface Plasmon resonance, well separated from the interband transition. In Fig. 2 typical absorption spectrum from the silver nanorods is shown. A broad Plasmon absorption band centered at 427 nm can be observed.

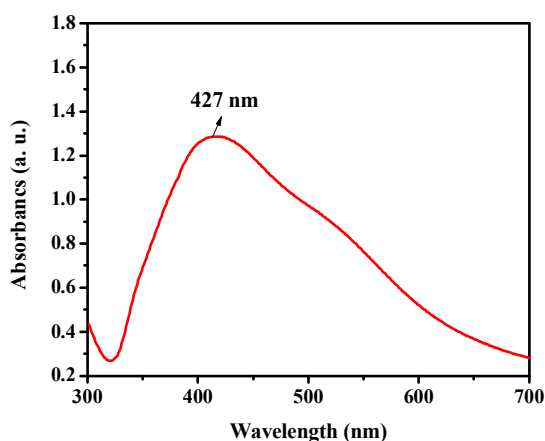


Fig. 2 UV-vis spectrum of Ag nanorods

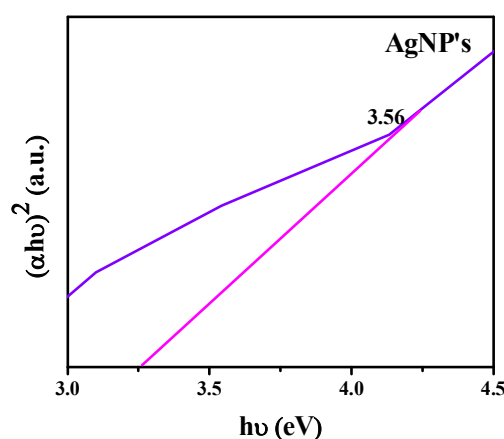


Fig. 3 Direct band gap plot of Ag nanorods

Fig. 3 shows the plot of absorption coefficient as a function of photon energy. These absorption spectra, which are the most direct and perhaps the simplest method for probing the band structure of semiconductors, are employed in the determination of the energy gap  $E_g$ . The  $E_g$  was calculated using the well-known Tauc's relation:

$$\alpha = A \frac{(h\nu - E_g)^n}{h\nu}$$

where A is a constant,  $h\nu$  is the photon energy, and  $\alpha$  is the absorption coefficient, while  $n$  depends on the nature of the transition. For direct transitions  $n=1/2$  or  $2/3$ , while for indirect ones 2 or 3, depending on whether they are allowed or forbidden, respectively. The best fit of the experimental curve to a band gap semiconductor absorption function was obtained for  $n=1/2$  to obtain direct band gap energy values. The obtained value is 3.56 eV.

### 3.2 FTIR spectrum of Ag nanorods

FT-IR spectroscopic studies were carried out to investigate the plausible mechanism behind the formation of these silver nanorods and offer information regarding the functional groups. The representative spectra of Silver nanorods are shown in Fig. 4. The very strong absorption peak at  $1599.19\text{ cm}^{-1}$  and the strong absorption peak at  $1659.54\text{ cm}^{-1}$ , can be assigned to the amide groups which may be from  $\text{AgNO}_3$  solution, the metal precursor involved in the Ag nanorods synthesis process. Strong interaction of water with the surface of silver could be the reason for the O-H stretching mode peaks at  $3547.21\text{ cm}^{-1}$  and  $589.15\text{ cm}^{-1}$  shows silver metal vibration<sup>20</sup>.

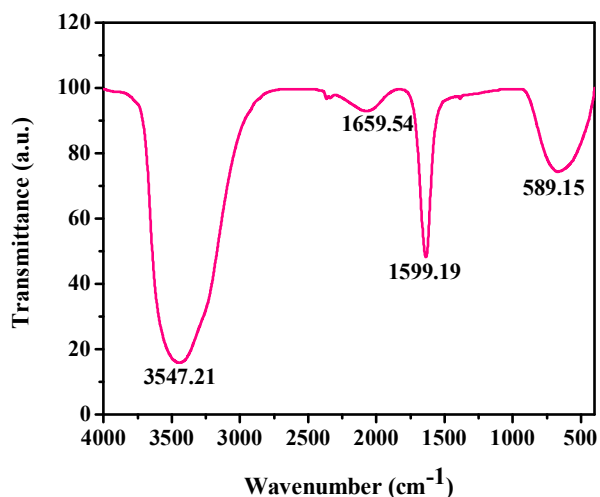


Fig. 4 FTIR Spectrum of Ag nanorods

### 3.3. XRD of Ag nanorods

The X-ray diffraction pattern of the silver nanorods synthesized by electrolysis method is shown in Fig. 5. A number of strong Bragg reflections can be seen which correspond to the (111), (200), (220) and (311) reflections of FCC silver. No spurious diffractions due to crystallographic impurities are found. All the reflections correspond to pure silver metal with face centered cubic symmetry. The high intense peak for FCC materials is generally (111) reflection, which is observed in the sample. The intensity of peaks reflected the high degree of crystallinity of the silver nanorods.

