



# Synthesis and Electrochemical Studies of Spirooxindole Derivatives using Efficient and Recoverable Nanocatalyst

Aayushi Chanderiya, Atish Roy, Pratibha,  
Arunesh K. Mishra, Hemlata Dangji, Ratnesh Das\*

Dr. Harisingh Gour University Sagar (M.P.)

**Abstract :** Herein, we have reported a One-pot multi-component Reaction of Spirooxindole derivatives using Isatin, active methylene compounds and 1,3diketones in alcohol, under reflux and room temperature. Spirooxindoles are pharmacologically active substances with several biological activities and electrochemically active compounds. The key feature of this process is mild reaction conditions and the use of Nanoparticles as a catalyst as they showed excellent catalytic activity due to more surface area. The electrochemical study of the synthesized product has been done by cyclic voltammetry.

**Keywords** - Spirooxindole derivatives; pharmacologically active; biologically active; Cyclic voltammetry.

## Introduction

Multi-component reactions (MCRs) are a modern, easy, and efficient solution for producing active biological molecules that have become a high-priority area of research in organic, multidisciplinary, and pharmaceutical applications. [1]. Due to its versatile, divergent, and atom-efficient characteristics, the MCRs approach has significant benefits over traditional sequential synthesis [2, 3]. Many pharmaceutical drugs and natural substances have a spirooxindole system at their foundation structure. [4,5]. As a result, spirooxindole has piqued the curiosity of synthetic and medicinal chemists. Many different catalysts, such as surfactant (Tri Ethyl Benzyl Ammonium Chloride) TEBA, ammonium chloride (NH<sub>4</sub>Cl), sodium stearate, mesoporous silica NPs (nanoparticles), (Chloroauric acid)HAuCl<sub>4</sub>, nanocrystalline MgO, and sulfated choline, have been used in the reaction to produce more efficient and greener techniques.

We have used ZnO for the synthesis due to their operational advantages, such as insolubility in water and organic solvents; heterogeneous catalysts have gained significant interest. In the heterocyclic synthesis, the active methylene moiety of

malononitrile performs a crucial and attempting to attack role. Because of the conversion of different functional groups into their corresponding carbanions. These functional groups are such as ketones, aldehydes, esters, Oxo and amines etc. Malononitrile molecule produces fundamental functional and spectral changes; thus, malononitrile has a particular interest in organic synthesis. The nature of the catalyst and solvent also are very important for the determination of the product and its selectivity.

## Material and methods

Chemicals were obtained from Sigma-Aldrich and Himedia. All these chemical and used without further purification. The pH of the solution was measured by digital pH meter. All electrochemical investigations were carried out on an electrochemical work station of Metrohm Autolab B.V. PGSTAT128N computer running software NOVA 1.11.2.

Cyclic voltammetry was performed using a carbon paste electrode (d = 0.2 cm) as the working electrode, a Platinum electrode as the Auxiliary electrode, and an Ag/AgCl (in 3 M KCl solution) as the reference electrode. Carbon paste electrodes (d = 0.2

\*Corresponding author :(E-mail: ratneshdas1@gmail.com)

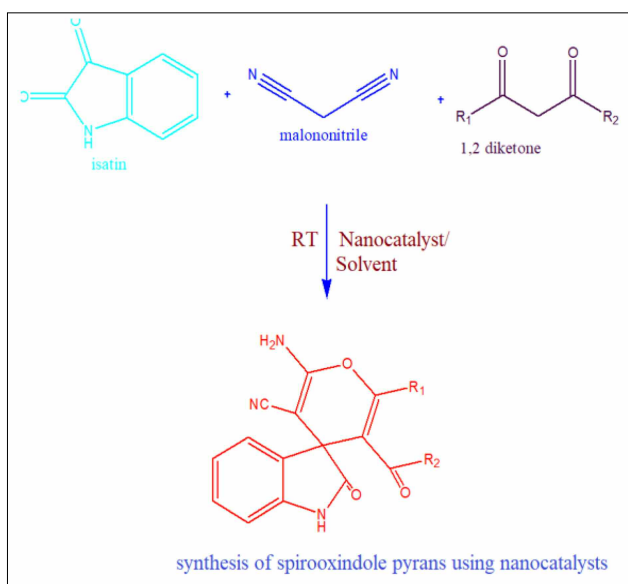
mm) were made by combining paraffin wax and graphite powder in a 3:7 ratio, sonicating it for 30 seconds in an ultrasonic bath and finally rinsing it with DI water. The carbon paste electrode was then mechanically treated before being installed in a three-cell arrangement.

### Experimental section

3 mmol isatin, 3 mmol malononitrile (0.198 g), 3 mmol acetyl acetone, and 0.3 mmol catalysts were combined in a round bottom flask with solvent and agitated at reflux at room temperature until all reactants were consumed. TLC was used to observe the reaction. The resultant slurry was dried by air. After that, the crude solid was kept on Whatman filter paper and purified with DI water. The solid product was collected by filtering and refined by crystallization from alcohol to get pure Spirooxindole derivatives after the reaction was completed.

