Received: 10 September 2018 | Revised: 17 October 2018 | Accepted: 18 October 2018
DOI: 10.1002/aoc.4698

FULL PAPER

WILEY Applied Organometallic Chemistry

Biosynthesis of Pd/MnO_2 nanocomposite using *Solanum melongena* plant extract and its application for the one-pot synthesis of 5-substituted 1*H*-tetrazoles from aryl halides

Mahmoud Nasrollahzadeh[1] | Fatemeh Ghorbannezhad[1] | S. Mohammad Sajadi[2]

[1] Department of Chemistry, Faculty of Science, University of Qom, Qom 37185-359, Iran

[2] Department of Petroleum Geoscience, Faculty of Science, Soran University, PO Box 624, Soran, Kurdistan Regional Government, Iraq

Correspondence
Mahmoud Nasrollahzadeh, Department of Chemistry, Faculty of Science, University of Qom, Qom 37185-359, Iran.
Email: mahmoudnasr81@gmail.com

In this work, for the first time, *Solanum melongena* plant extract was used for the green synthesis of Pd/MnO_2 nanocomposite *via* reduction osf Pd(II) ions to Pd(0) and their immobilization on the surface of manganese dioxide (MnO_2) nanoparticles (NPs) as an effective support. The synthesized nanocomposite were characterized by various analytical techniques such as Fourier transform infrared (FT-IR), X-ray diffraction (XRD), transmission electron microscopy (TEM), field emission scanning electron microscopy (FESEM), energy dispersive X-ray spectroscopy (EDS) and UV–Vis spectroscopy. The catalytic activity of Pd/MnO_2 nanocomposite was used as a heterogeneous catalyst for the one-pot **synthesis of** 5-substituted 1*H*-tetrazoles **from** aryl halides containing various electron-donating or electron-withdrawing groups **in the presence of K_4[Fe (CN)$_6$] as non-toxic cyanide source and sodium azide. The products were obtained in good** yields via a simple methodology and easy work-up. The nanocatalyst can be recycled and reused several times with no remarkable loss of activity.

Highlights:

- Green synthesis of Pd/MnO_2 nanocomposite using *Solanum melongena* extract.
- Pd/MnO_2 nanocomposite was characterized by FT-IR, XRD, FESEM, EDS and TEM.
- One-pot synthesis of 5-substituted 1*H*-tetrazoles from aryl halides using Pd/MnO_2 nanocomposite.
- The catalyst can be easily recycled and reused several times without sensible loss in its catalytic efficiency.

KEYWORDS

5-substituted 1*H*-tetrazole, aryl nitriles, Pd/MnO_2 nanocomposite, sodium azide, *Solanum melongena*

© 2018 John Wiley & Sons, Ltd.

1 | INTRODUCTION

The field of heterocyclic synthesis has detected as enormously important field in recent years. Tetrazoles as one of the important five-membered ring compounds are classified into heterocycles. This nitrogen-rich heterocyclic is represent an increasingly popular functionality owing to their multi-connectivity abilities and various applications in medicinal as well as synthetic chemistry.[1] Among heterocycles, tetrazoles have been used as carboxylic acid isosters[2] hence biological properties can be reclaimed by replacement of C-terminal amino acid with a tetrazole. The N-containing rings heterocyclic comprehensively are applied in molecular design and synthesis of modified amino acids and peptidomimetics due to metabolically stable alteration in compared with the carboxylic acid group.[3,4] Furthermore, tetrazole moieties are beneficial to approachability more complex heterocycles through various rearrangements.[5,6] In a quest for investigation on high energy-density materials (HEDM), N-containing heterocycles are promising candidates. Tetrazoles energetic can be acquired of extrusion of nitrogen gas as an end product and avoiding environmental pollution.[7–10]

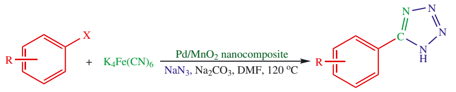
Because of advantage the tetrazoles, several synthetic paths have expanded due to their construction of frameworks. 5-Substituted 1*H*-tetrazoles are the most N-containing heterocyclic compounds favorite. Standard method for the synthesis of 5-substituted 1*H*-tetrazoles is the [3 + 2] cycloaddition of organometallic between nitriles and azides.[11–13] In generally, aluminium azide,[13] tin azide[13–16] or silicon azide[17–20] were used as the sources of azide which have follow drawbacks including toxic organometallic reactants, difficult to obtain and/or prepare starting materials, tedious workup procedures and expensive materials. In 2001, Sharpless and co-workers[21] had introduced sodium azide for synthesis of 5-substituted 1*H*-tetrazoles with stoichiometric amounts of zinc salts as catalyst under aqueous conditions. In recent years, [3 + 2] cycloaddition of nitriles and azides enormously have been studied *via* homogeneous and heterogeneous catalysts[22–30]. However, despite wide advances for synthesis of 5-substituted 1*H*-tetrazoles, there is no report on their *in situ* preparation from aryl halides using metal nanocomposites.[31,32] So, it is more desirable to develop a more efficient and simple catalytic system for the one-pot synthesis of 5-substituted 1*H*-tetrazoles from aryl halides *via* the formation of benzonitriles as intermediate.

