

Proceeding Paper

Cobalt (II) Complex on Nanodiamond-Grafted-Polyethyleneimine@Folic Acid: As Extremely Effective Nanocatalyst for Green Synthesis of 5-Substituted 1*H*-Tetrazole Derivatives [†]

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[†] Presented at The 28th International Electronic Conference on Synthetic Organic Chemistry (ECSOC 2024), 15–30 November 2024; Available online: <https://sciforum.net/event/ecsoc-28>.

Abstract: In this paper, a novel, cost-effective, and green methodology has been investigated for preparation of cobalt (II) nanoparticles supported on the nanodiamond carbon structure-grafted-polyethyleneimine@folic acid (ND-g-PEI@FA@Co(II)) nanocomposite. Some of the physicochemical characteristics of the synthesized efficient heterogeneous nanocatalyst, including bond formation and functional groups, percentage of elements, crystalline phase, and surface morphology were studied using techniques such as Fourier Transform Infrared Spectroscopy (FT-IR), Energy dispersive X-ray spectroscopy (EDS), X-ray diffraction (XRD), and Field emission scanning electron microscopy (FE-SEM). Following the principles of green chemistry, this nanocatalyst has been used in the production of 5-substituted 1*H*-tetrazole derivatives using different benzaldehyde derivatives, sodium azide and malononitrile agents in ethanol eco-friendly solvent with high efficiency. The mechanism of tetrazole synthesis is carried out through cascade condensations, such as Knoevenagel condensation, 1,3-dipolar cycloaddition, and tautomerization reactions. The main advantages of ND-g-PEI@FA@Co(II) nanocatalyst include facile preparation, easy separation, low consumption of catalyst for this multicomponent reaction (MCR), use of cheap and recyclable materials, excellent product yield, and reusability up to 4 times with good efficiency. The substrate used in this heterogeneous catalyst (ND) with appropriate thermal stability, abundant availability in large quantities, non-toxicity are prominent features of the synthesized nanocomposite.

Keywords: nanocatalyst; nanodiamond; polyethyleneimine; folic acid; multicomponent reaction; tetrazole derivatives

Citation: Nasri, Z.; Ramezani, A.; Ghafuri, H. Cobalt (II) Complex on Nanodiamond-Grafted-Polyethyleneimine@Folic Acid: As Extremely Effective Nanocatalyst for Green Synthesis of 5-Substituted 1*H*-Tetrazole Derivatives. *Chem. Proc.* **2024**, *6*, x.

<https://doi.org/10.3390/xxxxx>

Academic Editor(s): Name

Published: 15 November 2024



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1. Introduction

Tetrazoles are a group of heterocyclic compounds with a five-membered ring structure containing four nitrogen atoms and one carbon atom attached to the main structure of the molecule [1,2]. According to biological properties, tetrazole derivatives have antifungal [3], antibacterial [4], antiviral, anti-inflammatory, anticancer [5–8], antitubercular [9], antiHIV [10], antidiabetic and antihypertensive activities. In addition, tetrazole derivatives are also used for the production of medicines needed by patients who have immunodeficiencies [11]. Therefore, the synthesis of tetrazoles is of special importance. Tetrazoles are synthesized through a multicomponent reaction between aldehydes or nitriles and sodium azide in three steps [12–14]. Compared to nitriles, aldehydes have attracted more attention from researchers due to their lower toxicity and easier access

[15,16]. Meanwhile, the use of an excellent and suitable catalyst to increase product efficiency and reaction rate in the synthesis of tetrazole derivatives can be very important.

Among the nanomaterials that have been reported for the synthesis of tetrazoles by other researchers, we can mention boehmite based nanoparticles (NPs) [17], magnetic NPs, copper based NPs [18], MCM-41 [19] based NPs, carbon based NPs, ZnO NPs, and nanocomposites [20].

From the point of view of green chemistry, a catalyst must have outstanding features such as high selectivity and efficiency, good stability, high recyclability and excellent activity. In this work, a nanocatalyst based on nanodiamond carbon substrate was prepared. During the recent years, carbon materials have been developed in different directions and different types of carbons have emerged at the nanoscale, including nanotubes, fullerene, graphene, non-graphite nanostructures, and nanodiamonds [21]. The coordination number of nanodiamond carbon atoms is 4 and they have quasi-zero-dimensional and quasi-one-dimensional structures. Recently, these nanoparticles have attracted a lot of attention in scientific and industrial fields due to their special characteristics. Compared to other nanoparticles, nanodiamond has a very diverse and suitable surface chemistry, which can create different chemical and physical properties by adjusting and controlling the reaction, leading to increased stability and compatibility with the environment, etc. This surface feature in nanodiamond has caused its wide applications in catalysis.

Nanodiamonds have high thermal conductivity, chemically active surface and spherical structure, which makes it used to improve polymer properties and prepare nanocomposite coatings [22]. These compounds have high mechanical strength, electrochemical resistance and high chemical stability against corrosion and can be produced in large quantities at a low cost. Among other advantages of these nanoparticles, we can mention the large relative surface area and its non-toxicity [23].

