Asian Journal of Chemistry; Vol. 29, No. 10 (2017), 2133-2137
ASIAN JOURNAL OF CHEMISTRY
https://doi.org/10.14233/ajchem.2017.20644

Electrochemical Reduction of Nitroanisaldehyde at Zinc Cathode with Surface Morphology and Biological Activity

S.A. SRIKANTA[1,*], P. PARAMESHWAR NAIK[1] and T.V. VENKATESH[2]

[1]Department of Chemistry, Sahyadri Science College, Shivamogga-577 203, India
[2]Department of Chemistry, Kuvempu University, Jnanasahyadri, Shankaraghatta-577 451, India

*Corresponding author: E-mail: shreekanta.camistry@gmail.com

Received: 13 March 2017; *Accepted*: 19 May 2017; *Published online*: 31 August 2017; AJC-18506

Crystalline and sphere like morphologies of smaller molecules have many applications. Particle size determination is essentially and important while working with nanomaterials. The information on many physical properties including the size, morphology, surface texture, roughness and chemical composition of materials is the important area of research. Moreover, advanced manipulation of the samples during the SEM experiments can provide key information about the morphology of the crystals at the micro and nanometer scale. The electrochemical reduction of nitro aromatic compound to its amine derivative is of great importance in studying the conductivity and the surface morphology of the cathode. The measurement of the variation of current and electrode potential with time during the electrolysis is also the important area of research. The particle size variation in the reduction product of a nitro aromatic compound increases the biological activity may be due to their particle size. The study of biological activity of the organic molecule before and after electrolysis is an interesting subject in the pharmaceutical industry.

Keywords: Cathode surface, Electrochemical reduction, Surface morphology.

INTRODUCTION

Crystalline, sphere like morphologies of small molecular organic compounds have applications in many fields. The experimental approach opens a new route for exciting applications of small molecular organic compounds in optical coatings, textured surfaces with controlled wettability, pharmaceutical and food substance printing and others, where thick organic films and particles with high surface area are needed [1].

As in the last several decades, chemists have shown their interest in the electrochemical reduction of organic compounds. These molecules are brought into contact with a cathode, wherein the cathode comprises a support made of an electrically conductive material [2].

The electrochemical reduction of nitro organic compounds has been used for the cathode dimerization of acrylonitrile, but yields were too low, hydrogen was being formed, selectivities with a view to a number of possible reduction steps were too low, the special catalytically active cathodes were not sufficiently available on a technical scale. At present more information is required on electrochemical behaviour for electrochemical reduction on cathodes to be utilized industrially [3].

It is also known, from literature in preparative organic electro chemistry that anodes and cathodes used in preparative electro chemistry must have special electrochemical characteristics. Such electrodes are often used for metal organic frameworks represent a class of hybrid materials comprised of ordering networks formed *via* combining metal ions with organic ligands. Metal organic frameworks have been used as efficient electrodes in fuel cell systems [4].

The electrodes and electrolytes are crucial in electro catalysis and different electrodes and electrolytes can induce different products. Modifying the surface of electrodes to provide some control over how the electrode interacts with its environment has been one of the most active areas of research interest in electro chemistry during the last 30 years [5-11].

The absorption of the drugs is especially affected by particle size because the bioavailability is, in most of the cases, dissolution rate controlled. In the pharmaceutical industry several conventional techniques have been utilized for particle size reduction, such as spray drying, freeze drying and liquid antisolvent precipitation [12].

A drawback of these established fabrication methods is that the electrodes, after inactivation of the catalytically active layer, often have to be removed from the electrolytic apparatus and subjected to external regeneration, so that the short catalyst

on stream times preclude the economic utilization of the electrochemical synthesis system. A further drawback consists in the laborious preparation of the catalytically active layer as such and the difficulties in achieving adequate bonding to the support electrode. The development effort for a classic electrode coating process can in many cases be justified in economic terms only with major industrial processes such as chlorine-alkali electrolysis or the cathodic dimerization of acrylonitrile [13-15].

In view of the above it is an object of the present study to provide a process for reducing organic compounds, which on the one hand gives high space, time yields, permits high selectivity in case of multiply reducible compounds, which avoids the formation of hydrogen during the reduction and can be used on an industrial scale.