Aryl nitriles are important key constituents of pharmaceuticals, agrochemicals, dyes, and natural products.[33,34] The successful examples for the synthesis of benzonitriles were reported using superstoichiometric amount of toxic cyanide sources under harsh reaction conditions.[35–37] Among cyanide sources, $K_4[Fe\ (CN)_6]$ is attractive candidate in synthetic chemists as non-toxic cyano source.[38–40] There are several methods for the synthesis of aryl nitriles using $K_4[Fe\ (CN)_6]$ in the presence of homogeneous catalysts.[38–40]

In recent years, there has been an immense upsurge interest of separation of the catalyst and its reusability in further runs as heterogeneous catalysis in various chemical transformations. Metal nanoparticles (MNPs) as heterogeneous catalysts are being employed because of their high surface-to-volume ratio and the fact that are exceedingly active upon their surfaces.[41–44] Biosynthesis of MNPs as green nanobiotechnology are developed with growing concern use of environmental-risk substances. Biological-based synthesis of nanoparticles is utilized an ambient aqueous, plant extracts, biological systems and microwave assisted synthesis.[45–47] The biological synthesis as a simple and environmentally safe method have advantages such as utilization of non-toxic solvents, simple methodology, mild reaction conditions (avoidance of the high pressure and temperature), easy work-up, long-term stability, elimination of expensive and toxic reducing agents, avoidance of expensive capping agents and organic surfactants. However, the agglomeration of MNPs is inevitable. To circumvent this drawback, an ideal support is needed to decrease MNPs agglomeration and suitable catalytic activity.[48–51] Therefore, the importance of synthetic methods is to establish environment friendly benign methods by choosing suitable nanocatalyst to avoid all harm conditions and give good results. Herein, in continuation of our efforts to develop eco-friendly synthetic methodologies, we are used *Solanum melongena* plant extract for the synthesis of Pd NPs on MnO_2 NPs.

Solanum melongena (Eggplant), commonly known as melongene (Figure 1) plays an important role in the

FIGURE 1 Image of *Solanum melongena* plant



SCHEME 1 One pot synthesis of 5-substituted 1*H*-tetrazole from aryl halides in the presence of bio-catalyst

$$\mathrm{nFlOH} + \mathrm{Pd}^{+2} \longrightarrow \mathrm{nFlO\ (radical)} + \mathrm{nPd}^{0}$$

$$\mathrm{nFlO\ (Radical)} + \mathrm{Pd}^{+2} \longrightarrow \mathrm{nFlOX} + \mathrm{nPd}^{0}\ \mathrm{(Nucleation)}$$

$$\mathrm{nPd}^{0} + \mathrm{Pd}^{+2} \longrightarrow \mathrm{Pd_n}^{+2}\ \mathrm{(Growth)}$$

$$\mathrm{Pd_n}^{+2} + \mathrm{Pd_n}^{+2} \longrightarrow \mathrm{Pd_{2n}}^{+2n}$$

$$(\mathrm{Pd_{2n}}^{+2n})_n + (\mathrm{FlOH})_n \longrightarrow \mathrm{Palladium\ NZV}$$

SCHEME 2 Reducing ability of antioxidant phenolics to produce Pd NPs where FlOH and NZV are flavonoid and nano zero valent, respectively

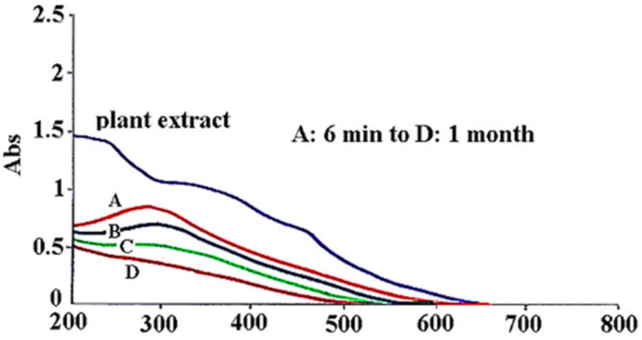


FIGURE 2 UV–Vis spectrum of plant extract and green synthesis Pd NPs at different times