In this research, nanodiamond substrate was grafted with polyethyleneimine (PEI) polymer. PEI was added to the catalyst in order to increase stability, more strength and create many active sites for better metal complexation. In the next step, folic acid (FA) was attached to the substrate as a result of the amidation reaction, and finally cobalt (II) metal was coordinated with active groups. This catalyst was used for the synthesis of 5-substituted 1*H*-tetrazole derivatives with excellent efficiency and suitable solvent.

2. Experimental

2.1. Reagents and Apparatus

All chemicals were purchased from Merck or Aldrich (St. Louis, MO, USA) with high purity and utilized as received without further purification. The functional groups were investigated by fourier transform infrared (FT-IR) spectrometer (S8400, Shimadzu, Japan). The percentage of elements was recorded on an energy dispersive X-ray Spectroscopy (EDS) analysis (Numerix DXP-P10X model and equipped with EDS detector). The phase and crystallinity of ND-g-PEI@FA@Co(II) nanocomposite were identified by X-ray diffraction (XRD) pattern (D8 Advance, Bruker, Berlin, Germany). The morphology and surface image was monitored by field emission scanning electron microscope (FE-SEM) analyzer (TESCAN-MIRA3).

2.2. Preparation of ND-g-PEI

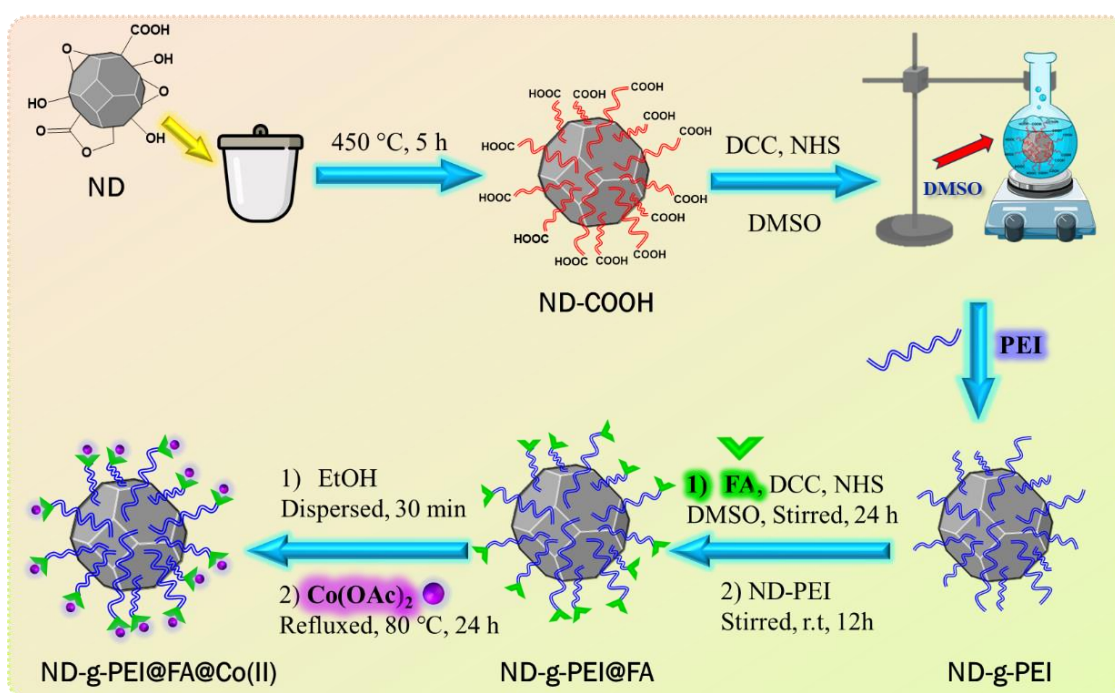
Initially, 0.5 gr of ND was placed into the furnace at 450 °C for 5h at rate of 1 °C/min. In the second step, the oxidized ND (0.3 gr), 0.31 gr of *N,N'*-dicyclohexylcarbodiimide (DCC), and 0.4 gr of *N*-hydroxysuccinimide (NHS) were poured into round-bottomed flask and 10 mL of DMSO solvent was added to it. This mixture was stirred at room temperature for 24 h. After 24 h, 1.0 gr of PEI was added and the reaction mixture was stirred for 8 h. In order to separate the ND-g-PEI nano polymer, it was centrifuged and then dried inside at 60 °C for 24 h.

2.3. Preparation of ND-g-PEI@FA

In this step, 0.265 gr of FA powder, 0.31 gr of DCC, and 0.4 gr of NHS were added to 10 mL of DMSO and stirred at room temperature for 24 h. Next, 1.0 gr of ND-g-PEI nano polymer was added to the mixture and stirred under previous condition for 12 h. The ND-g-PEI@FA nanocomposite was washed with EtOH and dried in oven at 60 °C for 24 h.

