AASCIT Communications
Volume 3, Issue 5
ISSN: 2375-3803

American Association for Science and Technology

Cyclic Voltammetry of Nano Silver Nitrate with Glyclglycine (GG) Using Glassy Carbon Electrode

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Received: May 19, 2016; **Accepted**: June 3, 2016; **Published**: September 13, 2016

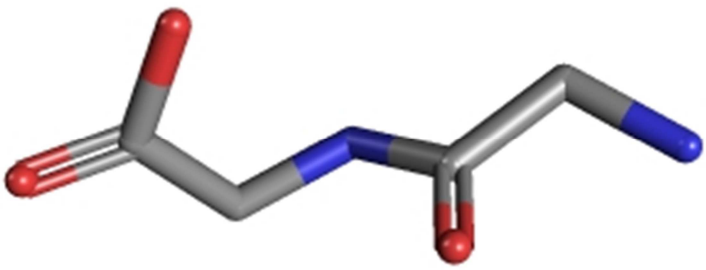
Keywords

Cyclic Voltammetry, Nano Silver Nitrate, Glassy Carbon Electrode, Glyclglycine (GG)

The nano silver nitrate was prepared by ball milling of normal $AgNO_3$. The redox behavior for nano silver nitrate was examined by cyclic voltammetry in presence and absence of glyclglycine (GG) using glassy carbon electrodes in 0.1 M KCl supporting electrode. Scan rates were done for the redox behaviors for silver nitrate in absence and in the presence of amino acid glyclglycine. Stability constants for the interaction of silver ions with glyclglycine (GG) were evaluated. All mechanisms were discussed.

Introduction

Silver salts have antiseptic properties as written in Wikipedia [1]. In 1881 using dilute solutions of $AgNO_3$ in newborn babies' eyes at birth to prevent contraction of gonorrhea from the mother, which could cause blindness. (Modern antibiotics now are used instead. [2] [3] Fused silver nitrate, shaped into sticks, was traditionally called "lunar caustic Dentists sometimes use silver nitrate infused swabs to heal oral ulcers. Silver nitrate is also used by some podiatrists for killing cells llive in the nail bed. Silver nitrate is also used to cauterize superficial blood vessels in the nose to help prevent nose bleeds [3]. Nanoparticles with high surface energy properties compared to bulk materials, lead to instability [5]. Therefore nano particles need capping agents to help their stabilization. Capping agents work through different mechanisms, electrostatic, steric stabilization, also stabilization by Van der Waals forces, depletion stabilization, stabilization through hydration forces [4]. The choice of capping agents on nanoparticles is important, because the properties as size, shape and interaction of solvent are strongly influenced it [5], which is our aim of the work. Many works on toxic behaviors of silver nanoparticles which include algae, bacteria, fungi, fish and health humans [6-8]. Research concentrated on the interaction with cell walls [9, 10]. Studying physico chemical behaviors' of the nanoparticles is important to illustrate many conditions necessary. Glyclglycine has also been reported to be helpful in solubilizing recombinant proteins in E. coli. Using different concentrations of the glyclglycine (GG) improvement in protein solubility after cell lyses has been observed [11]. Its structure is shown in Fig. 1 [12].