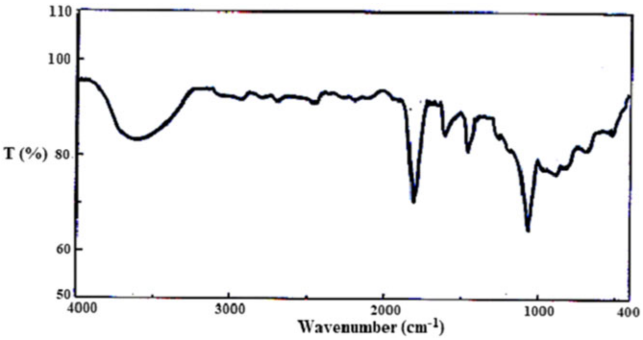


FIGURE 3 FT-IR spectrum of green synthesized Pd NPs

treatment of human disease since ancient time.[52–56] The phytochemical constituents like tannins, proteins, alkaloids, flavonoids and saponins of these species in dry and shady areas were investigated qualitatively.[52–55] Thus, through this research we decided to use the *Solanum melongena* aqueous extract as a biomedia and bioreducing agent to phytosynthesis of Pd NPs.

So, having the above point in mind, we have chosen a biological procedure for preparation of the Pd/MnO_2 nanocomposite using *Solanum melongena* aqueous extract and its application as a heterogeneous catalyst for the one-pot synthesis of 5-substituted 1*H*-tetrazoles from aryl halides by using $K_4[Fe\ (CN)_6]$ as non-toxic cyano source and sodium azide as a azide source (Scheme 1). The Pd/MnO_2 nanocomposite was prepared via immobilization of Pd NPs onto MnO_2 nanostructure using *Solanum melongena* aqueous extract.

2 | RESULTS AND DISCUSSION

2.1 | Characterization of *Solanum melongena* plant extract and biosynthesized Pd NPs

During this work, with the aim of improving the synthetic methods we successfully introduced the Pd/MnO_2 nanocomposite as a nanocatalyst heterogeneous using *Solanum melongena* plant extract for conversion aryl halides to aryl tetrazoles without aryl nitriles intermediate separation. The Pd^{2+} ions are reduced to Pd^o in the presence of the *Solanum melongena* plant extract as reducing agent instead of the conventional environmentally polluting ones. Nanocomposite are generally characterized by their shape, size, and dispersity by XRD, TEM, EDS, FESEM and FT-IR.

In this work, we have employed *Solanum melongena* plant extract as a reducing agent and efficient stabilizer. As shown in Scheme 2, metal ions were reduced to nano zero valent (NZV) metallic particles using flavonoid (FlOH) contents of the plant as green chemical component.

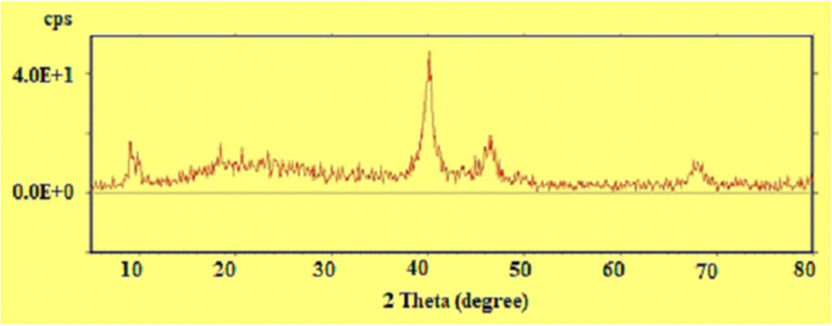


FIGURE 4 The XRD powder pattern of the Pd/MnO_2 nanocomposite

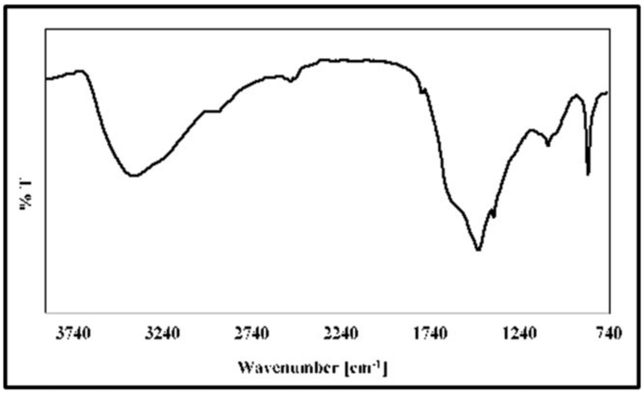


FIGURE 5 FT-IR spectrum of biosynthesized Pd/MnO_2 nanocomposite

The progression of the formation and stability of Pd NPs were investigated by UV–Vis. Figure 2 shows the UV bonds of the extract at 340 nm (bond I) and 255 nm (bond II) due to the cinnamoyl and benzoyl systems, respectively. In fact, they are concerned to the $\pi \rightarrow \pi^*$ transitions of polyphenolics. The UV–vis spectrum of biosynthesized Pd NPs shows the effect of surface Plasmon resonance following the appearance of maximum wavelength around 305 nm. Also, the study of stability of nanoparticles revealed that they have a good stability even for more than one month because the wavelength of nanoparticles shows no significant deviation or disruption during this time and keeps its symmetry. This stability is for possible adsorption of