FTIR (KBr) ( $\nu_{\max}$   $\text{cm}^{-1}$ ) 3200(N-H stretching), 2300(CN), 1700 (C=O), 1590(NH<sub>2</sub>), 1100(CN)

- The scheme of reaction is shown



### Synthesis of catalyst

Zinc acetate solution (0.05M) was combined with Dextrose solution (0.01 M) in TWEEN 80 (C<sub>6</sub>H<sub>12</sub>O<sub>26</sub>) (0.05 M) in conventional synthesis. The solution was prepared to a volume of 50 mL with DI water and vigorously stirred for 30 minutes. The hazy solution resulting was then treated to a solution combustion method similar to those described in previous papers. Subsequently, 50 mL of the turbid mixture was put into a glass beaker and burned to 250 °C in a muffle furnace. The sample momentarily ignites due to the presence of

Dextrose, and the subsequent deflagration correlates to the creation of ZnO nanoparticles. 10

### SEM and EDX characterization of nanocatalyst

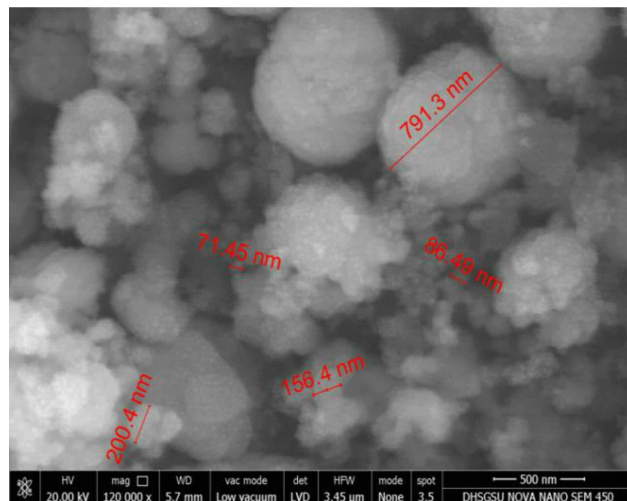


Fig - 1 SEM characterization of nanocatalyst

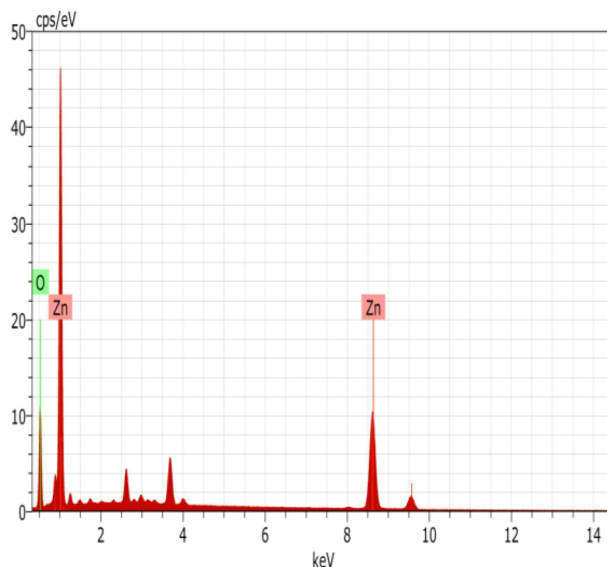


Fig - 2 EDX characterization of nanocatalyst

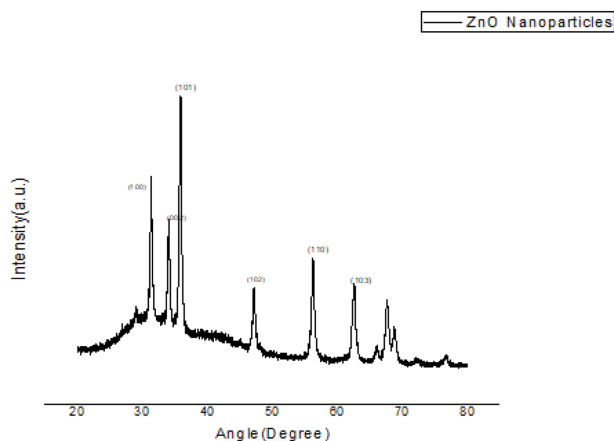


Fig - 3 XRD analysis of Synthesized ZnO catalyst

## Electrochemical study of synthesized compounds

- An electrochemical method which measures the current that arises in an electrochemical cell when the voltage exceeds that described by the Nernst equation is known as Cyclic voltammetry.
- CV solutions were made by combining 14.0 mL of  $K_3Fe(CN)_6$  solution (0.01 M), 2.0 mL of KCl solution (0.1 M) as a supporting electrolyte, and 4.0 mL of phosphate buffer (0.1 molL<sup>-1</sup>). all these electrochemical measurements were carried out At room temperature
- The product's cyclic voltammogram reveals a reversible redox reaction various scan rates.
- By performing cyclic voltammetric measurements for  $K_3Fe(CN)_6$  (1.0 mM) probe in M KCl (0.1 M) electrolyte at varied scan speeds, the surface area of the electrodes can be estimated by using the Randles-Sevick equation:
- $I_{pa} = 0.4463 (F^3/RT)^{1/2} n^{3/2} A_0 D_0^{1/2} C v^{1/2}$