2.4. Preparation of ND-g-PEI@FA@Co(II)

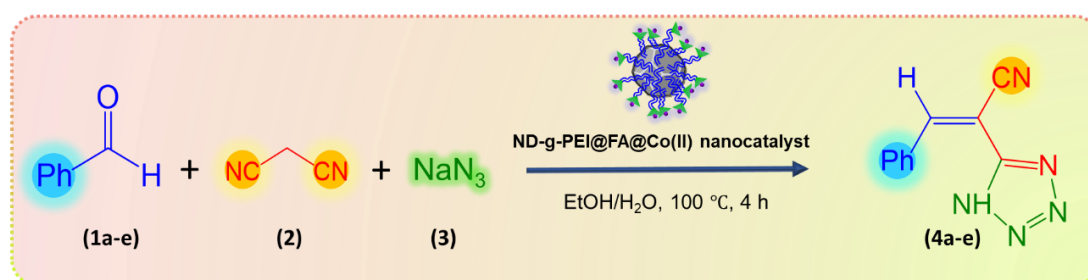
To complex the cobalt (II) on the prepared ND-g-PEI@FA nanocomposite, 0.5 gr of ND-g-PEI@FA was dispersed in 10 mL of EtOH for 30 min. On the other hand, 0.5 g of $\text{Co}(\text{OAc})_2$ was dissolved in 10 mL of deionized water and the resulting solution was added to the dispersed nanocomposite. The reaction mixture was refluxed at 80 °C for 24 h. After the completion of the reaction, the catalyst was washed once using EtOH solvent and dried at 70 °C.



Scheme 1. Preparation steps of ND-g-PEI@FA@Co(II) nanocomposite.

2.5. General Procedure for the Synthesis of 5-Substituted 1H-Tetrazole Derivatives

For this purpose, benzaldehyde derivatives (**1a–e**, 1 mmol), malononitrile (**2**, 1 mmol), NaN_3 (**3**, 1.2 mmol) and 40 mg of the ND-g-PEI@FA@Co(II) nanocomposite were added to round-bottom flask, and stirred in a mixture of EtOH and H_2O green solvent a ratio of 1:1 for 4 h. The reaction progress was controlled by thin layer chromatography (TLC) technique. After completion, the reaction mixture was diluted by HCl (10 mL, 2 M), and the catalyst was separated by filtration. 10 mL of EtOAc was added to the solution under filtration and decanted. The EtOAc was evaporated and the final product was recrystallized for further purification with the mixture of H_2O and EtOH.



Scheme 2. Multicomponent reaction for synthesis of 5-substituted 1H-tetrazole derivatives.

2.6. Spectral Data

(E)-3-(2-chlorophenyl)-2-(1H-tetrazol-5-yl) acrylonitrile (4a). FT-IR (KBr, cm⁻¹): 3420, 2926, 2222, 1564. Observed Mp (°C): 165–167 (Figure 6).

3. Result and Discussion

3.1. FT-IR Spectroscopy

The FT-IR spectra of oxidized ND (ND-COOH) is shown in Figure 1a. The stretching vibrations in the range of 3628–3010 cm⁻¹ are attributed to O–H bonds of carboxylic acid groups. Also, the adsorption bonds at 2914 and 2848, 1708, and 1222 cm⁻¹ are related to the asymmetric and symmetric of aliphatic C–H groups, stretching vibration of C=O carboxylic acid, and C–O bond in the oxidized ND structure.

As indicated in Figure 1b, the broad peak appearing in 3659 to 3104 cm⁻¹ are related to stretching vibration of O–H and N–H bonds. Furthermore, the adsorption bonds in 2917 and 2850 cm⁻¹ are related to asymmetric and symmetric of –CH₂– groups. Also, the characteristic peaks in 1651, 1630, 1023, and 954 cm⁻¹ are attributed to the stretching vibration of the C=O functional group results from the nucleophilic attack of the amine groups present in PEI on the carboxylic acid groups present in oxidized ND and the formation of the amide bond, bending vibration of –NH– in the PEI structure [24,25], stretching vibration of C–N, and wagging of –NH₂ groups in PEI, respectively [26,27].

In Figure 1c, the FT-IR spectra of ND-g-PEI@FA nanocomposite can be observed. The adsorption peak in the range of 3654 to 3223 cm⁻¹ are belonging to O–H bonds of carboxylic acid functional group of FA and NH bonds of PEI and FA. On the other hand, the stretching vibrations in 2927 and 2850 cm⁻¹, 1708, 1623, 1437, 1313 and 1089 cm⁻¹ are corresponded to asymmetric and symmetric vibration of –CH₂–, stretching vibration of carboxylic acid C=O, stretching vibration mode of C=O bond of amide group, the benzene ring stretching vibration of FA, and the C–O bonds of carboxylic acid in FA structure [28].