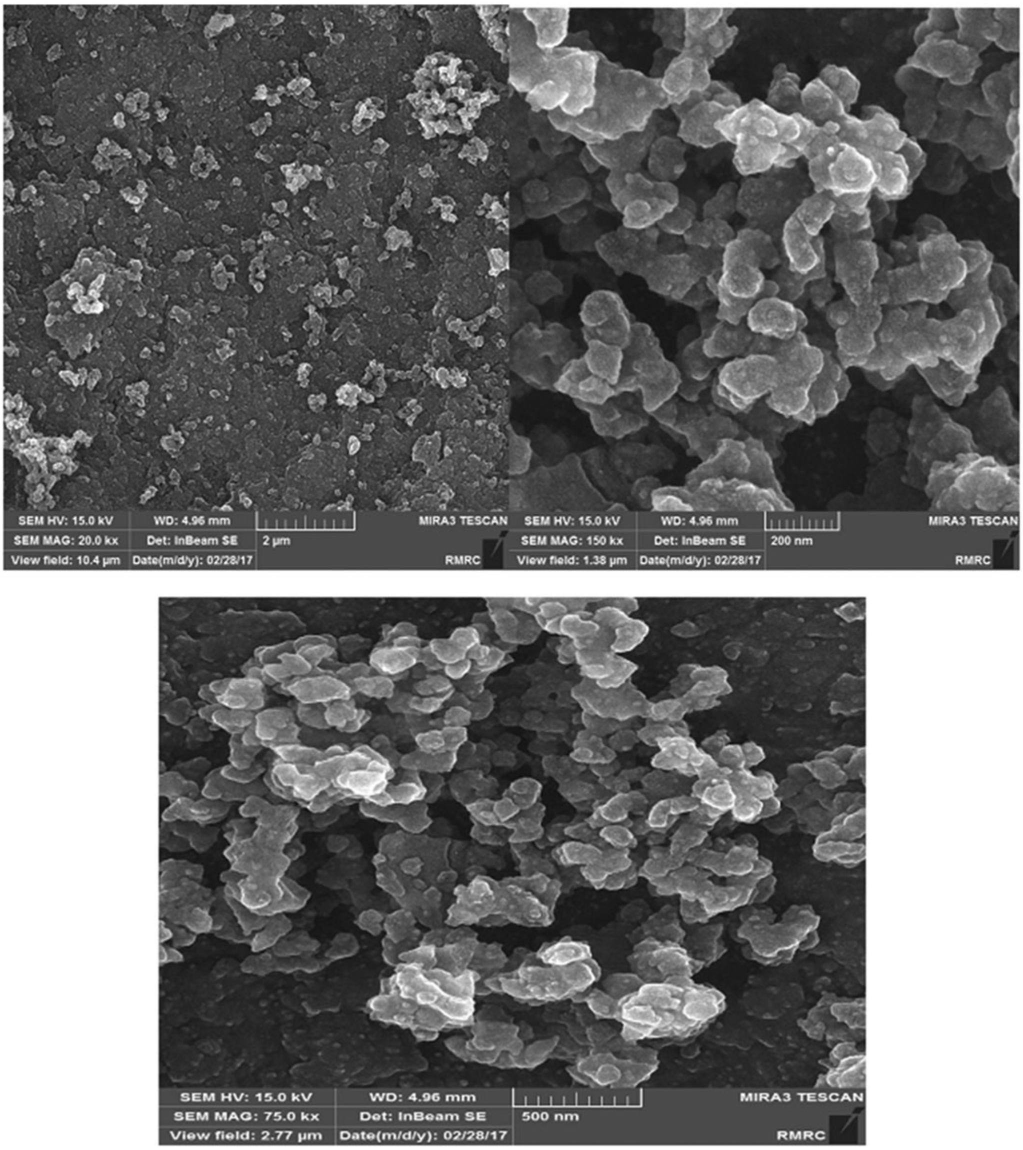


FIGURE 6 FESEM images of the Pd/MnO_2 nanocomposite

antioxidant phytochemicals on nanosurface and their protection effect to prevent decomposition and deformation processes on nanostructures for a special period of time.

Figure 3 shows the FT-IR signals of Pd NPs synthesized by *Solanum melongena* plant extract. The main signals around 3600, 1790 and 1495–1580 cm^{-1} are assigned to the OH, carbonyl group (C=O) and C=C aromatic ring vibrations, respectively. The sharp peak about 1100 cm^{-1} attributed to C-O stretching vibrations. These signals clearly confirm the presence of plant phytochemicals on the surface of Pd NPs and their effect on protection and stability of nanoparticles.