Nanotechnology is emerging as a rapidly growing field with its application in science and technology for the purpose of manufacturing new materials at the nanoscale level [16]. Recently, biosynthetic methods employing either biological microorganisms such as bacteria [17] and fungus [18] have emerged as a simple and viable alternative to more complex chemical synthetic procedures to obtain nanomaterials

This object is achieved according to the invention by means of a process for the electrochemical reduction of an organic compound by bringing the organic molecule into contact with a cathode, wherein the cathode comprises a support made of a conductive material.

The mean particle size of the conductive particles is generally from 1 to 400 μm, preferably from about 30 to 150 μm and the thickness of the layer is generally from 0.05 to 20 mm, preferably from 0.1 to 5 mm.

After the reduction is complete or when the catalytically active layer is spent, it can be separated from the support, by a simple switch of the flow direction and can be disposed off or regenerated, independently of the reduction. After the spent layer has been completely removed from the system, it is then possible once more to support with the particles forming the layer and, after said particles have been completely alluviated to continue the reduction of the organic compound.

Organic compounds suitable for use in the process according to the invention in principle comprise any organic compounds containing reducible groups as starting materials. The products which can be obtained in the process include, depending on the total electric charge introduced, both partially reduced compounds and completely reduced compounds

Preferably, organic compounds are reduced which have reducible groups or bonds *e.g.*, nitro groups [19,20].

EXPERIMENTAL

Procedure for electrolysis: 0.01 mmol (0.182 g) of nitroanisaldehyde was taken in an undivided cell with 75 mL of ethanol and 25 mL of water. To this mixture an aqueous solution of potassium bromate (1 g) was added dropwise at room temperature. The undivided cell was equipped with a zinc cathode (0.014 cm^2), platinum anode (Pt^+) and calomel electrode. The constant potential was supplied with DC power supply (9.5 V, 300 mA). The reaction was electrolyzed with constant stirring using a magnetic stirrer for 1 h and electrolysis was stopped. The electrode along with product deposited was washed with water and dried and the surface of the electrode was characterized by SEM.

Procedure for antibacterial and anti fungal activity: The *in vitro* antibacterial activity carried out by a well diffusion method using nutrient agar as the medium, DMSO as the control and chloramphenicol used as a standard bactericide and fluconazole as standard fungicide. The electrolytic solutions were screened for antimicrobial activity against *Staphylococcus aureus*. *Bacillus aureus*, *Streptococcus* Sp, *Proteus mirabilis*, *Staphylococcus epidermidis*, *Enterobacter aerogenes*, *Shigella flexneri*, *Klebsiella pneumonia*, *Vibriocholerae* and species of fungi *Aspergillus flavius*, *Aspergillus niger*, *Cryptococcus neaformens*, *Curvularia* Sp, *Trichosporon* Sp, *Candida albicans* Well-in agar method. The synthesized compound (1 mg mL^{-1}) and the controlled drugs were dissolved in redistilled DMSO for determining the both antibacterial and antifungal activity. The zones of inhibition were determined at the end of an incubation period of 24 h at 37 °C. During this period, the test solution defused and the growth of inoculated microorganism was affected. The antifungal activities were determined at 26-28 °C.

RESULTS AND DISCUSSION

Electrochemical behaviour: The electrochemical of nitroanisaldehyde was carried out in an undivided cell and the electrode reactions were performed successfully in an undivided cell which is a simple beaker type apparatus. A simple, undivided cells equipped with 3 electrodes and a magnetic stirrer. The cell is connected DC suppliers which could be operated at a standard output of 0.5 to 2.5 A/0-35 V. These are connected with an ammeter and voltmeter in series. A magnetic stirring system is convenient and is used in almost all cases. The calomel electrode a reference electrodes is used to monitor the operating potential. Electrochemical measurements involved the three variables, namely electrode potential (E), current density (i) and time (t). In order to investigate the relationship between any pair of these variables, the potential of the working electrode is measured against a reference electrode.