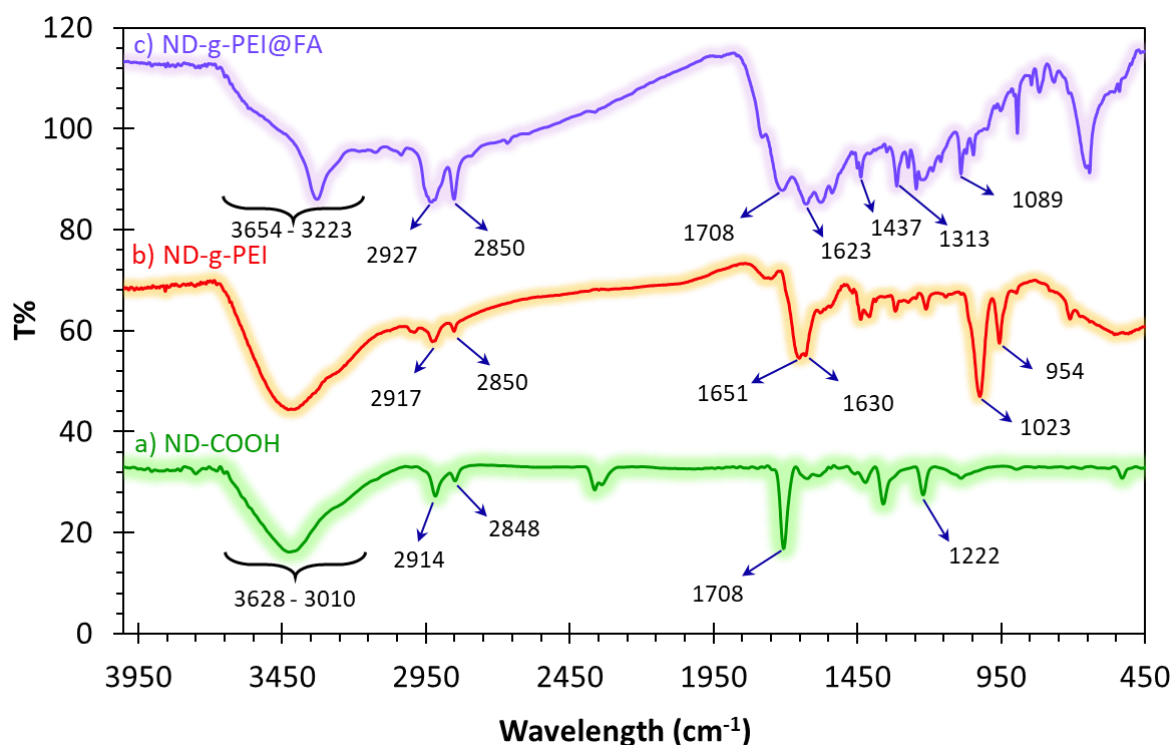


Figure 1. The FT-IR spectra of (a) oxidized ND, (b) ND-g-PEI, and (c) ND-g-PEI@FA nanocatalyst.

3.2. EDS Analysis

EDS spectrum of the synthesized ND-g-PEI@FA@Co(II) nanocomposite is shown in Figure 2. The peaks of carbon (54.97%), nitrogen (11.64%), oxygen (29.76%), sulfur (0.86%), and cobalt (2.78%) confirm the nanocomposite formation.

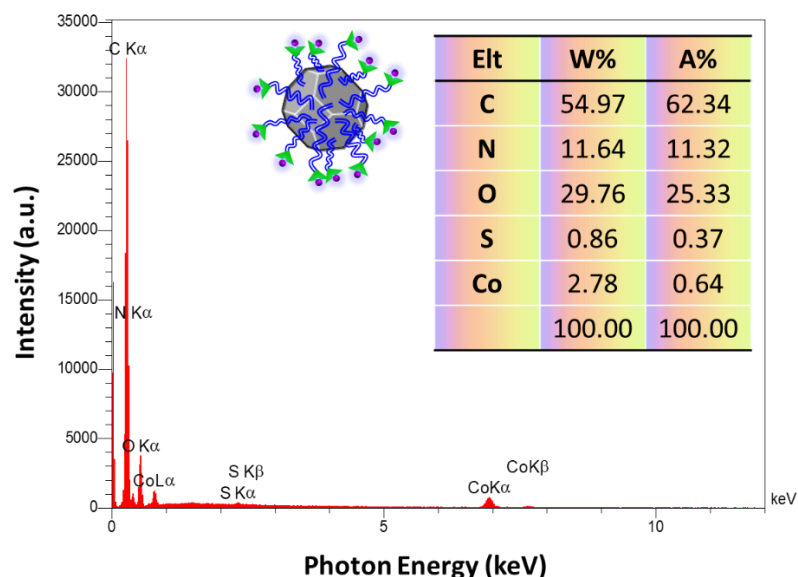


Figure 2. The EDS analysis of ND-g-PEI@FA@Co(II) nanocatalyst.

3.3. XRD Pattern

XRD pattern of synthesized ND-g-PEI@FA@Co(II) nanocatalyst was monitored in Figure 3. The characteristic peaks at $2\theta = 21.89^\circ$ and 43.80° are related to oxidized ND structure (JSPDS card No: 96-110-0920). On the other side, the peaks at $2\theta = 7.62^\circ, 14.60^\circ, 17.23^\circ$, and 28.8° can be attributed to crystalline structure of folic acid (JCPDS

card No: 96-222-0898) [29]. Also, the Co(II) XRD pattern were appeared at $2\theta = 15.35^\circ$ and 33.1° (JCPDS card No: 96-410-5685) [13,30]. PEI has an amorphous structure and does not appear in the XRD pattern of the this nanocatalyst [31,32].

