***Supporting information***

Ultrasound irradiation and green synthesized CuO-NiO-ZnO mixed metal oxide: An efficient sono/nano-catalytic system toward a regioselective synthesis of 1-aryl-5-amino-1*H*-tetrazoles

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1. **Experimental**
   1. **General**

All reagents, chemicals and solvents were purchased from Merck. The FT-IR spectra were recorded on Shimadzu FT IR-8400S spectrometer (400-4000 cm-1) with KBr pellets. The structure and crystalline nature of the obtained nanocomposites were evaluated by X-ray powder diffraction (XRD) with a Holland Philips Xpert X-ray powder diffraction (XRD) diffractometer, using CuKα radiation (λ=0.154 nm). The XRD patterns were usually collected with steps of 2°/min from 5° to 100° (2θ). The surface morphology of the obtained nanocomposites was recorded by the field emission scanning electron microscopy (FE-SEM) (ZEISS, model SIGMA VP). The elemental analysis (EDS) was performed with the Oxford Instrument detector (England). Thermogravimetric analysis (TGA) was carried out using STA 503 from Bähr GmbH, Germany. Progress of the catalytic process was monitored by thin-layer chromatography (TLC) using pre-coated plates of silica gel 60 F-254 (Merck) in the solvent system (ethyl acetate/n-hexane, 1:1). Melting points (°C) were determined in an open-glass capillary using an electro-thermal digital melting point apparatus and are uncorrected. 1H NMR and 13C NMR spectra were obtained in the DMSO-*d*6 solvent with a Bruker DRX-400, 500 spectrometers at 400 and 125 MHz respectively. The NMR spectra were obtained in DMSO-*d*6 solutions and are reported as parts per million (ppm) downfield from Me4Si as an internal standard.

* 1. **Preparation of mixed metal oxide nanoparticles**

The *Rheum ribes* leaves extracts were used for the synthesis of mixed metal oxide nanoparticles. For the preparation of aqueous extract, the *Rheum ribes* leaves were washed using double distilled water and after drying in a dust-free environment at room temperature, crushed by a grinding mill. Approximately 100.0 g of leaves powder was mixed with 200 mL of distilled water and was ultrasonicated to facilitate the extraction process. After 30 min ultrasonication, the mixture was stirred at 75℃ for 1 h. Finally, the prepared aqueous extract was centrifuged and kept in a refrigerator (at 4 °C) for further use. For the preparation of CuO-NiO-ZnO NPs, 5.0 mmol Cu(NO3)2.3H2O, 5.0 mmol Ni(NO3)2.6H2O, and 5.0 mmol  Zn(NO3)2.6H2O (with 1:1:1 ratio) were homogeneously mixed with 200 mL of aqueous plant extract and heated at 90 ℃ for 3 h. After that, the dried solid precursor was washed with double distilled water. Finally, the dried precipitate was calcined at 500 ℃ for 5 h to construct CuO-NiO-ZnO mixed metal oxide NPs.

* 1. **Analytical data data of new products**

***1-(3-chloro-2-methylphenyl)-1H-tetrazol-5-amine (1b-B isomer).***White crystals. m.p: 241-242 °C. Yield: (91%, Method A; 79% Method B). 1H NMR (400 MHz, DMSO-*d*6) δ (ppm): δH 7.70 (d, *J*= 7.80 Hz, 1H, Ar-H), 7.46-7.38 (m, 2H, Ar-H), 6.85 (s, 2H, NH2), 2.02 (s, 3H, CH3). 13C NMR (125.7 MHz, DMSO-*d*6) δ (ppm): δC 156.1 (C tetrazole), 135.1 (C), 134.3 (C), 133.7 (C), 131.6 (CH), 128.6 (CH), 127.3 (CH), 15.2 (CH3). Anal. Calc. for C8H8ClN5:C, 45.84; H, 3.85; N, 33.41; Found: C, 45.86; H, 3.87; N, 33.44.