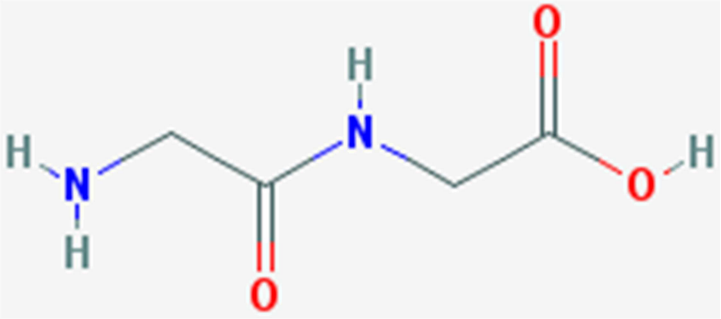


Fig. 1. *3 D and 2D of GG.*

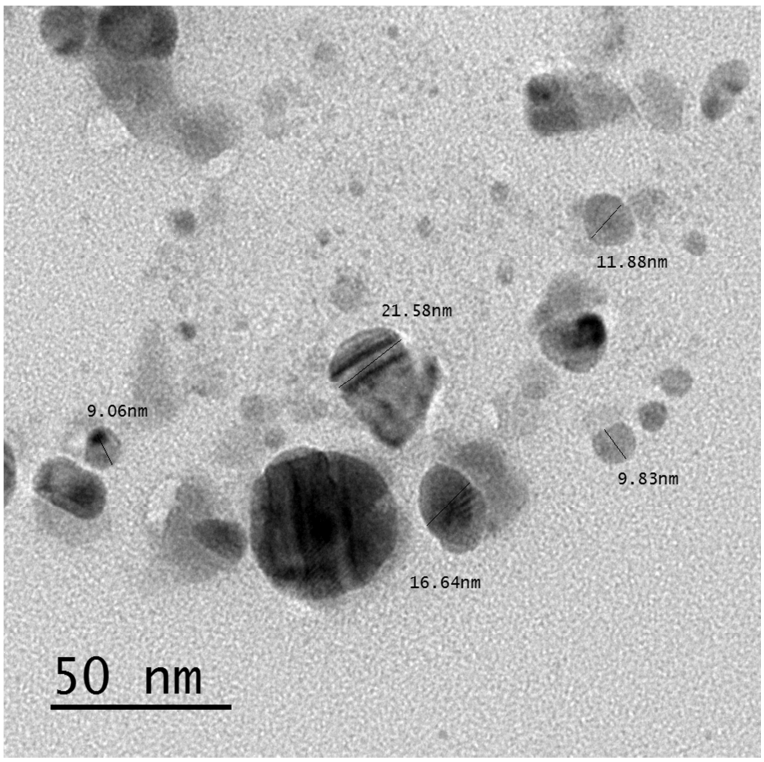


Fig. 2. *TEM Image of nano silver nitrate.*

Experimental

Preparation of Nano Silver Nitrate Material

The nano silver nitrate material studied in the study was prepared using ball milling technique using a Retsch MM 2000 swing mill with 10 cm^3 stainless steel double walled tube. The silver nitrate and nitric acid solutions used are prepared by the use Al Nasr Chemicals Company materials. In ball milling two balls stainless steel, dia-meter of 12 mm were used, the ball milling process was performed at 20225Hz and balling process was done usually at room temperature for one hour. The temperature was kept at room temperature during the material preparation.

Experimental Measurements

DY2000, DY2000EN Multichannel Potentiostat was used for voltammetry measurement Voltammetry analyzer using conventional three - electrode electrochemical cell to perform cyclic voltammetry (CV). Measurements were done by using glassy carbon made in our laboratory from pure carbon peace, polished with alpha aluminum oxide using wool peace, as working electrode with are of 0.64 cm^2, platinum wire electrode as counter electrode and Ag/AgCl standard electrode.

Cyclic Voltammetry Measurements (CV)

Cyclic voltammetry is the most common technique used to study the electrochemical systems obtained in undivided glass cell of 30 ml solution by utilizing the three electrodes mentioned above. Cyclic voltammetry experiments were carried out using different concentrations of nano silver nitrate in water at 19.3°C. HNO_3 (0.1M) as supporting electrolyte was used at different scan rates. After each run, the working electrode was cleaned and polished with aluminum oxide (α alumina), rinsed with distilled water to obtain reproducible results. Nitrogen gas was passed for (10) min. before each experiment.

Results and Discussion

TEM Images for Nano $AgNO_3$

The picture from TEM transmission electron microscope is presented for nano silver nitrate salt. The image in Fig. 2, which shows the crystalline forms of nano silver nitrate, indicates that nano silver nitrate is either in the form of irregular spheres or in the form of distorted spheres. In this image, boundaries ranging from 9.06 to 21.58 nm were shown.