Nitroanisaldehyde is reduced on the surface of zinc cathode. The surface morpholgy of electrode before and after electrolysis was studied at the electrode potential of -0.8 V. The surface morphology was analyzed by SEM analysis and it was observed that there is a difference in the morphology of the surface of zinc cathode, due to the reduction of nitroanisaldehyde on the surface of zinc cathode. The SEM image of aminoanisaldehyde on the surface of zinc cathode is shown in Fig. 1d (after electrolysis). The scanning electron microscope (SEM) images of surface of zinc cathode are shown in Fig. 1a (before electrolysis). The SEM image of nitroanisaldehyde are shown in Fig. 1b (before electrolysis). The unaffected aldehyde group of anisaldehyde was confirmed by IR spectrum as shown in Fig. 2. The variation of current with time and the variation of current with electrode potential is shown in Fig. 3a-c (Tables 1 and 2). As time proceeds more and more nitroanisaldehyde undergoes reduction on the surface of zinc cathode. The deposition of aminoanisaldehyde on the surface

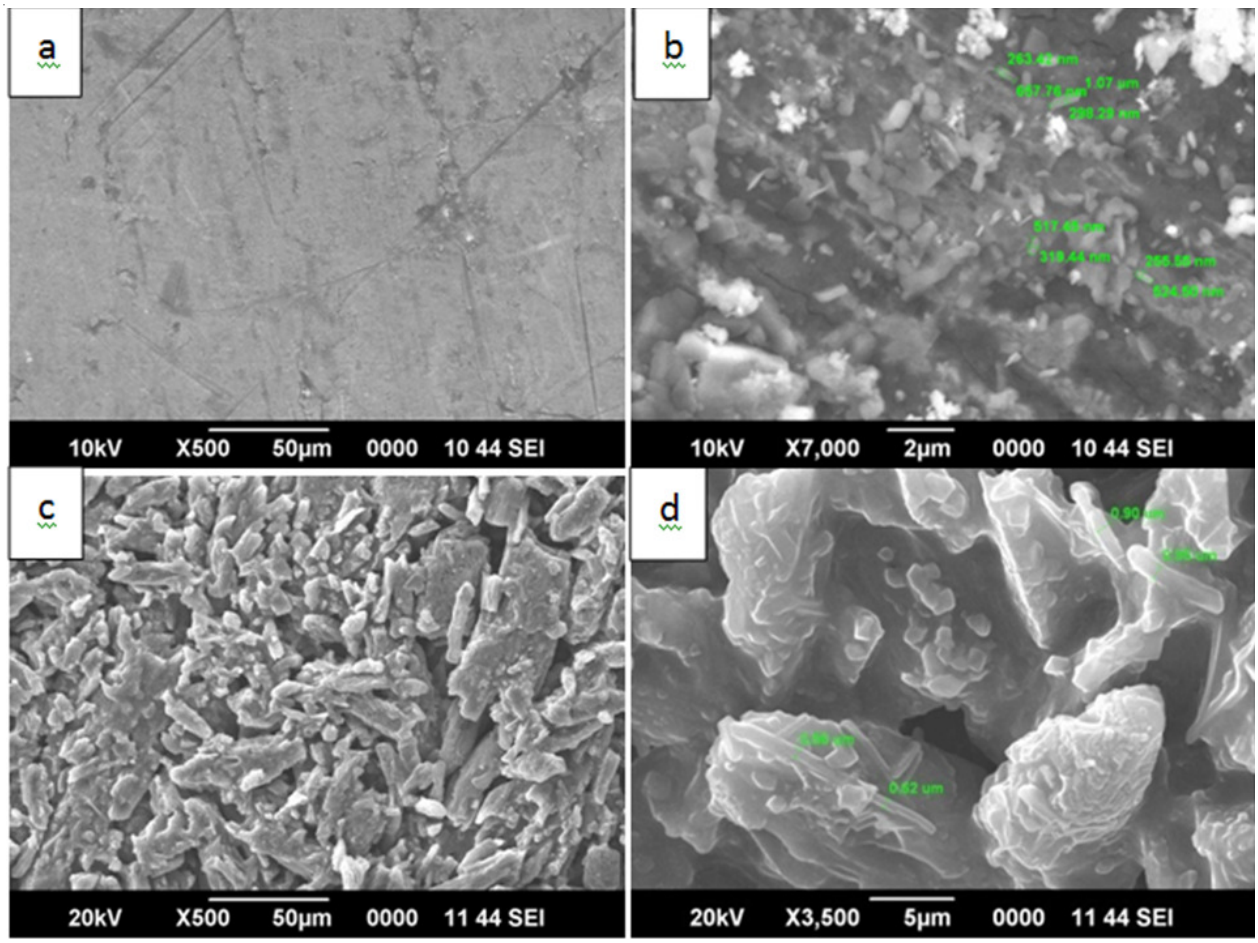

Fig. 1. (a) The SEM image of the morphologies of zinc electrode before electrolysis (b) The SEM image of the morphologies of nitroanisaldehyde before electrolysis (c) The SEM image of the morphologies of amino anisaldehyde on the surface of zinc cathode at 50 µm (d) The SEM image of the morphologies of amino anisaldehyde on the surface of zinc cathode at 5µm