***N-(5-chloro-2-methylphenyl)-1H-tetrazol-5-amine (2d-A isomer).***White crystals. m.p: 248-249 °C. Yield: (83%, Method B).1H NMR (400 MHz, DMSO-*d*6) δ (ppm): δH 14.98 (sbr, 1H, NH tetrazole), 9.06 (s, 1H, NH), 7.84 (d, *J*=1.74, 1H, Ar-H), 7.21 (d, *J*= 8.08 Hz, 1H, Ar-H), 7.00 (d-d, *J*= 8.00, 1.72 Hz, 1H, Ar-H), 2.23 (s, 3H, CH3). 13C NMR (125.7 MHz, DMSO-*d*6) δ (ppm): δC 156.04 (C tetrazole), 140.0 (C), 132.4 (CH), 131.1 (C), 126.7 (C), 122.5 (CH), 118.7 (CH), 17.8 (CH3). Anal. Calc. for C8H8ClN5: C, 45.84; H, 3.85; N, 33.41; Found: C, 45.81; H, 3.82; N, 33.44.

***1-(5-chloro-2-methylphenyl)-1H-tetrazol-5-amine (2d-B isomer).***White crystals. m.p: 240-241 °C. Yield: (91%, Method A). 1H NMR (400 MHz, DMSO-*d*6) δ (ppm): δH 7.78 (s, 1H, Ar-H), 7.11 (d, *J* = 8.1 Hz, 1H, Ar-H), 6.88 (d, *J* = 7.8 Hz, 1H, Ar-H), 6.20 (s, 2H, NH2), 2.15 (s, 3H, CH3). 13C NMR (125.7 MHz, DMSO-*d*6) δ (ppm): δC 154.11 (C tetrazole), 138.0 (C), 136.3 (CH), 132.9 (2CH), 128.8 (C), 128.3 (C), 117.1 (C), 17.8 (CH3). Anal. Calc. for C8H8ClN5: C, 45.84; H, 3.85; N, 33.41; Found: C, 45.79; H, 3.87; N, 33.38.

***1-(4-ethylphenyl)-1H-tetrazol-5-amine (2e-B isomer).*** White crystals. m.p: 213-214 °C. Yield: (94%, Method A; 86% Method B).1H NMR (400 MHz, DMSO-*d*6) δ (ppm): δH 7.44 (m, 4H, Ar-H), 6.83 (s, 2H, NH2), 2.68 (q, *J*= 7.57 Hz, 2H, CH2), 1.21 (t, *J*= 7.56 Hz, 3H, CH3). 13C NMR (125.7 MHz, DMSO-*d*6) δ (ppm): δC 155.3 (C tetrazole), 145.5 (C), 131.5 (C), 129.5 (2CH), 124.4 (2CH), 28.2 (CH2), 15.8 (CH3). Anal. Calc. for C9H11N5: C, 57.13; H, 5.86; N, 37.01; Found: C, 57.11, H, 5.85; N, 36.97.

***N-(naphthalen-1-yl)-1H-tetrazol-5-amine (2i-A isomer).*** Cream crystals. m.p: 240-241°C. Yield: (76%, Method A), 1H NMR (400 MHz, DMSO-*d*6) δ (ppm): δH 15.06 (sbr, 1H, NH tetrazole), 9.75 (s, 1H, NH), 8.19-8.17 (m, 1H, Ar-H), 7.95-7.92 (m, 1H, Ar-H), 7.77 (d, *J* = 7.5 Hz, 1H, Ar-H), 7.66 (d, *J* = 8.2 Hz, 1H, Ar-H), 7.56-7.47 (m, 3H, Ar-H). 13C NMR (125.7 MHz, DMSO-*d*6) δ (ppm): δC 154.7 (C tetrazole), 141.7 (C), 134.5 (C), 128.3 (CH), 128.1 (CH), 126.6 (CH), 126.3 (C), 126.2 (CH), 124.5 (CH), 121.5 (CH), 112.4 (CH). Anal. Calc. for C11H9N5: C, 62.55; H, 4.29; N, 33.16; Found: C, 62.51, H, 4.31; N, 33.19.