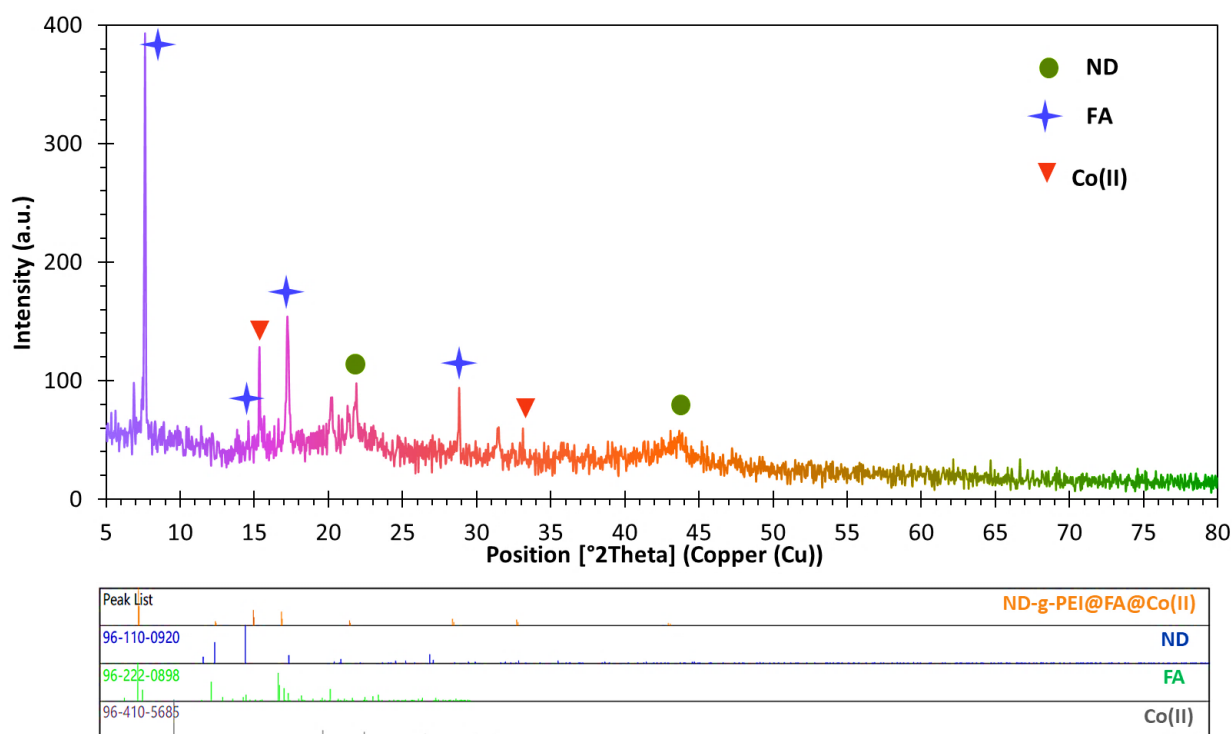


Figure 3. The XRD pattern of ND-g-PEI@FA@Co(II) nanocatalyst.

3.4. FE-SEM Analysis

Figure 4 shows the FE-SEM images of ND-g-PEI@FA@Co(II) nanocomposite. The FE-SEM images show that the ND nanoparticles are spherical, relatively uniform and with regular distribution on the surface. In addition, it is shown in these images that folic acid coating increases the particle size.

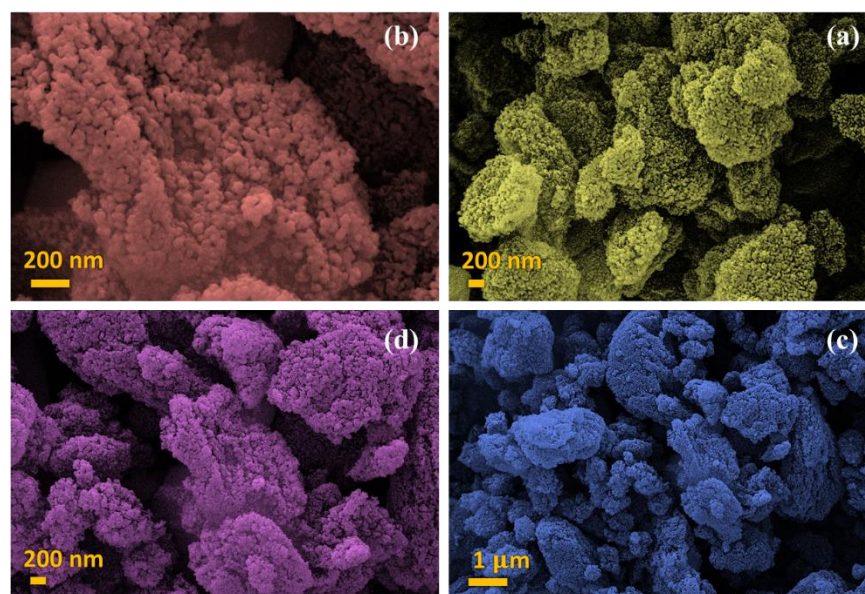


Figure 4. The FE-SEM images of ND-g-PEI@FA@Co(II) nanocatalyst.