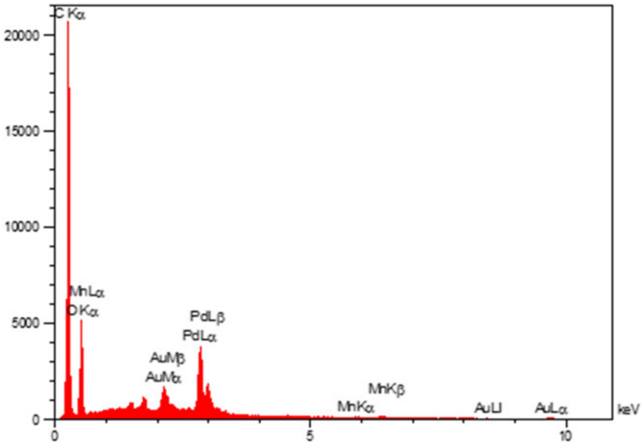


FIGURE 7 EDS spectrum of the Pd/MnO_2 nanocomposite

2.2 | Characterization of the Pd/MnO_2 nanocomposite

The bioreduction process of Pd (II) ions to Pd NPs and their immobilization on MnO_2 NPs surface was carried out by *Solanum melongena* plant extract. The nanocatalyst formation was fully characterized by XRD, TEM, FESEM, EDS and FT-IR.

Phase investigation of the crystallized product was carried out by powder XRD measurements. According to XRD analysis of Pd/MnO_2 nanocomposite as shown in