1. **Results and discussion** 
   1. **Green synthesis and characterization of CuO-NiO-ZnO mixed metal oxide**

Using biological sources as safe agents, environmentally being and sustainable contributors to the green synthesis of NPs have received considerable attention in recent years [1]. Among different potent biological sources, plant extracts have been reviewed several times [2]. Plant extract-mediated synthesis of NPs provides a hazard-free, non-toxic and environmentally friendly alternative for the production of NPs. The phytochemical content of plant extract functions as reduction agents for the preparation of NPs and provides capping agents to prevent their aggregation [3]. This study investigated the “green synthesis” of mixed metal oxide NPs of CuO-NiO-ZnO using an aqueous leaves extract of *Rheum ribes* as a potent precursor. The characterization of prepared mixed metal oxide NPs was comprehensively investigated such as general structure, crystalline phase nature, size and morphologies, chemical characterization and distribution of the elements and thermal degradation behavior.

The UV-vis spectroscopy technique was applied to the characterization of the *Rheum ribes* leaves extract (Fig. S1). The aqueous leaves extract of *Rheum ribes* contains a highly polar phenolic compound with conjugated double bonds (Fig. S2) [4]. The absorbance bands of plant extract at λmax 348 nm can be ascribed to π→π\* transition of double bonds within the cinnamoyl system. The existence of the absorption band at λmax 236 nm confirms the presence of phenolic compounds in the extract and was related to the π→π\* transitions of the benzoyl system. As previously reported in the literature, these signals were fingerprint characteristics of flavones nuclei being part and parcel of the *Rheum ribes* extract [5].

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**Fig. S1.** The UV-vis spectrum of the aqueous leaves extracts of Rheum ribes.

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**Fig. S2.** Some phytochemicals present in the Rheum ribes extract.

The presence of these phytoconstituents with their unique functional groups was responsible for the reduction of metal ions, which may be confirmed by using the Fourier Transform Infrared (FT-IR) spectroscopy. The structural and surface information were evaluated by the FT-IR spectra of the *Rheum ribes* leaves extract and then, the green synthesized CuO-NiO-ZnO NPs were produced (Fig. S3). The broad peak of the plant extract was at 2925 to 3370 cm-1 wavenumber which was attributed to the presence of C-H (Aliphatic, Aromatic, and/or Aldehyde), and O-H (alcoholic and/or phenolic) stretching vibrations of extract biomolecules [6]. The peak of 1616 cm-1 could be referred to stretching vibrations of C=C bonds of aromatic compounds. The stretching vibration from 1038 to 1232 cm−1 was C-X (C–H bending and C–O stretching) vibrations due to phenolic compounds are necessary for the nanoparticles synthesis [7]. The comparison between the FT-IR spectra of the mixed metal oxide-extract (sample before calcination) and plant extract confirmed the presence of phytoconstituents of plant extract on the surface of the particle through π-electron interactions [8]. As compared with the FT-IR spectra of plant extract, the presence of the absorption band (less than 426 cm−1) was related to the metal oxides (Cu-O, Ni-O, and Zn-O). The formation of mixed metal oxide nanoparticles was investigated by the XRD and FT-IR data [6].

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**Fig. S3.** FT-IR spectra of the Rheum ribes leaves extract and green synthesized mixed metal oxide of CuO/NiO/ZnO NPs before and after calcination.