3.5. Optimization of Reaction Conditions for the Synthesis of 5-Substituted 1H-Tetrazole Derivatives

As determined in Table 1, to obtain the optimal conditions for the synthesis of 5-substituted 1H-tetrazole derivatives, various parameters were investigated such as catalyst dosage, solvent, and reaction temperature. In order to, the multicomponent reaction between 4-chlorobenzaldehyde (**1b**) (1 mmol), malononitrile (**2**) (1 mmol), and NaN₃ (**3**) (1.2 mmol) was carried out in the presence of ND-g-PEI@FA@Co(II) nanocatalyst under different conditions. The progress of the reaction was evaluated using TLC technique. Based on the results of Table 1 (**entries 1–4**), the synthesis reaction of tetrazole derivatives was carried out in catalyst-free conditions with different solvents, but no product was obtained in a certain time. In **entries 8–12**, reactions were performed using different amounts of nanocatalyst, and the best efficiency was obtained for the amount of 40 mg of nanocatalyst. Next, in **entries 13–15**, the effect of solvent on product efficiency was investigated, and the best result was obtained with a mixture of H₂O and EtOH as a green solvent. Finally, the impact of temperature parameter on the synthesis reaction of tetrazole derivatives was evaluated in **entries 16–18**. According to the obtained results, the best conditions for the synthesis of 3-(4-chlorophenyl)-2-(1H-tetrazole-5-yl) acrylonitrile (**4b**) using ND-g-PEI@FA@Co(II) nanocatalyst can be seen in Table 1 (**entry 14**).

Table 1. Optimization of reaction condition for synthesis of 5-substituted 1H-tetrazole derivatives.

Entry	Catalyst	Catalyst Dosage (mg)	Solvent	T (°C)	Time (h)	Yield (%)
1	---	---	EtOH	r.t	4	N. R. ^a
2	---	---	Toluene	r.t	4	N. R.
3	---	---	DMF	r.t	4	N. R.
4	---	---	EtOH/H ₂ O	r.t	4	N. R.
5	ND-COOH	40	EtOH/H ₂ O	100	4	60
6	ND-g-PEI	40	EtOH/H ₂ O	100	4	72
7	ND-g-PEI@FA	40	EtOH/H ₂ O	100	4	70
8	ND-g-PEI@FA@Co(II)	10	EtOH/H ₂ O	80	4	80
9	ND-g-PEI@FA@Co(II)	20	EtOH/H ₂ O	80	4	87
10	ND-g-PEI@FA@Co(II)	30	EtOH/H ₂ O	80	4	89
11	ND-g-PEI@FA@Co(II)	40	EtOH/H ₂ O	80	4	91
12	ND-g-PEI@FA@Co(II)	50	EtOH/H ₂ O	80	4	90
13	ND-g-PEI@FA@Co(II)	40	EtOH	80	4	90
14	ND-g-PEI@FA@Co(II)	40	Toluene	Reflux	4	30
15	ND-g-PEI@FA@Co(II)	40	DMF	Reflux	4	50
16	ND-g-PEI@FA@Co(II)	40	EtOH/H ₂ O	70	4	78
17	ND-g-PEI@FA@Co(II)	40	EtOH/H ₂ O	90	4	95
18	ND-g-PEI@FA@Co(II)	40	EtOH/H ₂ O	100	4	97

Reaction conditions: 4-chlorobenzaldehyde (**1b**) (1 mmol), malononitrile (**2**) (1 mmol) and NaN₃ (**3**) (1.2 mmol), and nanocomposite. ^a No Reaction.

As evidenced from Table 2 for the synthesis of different tetrazole derivatives, various aldehydes with different electron donor and electron acceptor groups were used in the presence of nanocatalyst under optimization condition, structure and melting point are specified in Table 2.