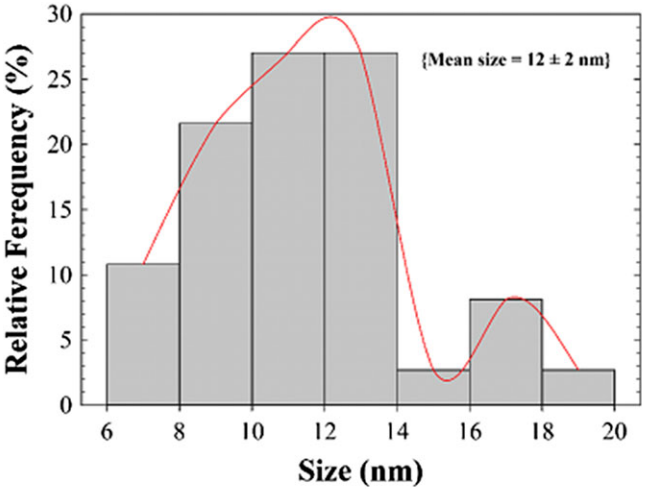


FIGURE 9 Histogram of particle size distribution of the Pd/MnO_2 nanocomposite

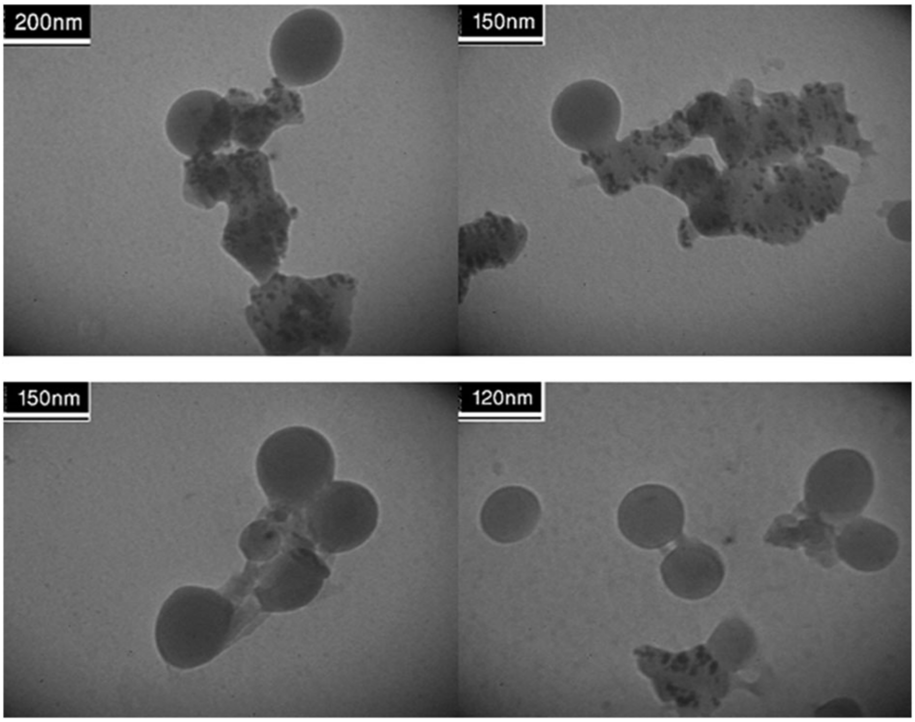


FIGURE 8 TEM images of the Pd/MnO_2 nanocomposite

Figure 4, strong and sharp peaks at 2θ values 40.05°, 46.5, 68.2° can be indexed to (111), (200) and (220) Bragg's reflections of face-centered cubic (*fcc*) Pd NPs (JCPDS No. 89–4897).[45] To confirm presence MnO_2 in sample, the typical XRD pattern show diffraction peaks at 9.8°, 18.6°, 24.0°, 29.0°, 35.1°, 41.1°, 46.0°, 47.0°, 50.6°, and 68.7° corresponding to (110), (200), (220), (310), (400), (420), (321), (510), (411), (541), respectively (JCPDS No. 44–0141).[57]

For confirmation of the polyphenolics present in *Solanum melongena* plant extract as reduction agent of metal salt, analysis of FT-IR spectrum was used (Figure 5). Oxides and hydroxides of metal nanoparticles generally gives absorption peak in the finger print region i.e. below wavelength of 1000 nm arising from inter-atomic vibrations. Absorption band observed at 856 cm^{-1} is corresponded to the surface –OH groups of Mn–OH for colloidal MnO_2 NPs.[58] The absorption peaks appearing at 3346, 1621, 1384 and 1047 cm^{-1} are assigned to the stretching vibrations of OH, carbonyl group (C=O), stretching C=C aromatic ring and C-O stretching vibrations, respectively. The adsorption of organic compounds in the extract on the surface of metal nanoparticles, feasibility by interaction through π-electrons interaction.

TABLE 1 Optimization of the reaction conditions for the synthesis of 5-phenyl-1*H*-tetrazole

Entry	Pd/MnO_2 (g)	Solvent	Base	Temperature (°C)	Yield (%)
1	0	DMF	Na_2CO_3	120	0
2	0.05	DMF	K_2CO_3	120	85
3	0.05	DMF	Piperidine	120	37
4	0.05	DMF	Et_3N	120	48
5	0.05	DMF	Na_2CO_3	120	90
6	0.05	DMSO	Na_2CO_3	120	87
7	0.05	NMP	Na_2CO_3	120	52
8	0.05	Toluene	Na_2CO_3	110	Trace
9	0.05	MeCN	Na_2CO_3	80	Trace
10	0.02	DMF	Na_2CO_3	120	72
11	0.08	DMF	Na_2CO_3	120	90

Reaction conditions: Iodobenzene (1.0 mmol), $K_4Fe(CN)_6$ (0.22 mmol), base (1.0 mmol), DMF (7.0 ml), NaN_3 (1.5 mmol), 12 hr.
bYields are after work-up.

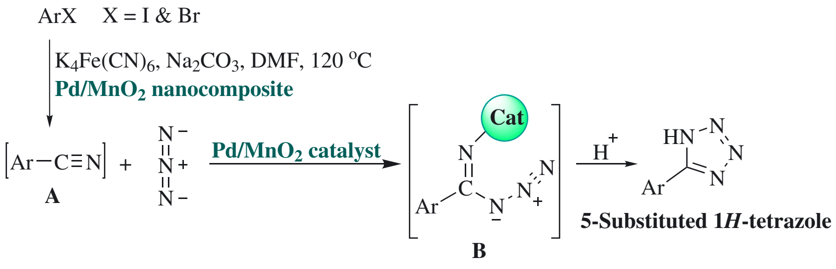
The morphology and uniformity of the Pd/MnO_2 nanocomposite were ascertained by FESEM. As shown in Figure 6, monodispersed spherical particles were produced extracellular by the *Solanum melongena* plant extract.

EDS analysis was used for more confirmation of the Pd/MnO_2 nanocomposite. As a result, the fabrication of the Pd NPs and their immobilization on the MnO_2 surface was confirmed through elemental analysis. As shown in Figure 7, the biosynthesized Pd/MnO_2 nanocomposite is composed of O, Mn and Pd elements.

The shape and size of nanoparticles are finest observed with the assistance of the TEM. TEM microscopic analysis showed the deposition of Pd NPs on the MnO_2 surface and formation of regularly spherical shaped nanoparticles with particle size distribution in nanoscale (Figure 8). As shown in Figure 9, the average size of particles is 12 nm.