The crystalline phase nature of the mixed metal oxide NPs was investigated by XRD patterns which were collected after annealing at 500 ℃ (Fig. S4). This nanocomposite included the mixture of the individual binary oxide phases. The CuO, NiO and ZnO phase were crystallized in the monoclinic crystal structure, cubic structure and a hexagonal structure, respectively. The CuO NPs peaked at 2θ values of 32.7, 35.8, 38.9, 49.0, 53.7, 58.4, 61.8 and 66.5 and assigned to crystal planes of (1 1 0), (0 0 2), (2 0 0), (-2 0 2), (0 2 0), (2 0 2), (-1 1 3) and (-3 1 1), respectively, consistent with the JCPDS No. 80-1917. The peaks appeared in 2θ of 37.4, 43.4, 62.9 and 75.4 correspond to the crystal planes of (1 1 1), (2 0 0), (2 2 0), and (3 1 1) which were consistent with cubic NiO (JCPDS No. 73-1523). Also, the peaks of hexagonal ZnO (JCPDS No. 80-0075) appeared in 2θ of 30.58, 34.71, 36.52, 47.80, 56.84, 62.98, 66.57, and 68.20 which ascribed to the crystal planes of (1 0 0), (0 0 2), (1 0 1), (1 0 2), (1 1 0), (1 0 3), (2 0 0), and (2 0 1), respectively. The summary of the 2θ peak position and full width at half maximum (*β*1/2) as well as the calculated crystallite size of particles using Debye Scherrer’s formula are shown in Table S1.

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**Fig. S4.** X-ray diffraction (XRD) patterns of green synthesized mixed metal oxide of CuO/NiO/ZnO NPs.

**Table S1.** The peak position, full width at half maximum (β1/2) and calculated crystallite size of the CuO-NiO-ZnO NPs.

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| **Element** | **CuO**  **(110)** | **CuO (002)** | **CuO**  **(200)** | **CuO**  **(-202)** | **CuO**  **(020)** | **CuO**  **(202)** | **CuO**  **(-113)** | **CuO**  **(-311)** |
| 2θ position (°) | 32.74 | 35.82 | 38.93 | 49.08 | 53.71 | 58.44 | 61.86 | 66.57 |
| *β1/2* (°) | 0.35 | 0.29 | 0.35 | 0.17 | 0.70 | 0.35 | 0.29 | 0.35 |
| Size (nm) | 24.72 | 30.08 | 25.15 | 53.68 | 13.29 | 27.18 | 33.37 | 28.37 |
| **Element** | **ZnO**  **(100)** | **ZnO**  **(002)** | **ZnO**  **(101)** | **ZnO**  **(102)** | **ZnO**  **(110)** | **ZnO**  **(103)** | **ZnO**  **(200)** | **ZnO**  **(201)** |
| 2θ position (°) | 30.58 | 34.71 | 36.52 | 47.80 | 56.84 | 62.98 | 66.57 | 68.20 |
| *β1/2* (°) | 0.23 | 0.17 | 0.17 | 0.17 | 0.23 | 0.35 | 0.35 | 0.29 |
| Size (nm) | 37.41 | 51.16 | 51.42 | 53.41 | 41.04 | 27.82 | 28.37 | 34.57 |
| **Element** | **NiO**  **(111)** | | **NiO**  **(200)** | | **NiO**  **(220)** | | **NiO**  **(311)** | |
| 2θ position (°) | 37.41 | | 43.44 | | 62.98 | | 75.44 | |
| *β1/2* (°) | 0.29 | | 0.29 | | 0.35 | | 0.35 | |
| Size (nm) | 30.22 | | 30.81 | | 27.82 | | 29.99 | |

The morphologies, [chemical characterization](https://en.wikipedia.org/wiki/Characterization_(materials_science)) as well as spatial distribution of the elements in the mixed metal oxide of CuO-NiO-ZnO NPs were investigated by FE-SEM, EDS, and element mapping (Fig. S5). The surface morphology of CuO-NiO-ZnO NPs was explored using Field-Emission Scanning Electron Microscopy (FE-SEM) images of low and high magnifications. Low magnifications images of CuO-NiO-ZnO NPs appeared a uniformly spherical NPs. Detailed morphology of CuO-NiO-ZnO NPs showed spherical NPs with sizes ranging between 20 and 50 nm. Energy-dispersive X‐ray spectroscopy (EDS) analysis data showed the composition of CuO-NiO-ZnO NPs, indicating the presence of Cu, Ni, and Zn, and also, confirmed the formation of CuO-NiO-ZnO metal oxide NPs. The amount of Cu, Ni, and Zn incorporated into the CuO-NiO-ZnO metal oxide NPs was 16.1, 40.8, and 21.6 wt %, respectively. On the other hand, the presence of phytochemicals of *Rheum ribes* leaves extract was detected as carbon signals in this analysis. Besides, the elemental mapping images clearly showed that the metal oxide content was distributed completely. The results of FT-IR, XRD, EDS and elemental mapping indicated and confirmed the successful synthesis of CuO-NiO-ZnO metal oxide NPs and also, demonstrated the potent application of *Rheum ribes* leaves extract for the preparation of green NPs.