Debye- Scherrer's formula was used to calculate crystallite size<sup>15</sup>:

$$D = \frac{0.9\lambda}{\beta \cos\theta}$$

Where  $\lambda$  is the wavelength of X-rays,  $\beta$  is the Full Width at Half Maximum (FWHM) of the peaks at the diffracting angle  $\theta$ . The crystallite size of the Ag nanorods estimated from the Debye-Scherrer formula is 28 nm.

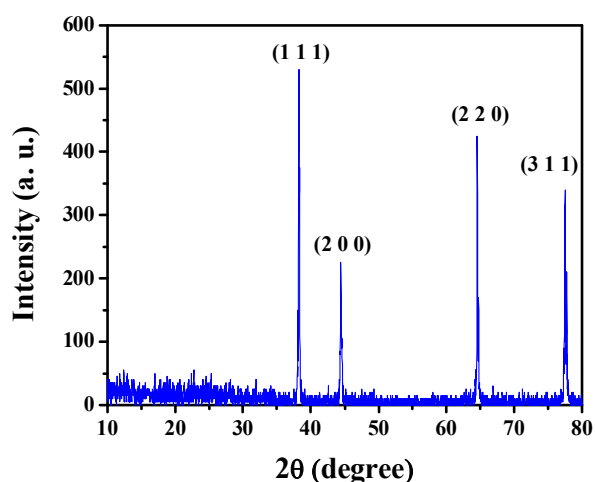


Fig. 5 XRD Spectrum of Ag nanorods

### 3.4. Cyclic voltammogram (CV) of Ag nanorods

The applicability of the best sample obtained in the optimized condition towards battery electrode application was tested through the electrochemical performance of the prepared sample. The cyclic voltammogram (CVs) of silver nanorods is shown in Fig. 6. The oxidation peak of Ag nanorods was found at 30  $\mu$  current, and the reduction peaks was observed at -5  $\mu$  current. The cyclic voltammogram obtained clearly indicates that these silver nano rods can be used for battery applications.