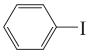
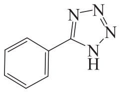
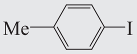
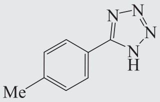
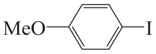
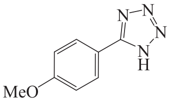
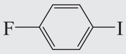
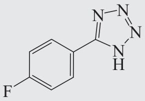
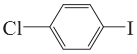
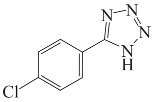
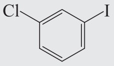
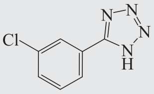
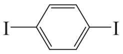
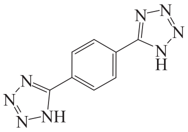
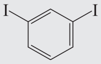
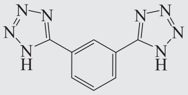
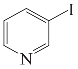
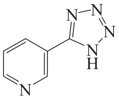
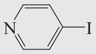
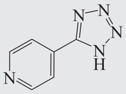
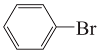
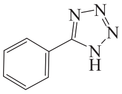
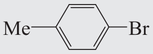
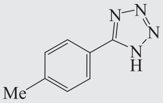
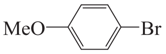
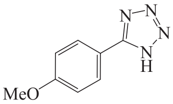
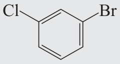
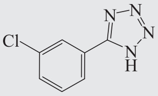
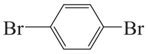
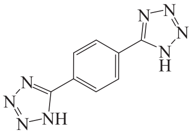
2.3 | Preparation of 5-substituted 1*H*-tetrazoles using Pd/MnO_2 nanocatalyst via a one-step method

In continuation of our recent effort on application of heterogeneous nanocatalysts for the development of synthetic methodologies, we introduced a green protocol for the preparation of Pd/MnO_2 nanocatalyst using *Solanum melongena* plant aqueous extract and its application for synthesis 5-substituted 1*H*-tetrazoles. To test this idea, we have focused our investigation on conversion iodobenzene to 5-phenyl 1*H*-tetrazole in the presence of the potassium hexacyanoferrate (II), sodium azide and Pd/MnO_2 nanocatalyst without benzonitrile intermediate work-up in present bio-catalyst. The reaction was not carried out in the absence of catalyst (Table 1, entry 1). The reaction conditions briefly were optimized and the best conditions were achieved with 0.05 g of the Pd/MnO_2 nanocomposite, 0.2 mmol of $K_4[Fe(CN)_6]$, 1.5 mmol of NaN_3, 1.0 mmol of iodobenzene, 1.0 mmol of sodium carbonate (Na_2CO_3) as base and 7.0 mL of DMF as solvent and the results are summarized in Table 1.



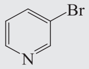
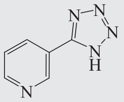
SCHEME 3 Proposed mechanism for the preparation of 5-substituted 1*H*-tetrazoles using Pd/MnO_2 nanocatalyst

TABLE 2 One-pot synthesis of 5-substituted 1*H*-tetrazoles from aryl halides using Pd/MnO_2 nanocomposite

Entry	Aryl halide	Product	Time (h)	Yield (%)
1			12	90
2			12	87
3			12	85
4			12	83
5			12	85
6			12	84
7			12	82
8			12	80
9			12	83
10			12	85
11			18	83
12			18	80
13			18	80
14			18	81
15			18	80

(Continues)

TABLE 2 (Continued)

Entry	Aryl halide	Product	Time (h)	Yield (%)
16			18	78

Reaction conditions: Catalyst (0.05 g), aryl halide (1.0 mmol), $K_4Fe(CN)_6$ (0.22 mmol), NaN_3 (1.5 mmol), Na_2CO_3 (1.0 mmol), DMF (5.0 ml), 120 °C.
bYields are after work-up.

To extend the scope and applicability of the heterogeneous catalysis, we examined a wide divertimento of substrates (Scheme 3). The optimal reaction conditions were applied to synthesis of 5-aryl 1*H*-tetrazoles and the results are summarized in Table 2. This strategy was general for a range of aryl halides having electron donating and withdrawing groups on benzene ring as well as heterocyclic ring. The reaction time and yields for aromatic nitriles bearing electron withdrawing and electron donating groups have no significant difference. As shown in Table 2, in comparison with aryl iodides, aryl bromides require much longer time. In all cases, the products were obtained in good yields under the standard reaction conditions.

A plausible mechanism is represented in Scheme 3. It is proposed that initially aryl halide was converted to aryl nitrile intermediate (**A**) by $K_4[Fe(CN)_6]$ in the presence of the Pd/MnO_2 nanocomposite. Then the tetrazole product was prepared from the [3 + 2] cycloaddition reaction between aryl nitrile intermediate with NaN_3 *via* the intermediate **B** in the presence of the Pd/MnO_2 nanocomposite. The catalytic reaction is supplemented by acidic work-up to afford the desired products.

The products were characterized by FT-IR, ^1H NMR and $^{13}CNMR$. The disappearance of an CN stretching band in the range of 2225–2370 cm^{-1} in the intermediate **B** and the appearance of NH stretching band in product structure in the FT-IR spectra confirmed the formation of the 5-substituted 1*H*-tetrazoles. $^{13}CNMR$ spectra showed one peak at 154–158 ppm corresponding to carbon of the tetrazole ring.