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**Fig. S5.** FE-SEM images at low and high magnifications (A, B, and C), EDS spectra (D), and elemental mappings of Ni, Zn, Cu, and O on the CuO-NiO-ZnO NPs (E).

The thermal gravimetric analysis/ differential thermal analysis (TGA/DTA) was conducted to investigate the thermal degradation behavior of the as-prepared mixed metal oxide NPs of CuO-NiO-ZnO NPs before and after calcination (Fig. S6). The mixed metal oxide-extract (sample before calcination) initially experienced a rapid weight decay at 70-150 ℃, due to the evaporation of absorbed water. The second region of weight loss at ~220-380 °C was attributed to the decomposition of capped biomolecules of extract, which were connected onto the surface of the nanoparticles. The final step of decomposition was attributed to the complete decomposition of pure salts and the formation of the metal oxide NPs, as confirmed by FT-IR and XRD analyses [9]. On the other hand, the CuO-NiO-ZnO NPs (after calcination) exhibited a steady weight-loss trend when compared to the precursor sample and it can be found that the surface of mixed metal oxide-extract (before calcination) was covered with the plant metabolites (phytochemicals).

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**Fig. S6.** TGA and DTA curves of CuO-NiO-ZnO NPs before calcination (A) CuO-NiO-ZnO NPs after calcination (B) and TGA curves of CuO-NiO-ZnO NPs before and after calcination (C).

Characterization of nanocatalyst confirmed the formation of CuO, NiO, and ZnO NPs through the green method using aqueous leaves extract from *Rheum ribes*. Great phytochemical of this plant extract showed the presence of pyrocatechol, chrysophanol, physcion, emodin, rutin and quercetin as a potent antioxidant which was responsible for the redox reactions and reduction of metal ions to metal-NPs [5]. The formation of NPs with phenolic constituents in the extract was checked several times and relatively well known [1]. The proposed mechanism for the formation of metal oxide NPs of Cu, Ni, and Zn is proposed in Scheme S1. As we know, *Rheum ribes* containing the reducing phytoconstituents such as rutin, querecetin-3-O-galactoside, querecetin-3-O-rhamnoside, emodin, chrysophanol, quercetin and physcion. After mixing of *Rheum ribes* leaves extract and metals salt solution, the phenolic components can able to form stable complexes with M2+, subsequently the stable metal-phenolic adduct oxidized and decomposed to metal oxide NPs (CuO, NiO and ZnO) at 500 °C [10].



**Scheme. S1.**Proposed mechanism of synthesized CuO-NiO-ZnO NPs using phenolic constituents of *Rheum ribes* leaves extract.