Cyclic Voltammetry Analysis

The interaction of nano silver nitrate with glyclglycine (GG) has been studied using cyclic voltammetry technique in the potential range (+0.8 to - 0.5) V at different scan rates in water at 292.25K using HNO_3 (0.1M) as supporting medium and glassy carbon as a working electrode. The study is valuable for evaluating various thermodynamic properties [13-18].

Mechanism of redox reaction:

The silver ions used show reversible redox processes (Figs. 3-6) with main oxidation peak at 0.45 V mV and the main reduction one electron peak at 0.17 V. These processes corresponding to the oxidation of silver zero valent (uncharged) to monovalent (Ag^+) [19]. The main reduction peak is the reduction of silver monovalent ion to silver zero valent in this media versus silver/silver chloride electrode as follows:

$$Ag^+ (aq.) + e^- = Ag^o \quad (1)$$

$$Ag^0 = Ag+ (aq.) + e^- \quad (2)$$

It was shown that adding amino acid Glyclglycine (GG) caused decreases in both peak heights, which indicate the reaction between nano silver nitrate and Glyclglycine (GG).

Different scan rates were discussed for the redox reaction for 2 mM nano copper sulphate alone were done in water and the resulted values are shown in Fig. (3). Straight lines were obtained by drawing the relation between Ip, a & Ip, c against scan rate. From this relation the diffusion coefficient was confirmed and found to be in the range from 0.47 to 0.5 Different additions of Glyclglycine (GG) from 1mm to 6 mM were made and different scan presented by using 1:3 molar ratio of silver ion to Glyclglycine (GG). The analysis of the complex formation voltamogram were done.

The mechanism of silver dissolution under our experiment has been supported as in literature, as it shown that the reduction of dissolved oxygen provides the electrons required for dissolution through the following mechanism [20-22].

$$Ag = Ag^+ + e^- \quad (3)$$

$$O_2 + 2H^+ + 2e^- = H_2O_2 \quad (4)$$

The oxidative dissolution of silver was shown to be influenced by the reduction of oxygen, also in the presence of micro quantities of oxygen still present after extensive deairation of nitrogen. Also the redox mechanisms were proved to be reversible one in absence and presence of amino acid from the voltamogram at different scan rates.

The total stability constants for the interaction [23-30] of nano silver nitrate with Glyclglycine (GG) were calculated by applying DeFord-Hume equation [30-35]. These calculation data together with the Gibbs free energies obtained for the complex formation nano silver nitrate and Glyclglycine (GG) [35] have been presented in Table (1). The Gibbs free energy of interaction for nano silver nitrate with Glyclglycine (GG) are given in Table (1) found to be in the range of -97 to -116 kJ/mole at different concentrations of Glyclglycine (GG) indicating specific strong complexation formed.