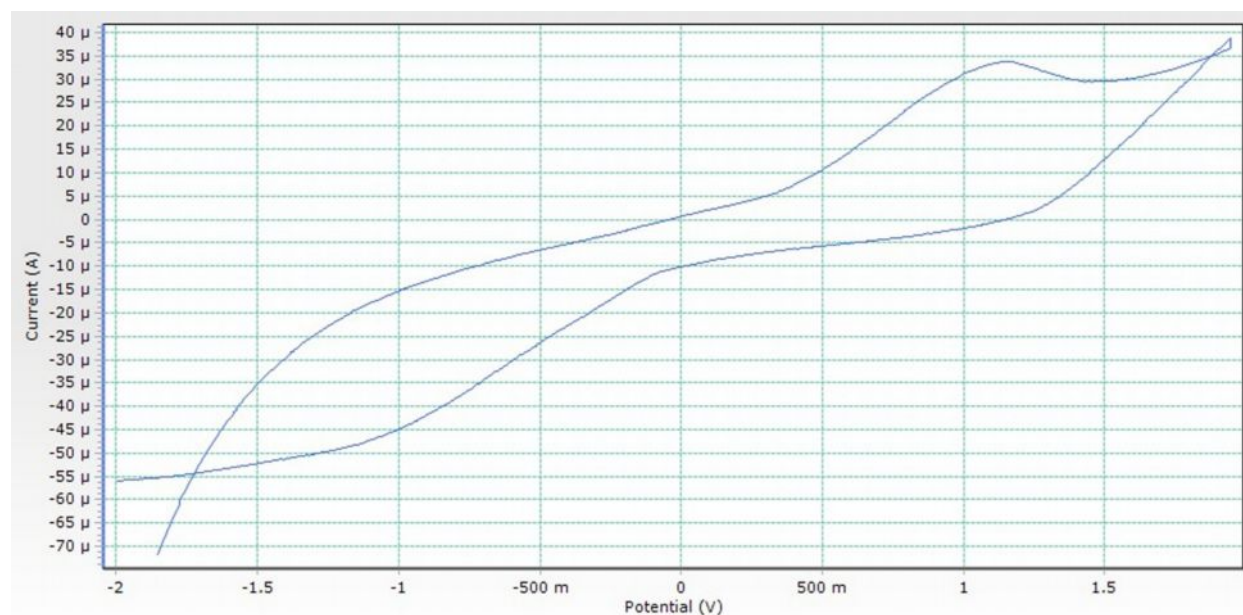
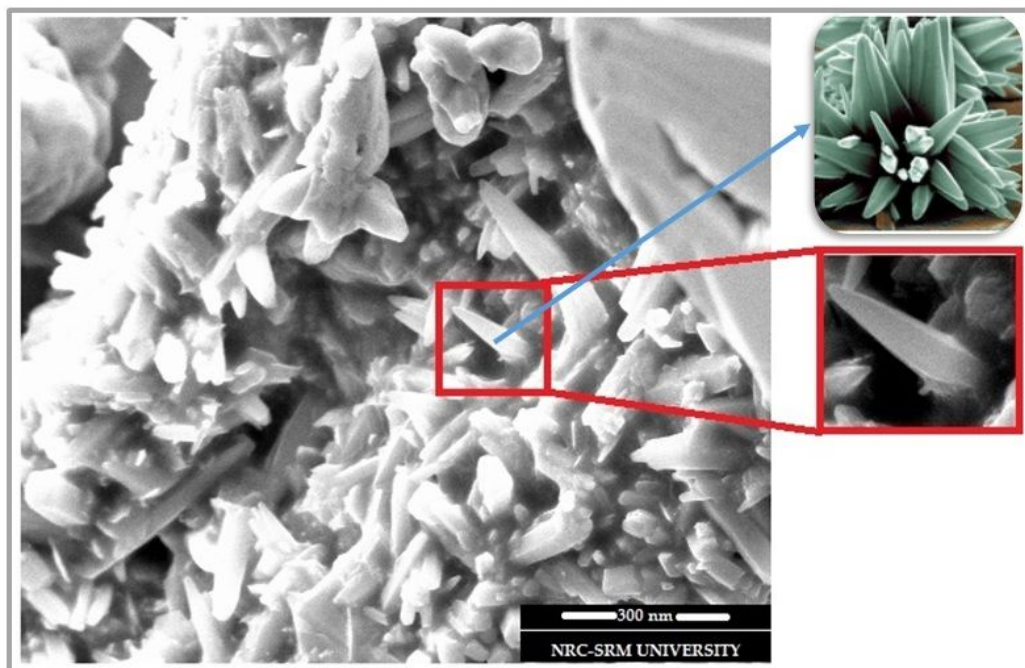


Fig. 6 CV Spectrum of Ag nanorods

### 3.5. FESEM image of Ag nanorods

Results of surface morphological and nonstructural studies using FESEM are summarized in Fig. 7. The results indicate that mono-dispersive and highly crystalline silver nanorods are obtained. FESEM image confirm the prepared sample contains silver nanorods as well as the nanowires in large quantity.



**Fig. 7**FESEM image of Ag nanorods

#### 4. Conclusion

In our research, we came to know that silver nanoparticles can be synthesized using simple, fast and economical electrolysis method. We were able to synthesize well-structured Ag nanorods because of using Pt/Ag electrodes, comparing other technique, large amount of nanorods were synthesized by this technique. As we are not utilizing any other hazardous chemicals, the Ag nanorods synthesized by us are free from toxicity. There is no need to use high pressure, energy, temperature, toxic chemicals, downstream processing etc. Handling of the nanorods is also much easier than other methods. Based on this study, some other metal nanorods may be prepared in future. Their characterizations have been successfully done using UV, CV, XRD, FESEM and FTIR spectroscopic techniques. The electrochemical analysis also reveals that this material can be used for battery application in near future.