* 1. **Catalyst recyclability**

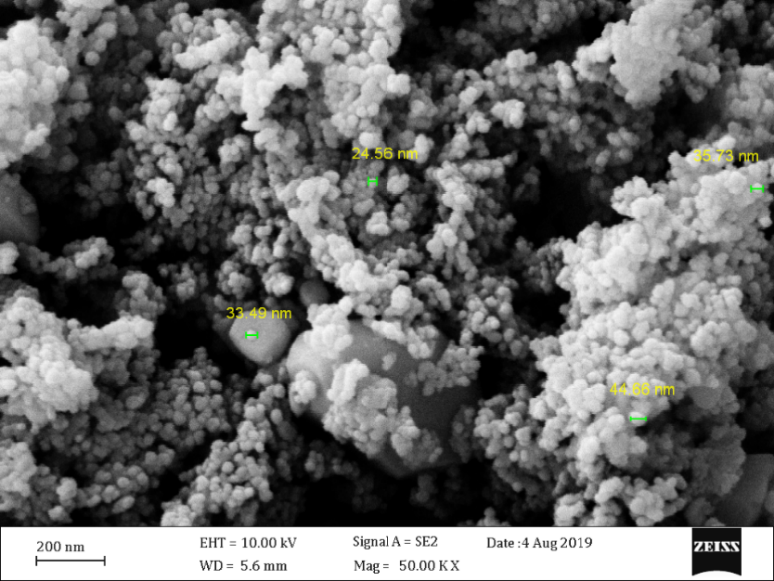
Recovery of the catalyst is an essential criterion because of the environmental and economic aspects, so the recyclability of the CuO-NiO-ZnO catalyst was investigated in the [3+2] cycloaddition reaction of *N*-(4-bromophenyl) cyanamide (**1a**) and sodium azide under optimized conditions in the presence of US irradiation. After completion of the reaction, the catalyst was separated from the reaction medium with centrifuge and washed with ethanol and dried at 70 ° C, then was reused in subsequent reactions. After six runs, the catalyst demonstrated approximately the same activity and leaded the desired product in high yields (Table S2). These data indicated excellent catalytic activity of the CuO-NiO-ZnO NPs during the synthesis of various aminotetrazole derivatives. The CuO-NiO-ZnO NPs exhibits no remarkable change in the morphology, shape and size after six runs, which is confirmed by the FE-SEM image of the recycled catalyst (Fig. S7).

**Table S2.** Reusability and recoverability of CuO-NiO-ZnO NPs for the synthesis of N-(4-bromophenyl)-1H-tetrazole-5-amine (2a)a.

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| Recycle | First | Second | Third | Fourth | Fifth | Sixth |
| Yield b (%) | 95 | 95 | 93 | 91 | 91 | 89 |

a Reaction conditions: **1a** (1.0 mmol), NaN3 (1 mmol), and 0.03 g CuO-NiO-ZnO in water (5.0 mL) under US irradiation at 70-80℃ for 1 h.

b Isolated yield.



**Fig. S7.**The FE-SEM image of recycled CuO-NiO-ZnO NPs.

**Table S2**

|  |  |  |
| --- | --- | --- |
| ***N*-arylcyanamides** | **Under US irradiation (methode A)** | **Under reflux condition (methode B)** |
|  | **2a, B isomer** | **2a, B isomer** |
|  | **2b, B isomer** | **2b, B isomer** |
|  | **2c, B isomer** | **2c, B isomer** |
|  | **2d, B isomer** | **2d, A isomer** |
|  | **2e, B isomer** | **2e, B isomer** |
|  | **2f, B isomer** | **2f, B isomer** |
|  | **2g, B isomer** | **2g, B isomer** |
|  | **2h, B isomer** | **2h, B isomer** |
|  | **2i, B isomer** | **2i, A isomer** |

a Reaction conditions: **1** (1.0 mmol), NaN3 (1 mmol), and 0.03 g CuO-NiO-ZnO NPs in water (5.0 mL); conditions: **A**, under ultrasound irradiation with a power intensity of 60% at 70-80 ℃ for 1-2 h; **B**, under reflux condition for 2.5-4 h.

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1. **1H and 13C NMR spectra of new compounds**

***1-(3-chloro-2-methylphenyl)-1H-tetrazol-5-amine (1b-B isomer)***

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***N-(5-chloro-2-methylphenyl)-1H-tetrazol-5-amine (2d-A isomer)***

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***1-(5-chloro-2-methylphenyl)-1H-tetrazol-5-amine (2d-B isomer)***

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***1-(4-ethylphenyl)-1H-tetrazol-5-amine (2e-B isomer)***

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***N-(naphthalen-1-yl)-1H-tetrazol-5-amine (2i-A isomer)***

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