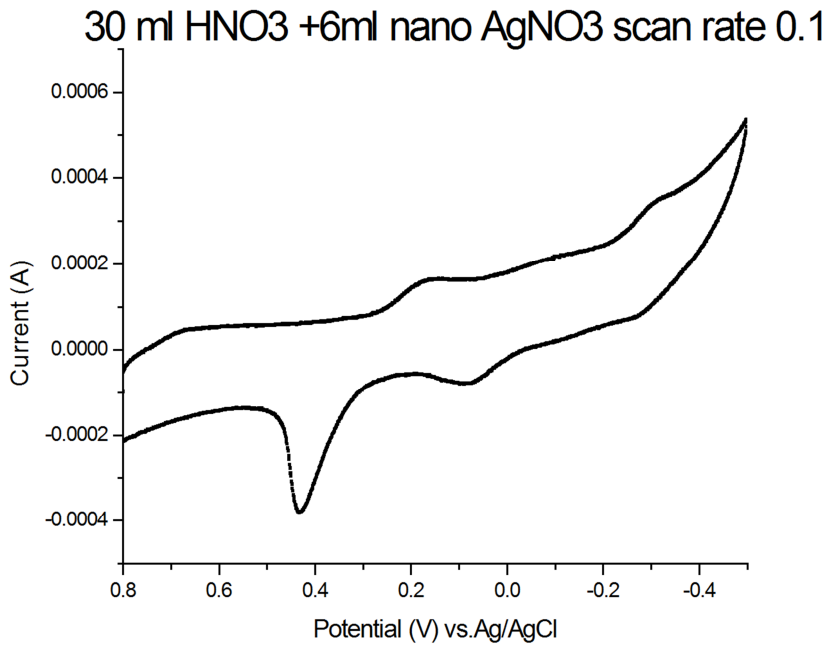


Fig. 3. *Cyclic Voltammetry for Nano $AgNO_3$ (concentration =$2x10^{-3}$) alone in 30 ml HNO_3 (0.1M) at scan rate 0.1 (V/Sec), Sens (A/V) = $1x10^{-3}$, initial E (V) = 0.8, high E (V) = 0.8 and low E(V) = -0.5.*

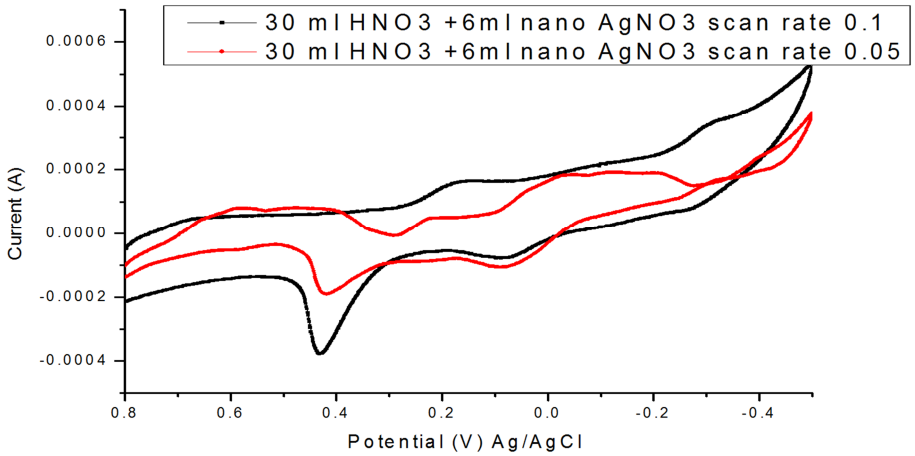


Fig. 4. *Effect of different scan rate for nano $AgNO_3$ at Concentration 2 mM. The scan rates were maintained at 0.1, 0.05 (V/Sec), Sens (A/V) = $1x10^{-3}$, initial E (V) = 0.8, High E (V) = 0.8 and low E(V) = -0.5.*

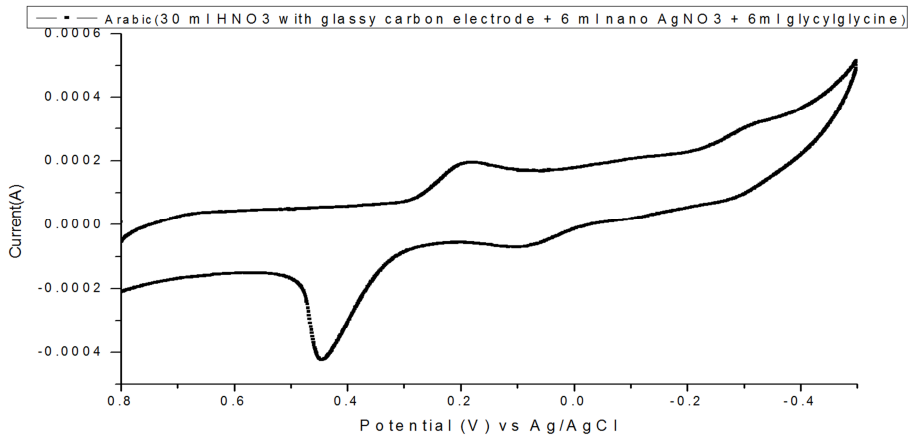


Fig. 5. *Cyclic voltammetry for Nano $AgNO_3$ $2x10^{-3}$ and Glycylglycine with concentration $1.6x10^{-3}$at scan rate 0.1 (V/Sec), Sens (A/V) = $1x10^{-3}$, initial E (V) = 0.8, high E (V) = 0.8 and low E(V) = -0.5.*