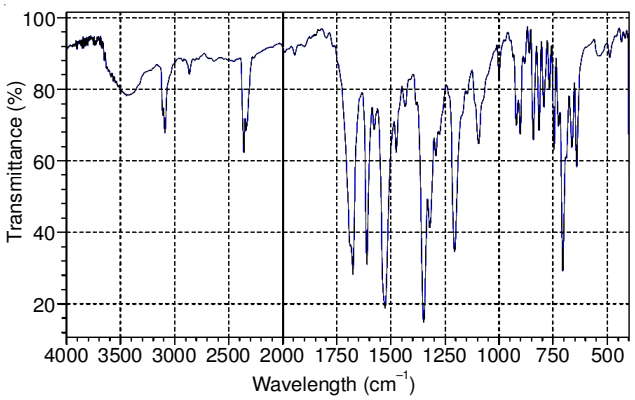

Fig. 2. IR spectra of aminoanisaldehyde on the surface of zinc cathode

of cathode and the transfer of electron from cathode to the nitro-molecule initiate electroreduction reaction. The conductivity of the cathode improved and hence current increases with time as shown in the Fig. 3c. The electro deposition on the cathode also responsible for the variation of current with time. A direct correlation between conductivity, structure and morphology was observed from the above result. The addition of supporting electrolyte potassium bromate further increases the current. As current is directly proportional to the current density, current density also increases. The rate of reaction is directly proportional to current density according to the equation:

$$r_A = ai/nF \quad (1)$$

$$i = (nFr_A)/a \quad (2)$$

where a is the stoichiometric coefficient of the reactant.

The current density is a very important factor for electrochemical reaction. The addition of $KBrO_3$ increased current density and the efficiency of the cathode. The following

TABLE-1
SUMMARY OF ANALYTICAL PARAMETERS OF ELECTROLYSIS WITH THE SUPPORTING ELECTROLYTE, POTASSIUM BROMATE ($KBrO_3$)

Time	Current (mA)	Electrode potential	pH	Source current	Source voltage
0	11.58	-0.74	7	1.15	28.2
10	14.28	-0.738	7	1.15	27.3
20	16.91	-0.735	7	1.15	26.1
30	17.67	-0.729	7	1.15	25.4
40	19.57	-0.726	7	1.15	24.8

TABLE-2
SUMMARY OF ANALYTICAL PARAMETERS OF ELECTROLYSIS WITHOUT THE SUPPORTING ELECTROLYTE, POTASSIUM BROMATE ($KBrO_3$)

Time	Current (mA)	Electrode potential	pH	Source current	Source voltage
0	2.56	-0.726	7	1.16	26.8
10	2.86	-0.619	7	1.16	26.2
20	3.93	-0.590	7	1.16	25.7
30	8.10	-0.573	7	1.16	25.6
40	10.08	-0.564	7	1.16	25.4