#### References

1. Mukherjee P, Roy M, Mandal BP, Dey GK, Mukherjee PK, Ghatak J, Tyagi AK, Kale SP. Green synthesis of highly stabilized nanocrystalline silver particles by a non-pathogenic and agriculturally important fungus *T. asperellum*. *Nanotechnology*, 2008: 075103.
2. Shirley, A. Dayanand, B. Sreedhar, Syed G Dastager. Antimicrobial activity of silver nanoparticles synthesized from novel streptomyces species. *Digest Journal of Nanomaterials and Biostructures*, 2010, 5: 447-451.
3. X. Chen, H.J. Schluesener. Nanosilver: A nanoparticle in medical application. *Toxicology Letters*, 2008, 176: 1-12.
4. L. M. Liz Marzan, I. Lado-Tourino. Reduction and stabilization of silver nanoparticles in ethanol by nonionic surfactants. *Langmuir*, 1996,12: 3585-3589.
5. M. Guzman, J. Dille, S. Godet. Synthesis of silver nanoparticles by chemical reduction method and their antibacterial activity. *International Journal of Chemical and Biological Engineering*, 2009, 2: 104-111.
6. G. N. Glavee, K. J. Klabunde, C. M. Sorensen, and G. C. Hadjipanayis. Borohydride reduction of cobalt ions in water. Chemistry leading to nanoscale metal, boride, or borate particles. *Langmuir*, 1993, 9: 162-169.

7. N. Leopold, B. Lendl. A new method for fast preparation of highly surface-enhanced raman scattering (SERS) active silver colloids at room temperature by reduction of silver nitrate with hydroxylamine hydrochloride. *The Journal of Physical Chemistry B*, 2003, 107: 5723-5727.
8. P. Jeevanandam, C. Srikanth, S. Dixit. Synthesis of monodisperse silver nanoparticles and their self-assembly through simple thermal decomposition approach. *Materials Chemistry and Physics*, 2010, 122: 402-407.
9. K. Akhbari, A. Morsali, P. Retailleau. Silver nanoparticles from the thermal decomposition of a two-dimensional nano coordination polymer. *Polyhedron*, 2010, 29: 3304-3309.
10. T. Edison, M. Sethuraman. Instant green synthesis of silver nanoparticles using *Terminalia chebula* fruit extract and evaluation of their catalytic activity on reduction of methylene blue. *Process Biochemistry*, 2012, 47:1351-1357.
11. V. Kotakadi, Y. Rao, S. Gaddam, T. Prasad, A. Reddy, D. SaiGopal. Simple and rapid biosynthesis of stable silver nanoparticles using dried leaves of *Catharanthus roseus*. *Linn. G. Donn and its anti microbial activity. Colloids and Surfaces B*, 2013, 105:194-198.
12. K. Shameli, M. Ahmad, E. Al-Mulla et al. Green biosynthesis of silver nanoparticles using *Callicarpamaingayi* stem bark extraction. *Molecules*, 2012, 17: 8506-8517.
13. R. Trbojevich, N. Pellegrini, A. Frattini, O. de Sanctis, P. J. Morais, R. M. Almeida. Preparation and isolation of gold nanoparticles coated with a stabilizer and sol-gel compatible agent. *Journal of Materials Research*, 2002, 17: 1973-1980.
14. D. Zhang, X. Liu, X. Wang, X. Yang, L. Lu. Optical properties of monodispersed silver nanoparticles produced via reverse micelle microemulsion. *Physica B*, 2011, 406: 1389-1394.
15. K. H. Baek, J. H. Kim, K. B. Lee, H. S. Ahn, C. S. Yoon. Surface plasmon resonance tuning of silver nanoparticle array produced by nanosphere lithography through ion etching and thermal annealing. *Journal of Nanoscience and Nanotechnology*, 2010, 15; 3118-3122.
16. M. L. Rodriguez-Sanchez, M. J. Rodriguez, M. C. Blanco, J. Rivas, M. A. Lopez-Quintela. Kinetics and mechanism of the formation of Ag nanoparticles by electrochemical techniques: a plasmon and cluster time-resolved spectroscopic study. *The Journal of Physical Chemistry B*, 2005, 109: 1183-1191.
17. M. Bordenave, A. Scarpettini, M. Roldan, N. Pellegrini, and A. Bragas. Plasmon-induced photochemical synthesis of silver triangular prisms and pentagonal bipyramids by illumination with light emitting diodes. *Materials Chemistry and Physics*, 2013, 139; 100-106.
18. I. Johnson, H. Joy Prabu, C. Bhagya Lakshmi, S. Arulappan. Tailoring of CdSe Nanoparticles by different Techniques. *International Journal of Scientific Research*. 2013, 18: 524-525.
19. Irudayaraj Johnson, H. Joy Prabu, S. Arulappan. Ultrasound tailoring of industrially important nanoparticles. *International Journal of Scientific Research Engineering & Technology*, 2013, 2: 056-059.
20. I. Johnson, H. Joy Prabu. Green synthesis and characterization of silver nanoparticles by leaf extracts of *Cycas circinalis*, *Ficus amplissima*, *Commelina benghalensis* and *Lippia nodiflora*. *Int Nano Lett*, 2015, 5: 43-51.

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