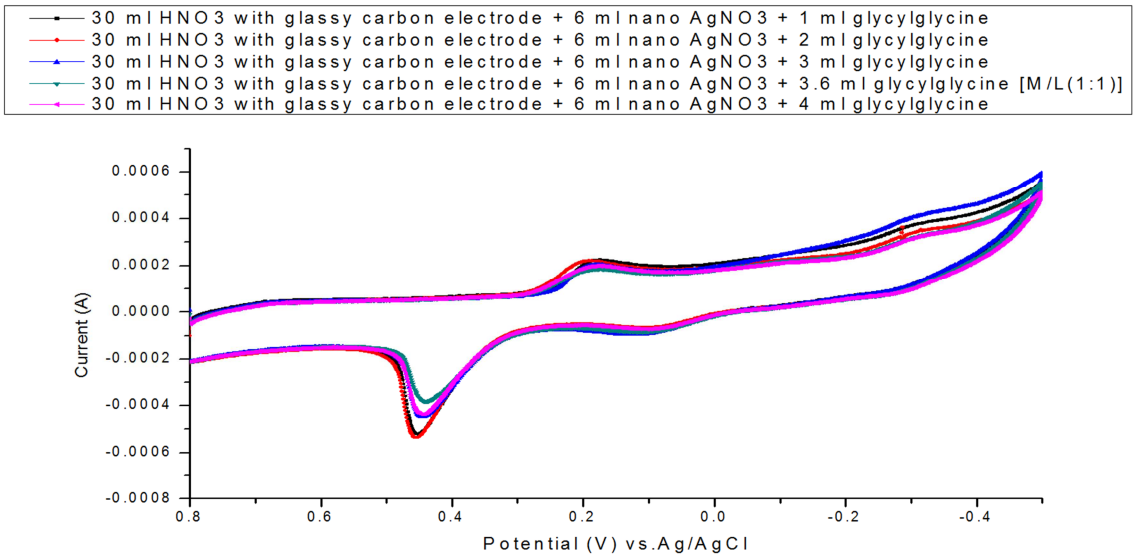


Fig. 6. *Comparison between adding different concentrations of ligand.*

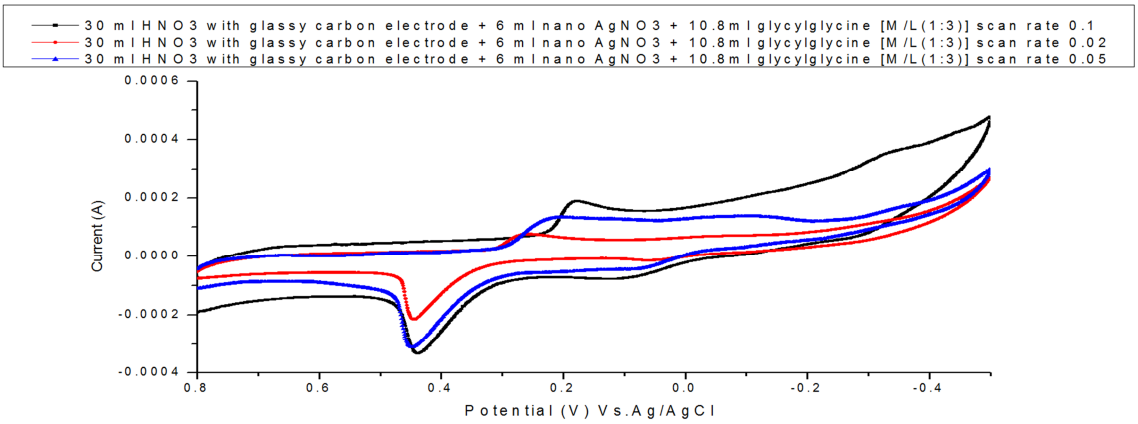


Fig. 7. *Effect of different scan rate for nano $AgNO_3$ ($2x10^{-3}$) with Glycylglycine ($3x10^{-3}$). The scan rates were maintained at 0.1, 0.05, 0.02 (V/Sec), Sens (A/V) = $1x10^{-3}$, initial E (V) = 0.8, high E (V) = 0.8 and low E(V) = -0.5.*