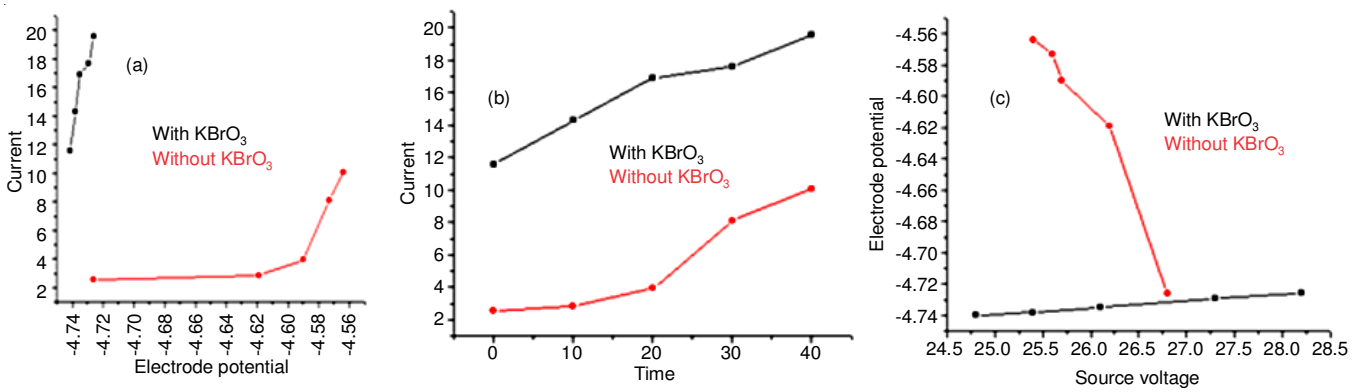

Fig. 3. (a) Graph showing the variation of current with electrode potential for the electrochemical reaction of nitroanisaldehyde with and without $KBrO_3$ in aqueous ethanol (b) Graph showing the variation of electrode potential with source voltage for the electrochemical reaction of nitroanisaldehyde with and without $KBrO_3$ in aqueous ethanol. (c) Graph showing the variation of current with time for the electrochemical reaction of nitroanisaldehyde with and without $KBrO_3$ in aqueous ethanol

oxidation reactions of potassium bromate increases the current density.

$$BrO_3^- + e^- + H_2O \longrightarrow BrO_2^- + HO^-$$

$$2BrO_2^- \longrightarrow BrO_3^- + BrO^-$$

$$BrO^- + BrO_2^- \longrightarrow Br^- + BrO_3^-$$

$$Br^- + BrO_2^- \longrightarrow 2BrO^-$$

$$2BrO^- \longrightarrow Br^- + BrO_2^-$$

Biological activity: The electrochemically produced aminoanisaldehyde is tested for biological activity as given in the experimental procedure.

The product shown enhanced biological activity which was compared by studying the biological activity of the compound (electrolysis solution) before and after electrolysis. The electrolytic solution containing nitroanisaldehyde that is before electrolysis and the electrolytic solution containing reduced nitroanisaldehyde that is after electrolysis were screened for antibacterial activity and antimicrobial activity (Tables 3 and 4).

TABLE-4
ANTIFUNGAL ACTIVITY OF THE NITROANISALDEHYDE BEFORE ELECTROLYSIS AND AFTER ELECTROLYSIS

S. No.	Fungal species	Compound before electrolysis	Compound after electrolysis	Compound after electrolysis with condensation
1	Yeast	–	–	–
2	*C. neoformons*	–	15	–
3	*A. flaeus*	–	–	–
4	*Trichosporon*	–	–	17

The biological activity may be due to reduction of nitroanisaldehyde and also depended on the particle size. The biological activity of unelectrolyzed and electrolyzed nitroanisaldehyde was shown in the Tables 3 and 4.

TABLE-3
ANTIBACTERIAL ACTIVITY OF THE NITROANISALDEHYDE BEFORE ELECTROLYSIS AND AFTER ELECTROLYSIS

S. No.		Bacterial species	Compound before electrolysis	Compound after electrolysis	Compound after electrolysis with condensation
1	Gram-negative	*Bacillus cereus*	10 mm	28 mm	14 mm
2	Gram-negative	*Pseudomonas aeruginosa*	12	10	13
3	Gram-negative	*Vibriocholerae*	–	–	–
4	Gram-negative	*Klebsiella pneumoniae*	–	20	4
5	Gram-positive	*B. cereus*	–	20	–
6	Gram-negative	*Shigella flexneri*	–	–	–
7	Gram-negative	*S. pyogens*			
8	Gram-negative	*Streptococcus*	–	20	–
9	Gram-positive	*Styphylococcus epidermidis*			
10	Gram-positive	*B. subtilis*			

Conclusion

This paper focuses on the particle size of reduced nitroanisaldehyde on the surface of zinc cathode. The surface morphology changes the cell current and the addition of potassium bromate increases the current density required for electrochemical reaction. The electrophore nitrogroup gets reduced to amine by reduction.The aminoanisaldehyde shows enhanced biological activity.The analytical study confirms that the electrolyzed product are biologically more active due to their particle size.

ACKNOWLEDGEMENTS

The authors are grateful to University Grant Commission, New Delhi, India for providing FIP assistance.

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