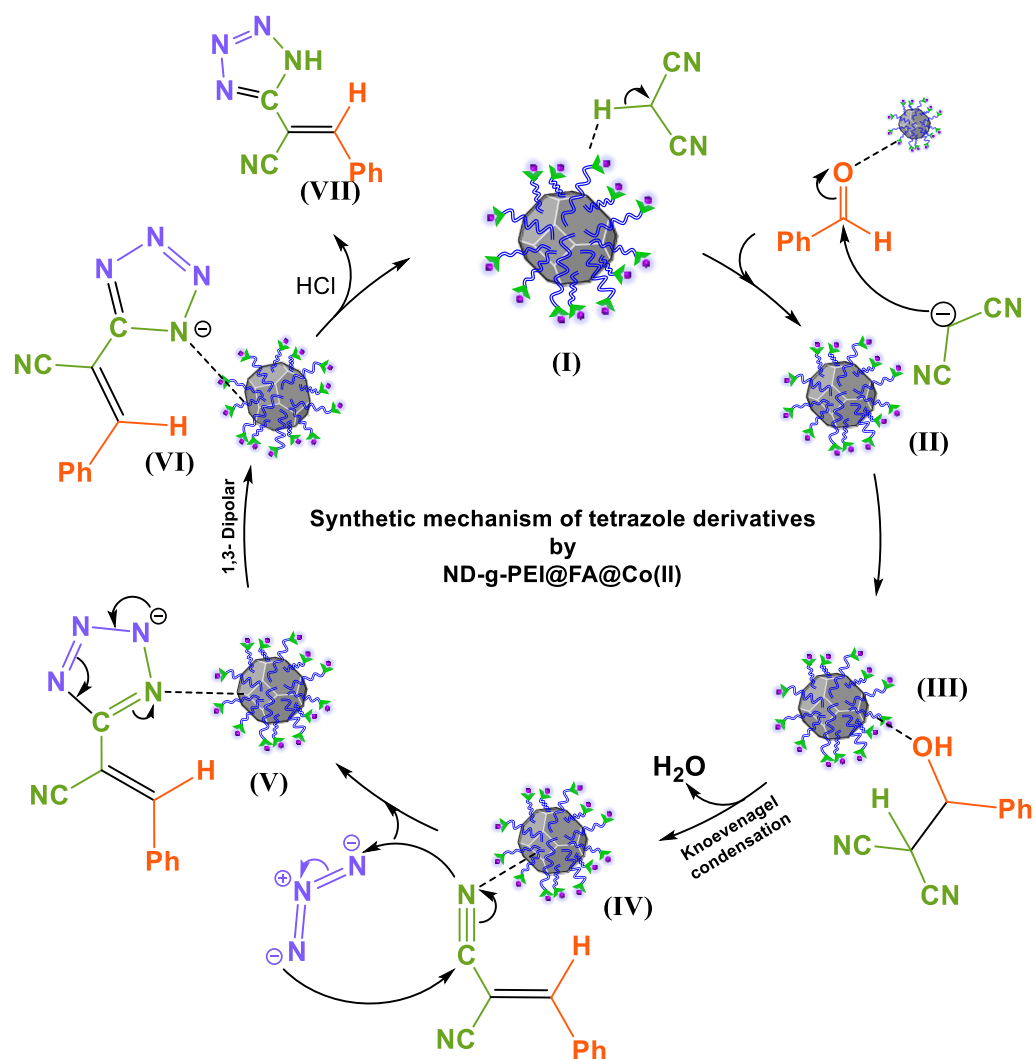
Table 2. Synthesis of different tetrazole derivatives in the presence of the ND-g-PEI@FA@Co(II) nanocatalyst.

Entry	Aldehyde (1a–m)	Product (4a–m)	Time (h)	Yield (%)	Mp (°C)	
					Observed	Literature
1			4	94	174–175	175–177 [33]
2			4	97	165–167	165–168 [33]
3			4	91	169–171	168–170 [34]
4			4	87	188–190	189–191 [35]
5			4	85	159–160	159–161 [36]

Reaction conditions: benzaldehyde derivatives (1a–e) (1 mmol), malononitrile (2) (1 mmol) and NaN₃ (3) (1.2 mmol), nanocatalyst (40 mg), and the mixture of EtOH/H₂O (10 mL).

3.6. The Plausible Mechanism for the Synthesis of 5-Substituted 1H-Tetrazole Derivatives

The mechanism of tetrazole synthesis is carried out through cascade condensations, such as Knoevenagel condensation, 1,3-dipolar cycloaddition, and tautomerization reactions. First, CH acid (malononitrile) and benzaldehyde are activated by using a nanocatalyst, and with the nucleophilic attack of malononitrile on the electrophilic group of aldehyde, intermediate (III) is formed, which is obtained by the Knoevenagel condensation and intermediate (IV). In the next step, as a result of nucleophilic cyclization, NaN_3 attacks one of the nitrile groups ($\text{C}\equiv\text{N}$) and intermediate (V) is produced. Finally, as a result of tautomerization and adding HCl (2 M), the 5-substituted 1H-tetrazole product (VII) is synthesized [37]. (Scheme 3)



Scheme 3. The proposed mechanism of the synthesis of 5-substituted 1H-tetrazole derivatives by ND-g-PEI@FA@Co(II) nanocatalyst.

3.7. Reusability of ND-g-PEI@FA@Co(II) Nanocatalyst

To emphasize the importance of reuse of ND-g-PEI@FA@Co(II) nanocatalyst in the production process of tetrazole derivatives, the catalyst was investigated. After separating the catalyst, it was washed using water and ethanol and then dried in an oven at 60 °C. The catalyst is reused 4 times. According to the results in Figure 5, the reaction efficiency has been accompanied by a slight decrease (from 97% to 81%).

In Table 3, the efficiency of prepared nanocatalyst in the synthesis of tetrazole was compared with different catalysts. In this work, the nanocatalyst has been able to perform

the tetrazole synthesis reaction in a short period of time using a green and environmentally friendly solvent with acceptable efficiency, which shows the importance of this nanocatalyst compared to other catalysts.