Table 1. *Analysis of the voltogramms for adding Glycylglycine (GG) to nano $AgNO_3$ in HNO_3.*

[M] *10^{-3}	[L] *10^{-3}	log γ±	γ±	(Ep, a)M	Ep, a)C)	Ip, a *10^4	ΔE1/2	n	Da	βMX	ΔG (kJ mol-1)-
2	0.278	-0.0309	0.931	0.431	0.456	-1.03	0.887	12	5.46E-17	1.32E+19	-105.135
2	0.556	-0.0163	0.963	0.431	0.454	-4.69	0.885	0	1.72E-10	6.10E+18	-103.287
2	0.833	-0.02	0.954	0.431	0.444	-3.7	0.875	0	1.06E-10	2.71E+18	-101.354
2	1	-0.0219	0.95	0.431	0.44	-3.05	0.871	0	7.30E-11	1.92E+18	-100.533
2	1.1	-0.0231	0.948	0.431	0.445	-3.83	0.876	0	1.19E-10	2.12E+18	-100.763
2	1.389	-0.0285	0.942	0.431	0.445	-3.83	0.876	0	1.19E-10	1.69E+18	-100.231
2	1.667	-0.0282	0.936	0.431	0.445	-3.56	0.876	0	9.94E-11	1.41E+18	-99.795
2	1.994	-0.0305	0.932	0.431	0.534	-3.83	0.965	1	4.45E-14	4.42E+19	-108.014
2	2	-0.0309	0.931	0.431	0.447	-3.81	0.878	0	1.17E-10	1.27E+18	-99.553
2	2.22	-0.03267	0.927	0.431	0.628	-7.27	1.059	0	1.21E-12	1.72E+21	-116.765
2	2.5	-0.0345	0.9233	0.431	0.448	-3.49	0.879	0	9.63E-11	1.06E+18	-99.116
2	2.778	-0.0365	0.9193	0.431	0.448	-3.53	0.879	0	9.88E-11	9.51E+17	-98.865
2	3	-0.0379	0.9163	0.431	0.437	-2.61	0.868	0	5.02E-11	5.69E+17	-97.62
[M] *10^3	[L] *10^3	log γ±	γ±	(Ep, a)M	Ep, a)C	Ip, a *104	ΔE1/2	N	Da	βMX	ΔG (kJ mol-1)
2	3.056	-0.03831	0.9156	0.431	0.438	-2.5	0.869	0	5.06E-11	5.81E+17	-97.672
2	3.333	-0.04001	0.9119	0.431	0.444	-3.04	0.875	0	7.64E-11	6.79E+17	-98.044
2	3.611	-0.04164	0.9085	0.431	0.444	-3.13	0.875	0	7.85E-11	6.23E+17	-97.853
2	3.889	-0.04322	0.9052	0.431	0.557	-1.36	0.988	1	1.14E-12	5.60E+19	-108.578
2	4	-0.04383	0.904	0.431	0.444	-3.08	0.875	0	7.66E-11	5.66E+17	-97.608

Conclusion

The nano silver ions used show reversible redox processes with main oxidation peak at 0.45 V mV and the main reduction one electron peak at 0.17 V. These processes corresponding to the oxidation of silver zero valent (uncharged) to monovalent (Ag^+). The main reduction peak is the reduction of silver monovalent ion to silver zero valent in this media versus silver/silver chloride electrode The stability constant and Gibbs free energy of interaction between silver with glyclglycine (GG) was estimated having mean values of -106 kJ for total Gibbs free energies of complexation.

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