where  $I_{pa}$  is the anodic peak current,  $n$  is the number of electrons transferred,  $A_0$  is the electrode surface area (cm<sup>2</sup>),  $D_0$  is the diffusion coefficient,  $C$  is the  $Fe(CN)_6^{3/4}$  concentration, and  $v$  is the scan rate;  $R$  is the molar gas constant (8.314 JK<sup>-1</sup> mol<sup>-1</sup>), and  $F$  is Faraday's constant (96,480 Cm<sup>-1</sup>).

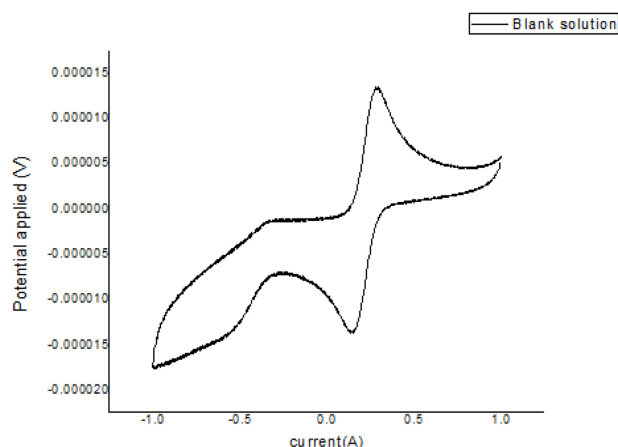


Fig 4 cyclic voltammogram of blank solution (without sample)

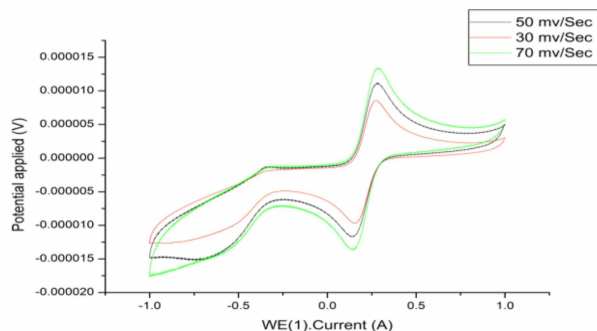


Fig 5 cyclic voltammogram of synthesized compound at different scan rate

- Spirooxindole shows two peaks, each having a one-electron reduction. The anodic half cycle and cathodic half-cycle show one extreme, as shown in Fig 5. The shift of cathodic peak potential towards more positive values with the increase in scan rate indicates the irreversible nature of the system 9. The Randle Sevick equation gives peak current for the irreversible system.
- Electrochemical studies of synthesized compounds revealed that the product is electro-active as it undergoes oxidation and reduction processes at a carbon paste electrode. The compound shows reduction and oxidation peaks.
- The value of cathodic and anodic peak current and potential at different scan rates is given in the table 1

Table 1 : The value of cathodic and anodic peak current and potential at different scan rates

Scan rate (In mv /sec)	$I_a$ (In $\mu A$ )	$E_a$ (V)	$I_c$ (In $\mu A$ )	$E_c$ (V)
30	9.07	0.22	-8.6	0.104
50	11.4	0.24	-10.6	0.086
70	13.1	0.29	-12.9	0.29

## Result and discussion

We report herein an efficient, Green and general method for synthesizing Spirooxindole derivatives in ethanol and their electrochemical study done by cyclic voltammetry. Electrochemical studies revealed that synthesized compounds are electro-active. This new method creates substituted spirooxindoles in an effective and convenient multi-component manner. This spirooxindole is a pharmacologically active molecule that promotes a sense, antihypertensive, anticoagulant, antitumor, and myositis properties and is a promising molecule for several biomedical fields. Simple equipment is used in this innovative multi-

component approach. It is simple to carry out and beneficial in ecologically friendly multicultural large-scale procedures.

### Conclusion

- The current methodology illustrates that moderate reaction conditions and operational simplicity can be used in cost-effective and environmentally sustainable methods for monumental industrial compositions.
- Since it is essential to find a simple, inexpensive, recoverable and reusable catalyst for synthesizing organic compounds.
- The reaction conditions are gentle, and the reaction delivers superior product yields.
- As a result, this process could be classified as sustainable development.
- There is no hazardous organic solvent used in this process. As a result, this process could be classified as sustainable development.

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