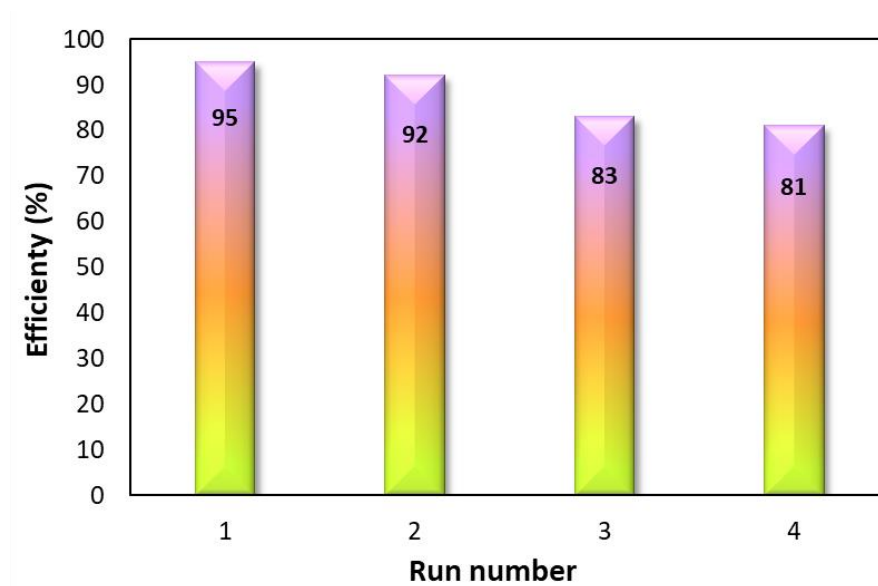


Figure 5. Reusability of the ND-g-PEI@FA@Co(II) nanocatalyst.

Table 3. Comparison of results by ND-g-PEI@FA@Co(II) nanocatalyst with various catalysts.

Entry	Catalyst	Solvent	Time (h)	Yield (%)	Ref.
1	Cu-P.bis(OA)@FeB-MNPs	PEG	2	97	[1]
2	Co(II)-diazido Intermediate	DMSO	12	99	[12]
3	Fe ₃ O ₄ @HT@AEPH ₂ -Co(II)	H ₂ O	1	95	[16]
4	Co-(PYT) ₂ @BNPs	PEG	2	98	[13]
5	ND-g-PEI@FA@Co(II)	EtOH/H ₂ O	4	97	This work

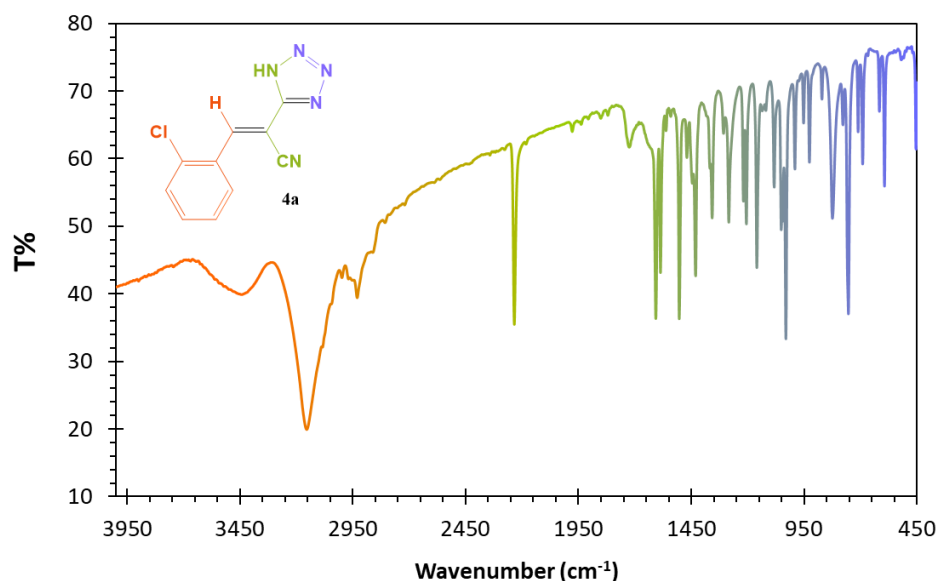


Figure 6. The FT-IR of (E)-3-(2-chlorophenyl)-2-(1H-tetrazol-5-yl) acrylonitrile.

4. Conclusions

In conclusion, a new and suitable nanocatalyst based on nanodiamond carbon substrate and polyethylene imine polymer with abundant amine groups was prepared for quick and green synthesis of tetrazole derivatives. Among the outstanding features of this work, we can mention the catalyst synthesis using environmentally friendly raw materials, the use of green and affordable solvents, stability and acceptable recyclability.

Author Contributions: H.G.: responsible writer; Z.N.: laboratory works and author; A.R.: laboratory works and author. All authors have read and agreed to the published version of the manuscript.

Funding: We are grateful for the financial support from the research council of Iran University of Science and Technology (IUST), Tehran, Iran.

Institutional Review Board Statement:

Informed Consent Statement:

Data Availability Statement:

Conflicts of Interest:

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