A comparison of the catalytic activities of various catalysts for the synthesis of 5-(4-methoxyphenyl)-1*H*-tetrazole is given in Table 3. It is clearly axiomatic from the Table 3 that the Pd/MnO_2 nanocomposite outperformed other catalysts that are reported in the literature.[18,21,59–64] The reaction was carried out in the presence of the Pd/MnO_2 nanocomposite in shorter time. The high yield of 5-(4-methoxyphenyl)-1*H*-tetrazole obviously have demonstrated excellent catalytic performance of the Pd/MnO_2 nanocomposite. The nanocomposite synthesized by a biological method which is a simple, green and ecofriendly procedure using aqueous extract of the leaves of *Solanum melongena* without using any harmful reducing or surfactant template. In addition, in comparison with some of the reported catalysts, the proposed nanocatalyst can be easily recovered and recycled for several times.

TABLE 3 Comparison of the Pd/MnO_2 nanocomposite with other previously reported catalysts in the synthesis of 5-(4-methoxyphenyl)-1*H*-tetrazole

Entry	Reaction conditions	Time (h)	Yield (%)	Ref.
1	(4-Methoxyphenyl) methanol, Cu $(NO_3)_2$, TEMPO/NH_3(aq.)/O_2, NaN_3, DMSO	24	63	59
2	4-Methoxybenzaldehyde, Cu $(NO_3)_2$, TEMPO/NH_3(aq.)/O_2, NaN_3, DMSO	24	61	59
3	4-Methoxybenzonitrile, Cu $(NO_3)_2$, TEMPO/NH_3(aq.)/O_2, NaN_3, DMSO	16	65	59
4	1-Bromo-4-methoxybenzene, $K_4[Fe\ (CN)_6]$, NaN_3, [Pd $(OAc)_2$], Na_2CO_3, dabco, $ZnBr_2$, DMF	24	60	32
5	4-methoxybenzaldehyde oxime, $(PhO)_2P(O)N_3$, DPPA, DBU, toluene, 110 °C	16	81	60
6	4-Methoxybenzonitrile, NaN_3 zinc salt, H_2O	48	86	21
7	4-Methoxybenzaldehyde, NH_2OH, NaN_3, $(NH_4)_2Ce(SO_4)_4.2H_2O$, DMF	8	65	61
8	4-Methoxybenzonitrile, Cu_2O, $TMSN_3$, MeOH/DMF, 80 °C	12	84	18
9	4-Methoxybenzonitrile, NaN_3, Yb $(OTf)_3.xH_2O$, DMF, 120 °C	24	69	62
10	4-Methoxybenzonitrile, NaN_3, $B(C_6F_5)_3$, DMF, 120 °C	14	84	63
11	1-Bromo-4-methoxybenzene, Zn $(CN)_2$, Pd $(PPh_3)_4$, NaN_3, NH_4Cl, DMF, 120 °C	31	68	64
12	1-Iodo-4-methoxybenzene, $K_4[Fe\ (CN)_6]$, NaN_3, Pd/MnO_2 nanocomposite, Na_2CO_3, DMF, 120 °C	12	85	This work

Yields are after work-up.

Compared with the other literature works on the synthesis of 5-substituted 1*H*-tetrazoles, the notable features of our method are:

- Elimination of toxic ligands and homogeneous catalysts;
- Avoidance of *in situ* formation of dangerous and harmful hydrazoic acid in reaction mixture
- The reaction system is simple;
- The yields of the products are high;
- The use of plant extract as an economic and effective alternative represents an interesting, fast and clean synthetic route for the synthesis of the Pd/MnO_2 nanocatalyst;
- The use of heterogeneous catalysts which can be easily recovered and reused;
- The synthesized Pd NPs by this method is quite stable and can be kept for one month.

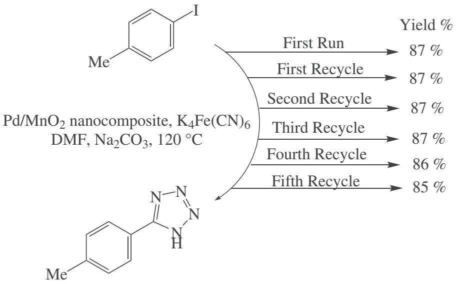


FIGURE 10 Reusability of Pd/MnO_2 nanocomposite for the synthesis of 5-(4-methylphenyl)-1*H*-tetrazole

2.4 | Catalyst reusability

In addition, we studied the reusability of the Pd/MnO_2 nanocomposite. The catalyst was recovered by simple filtration after completion of the reaction and re-used up to five times under the optimal reaction conditions (Figure 10). The recovered catalyst showed good

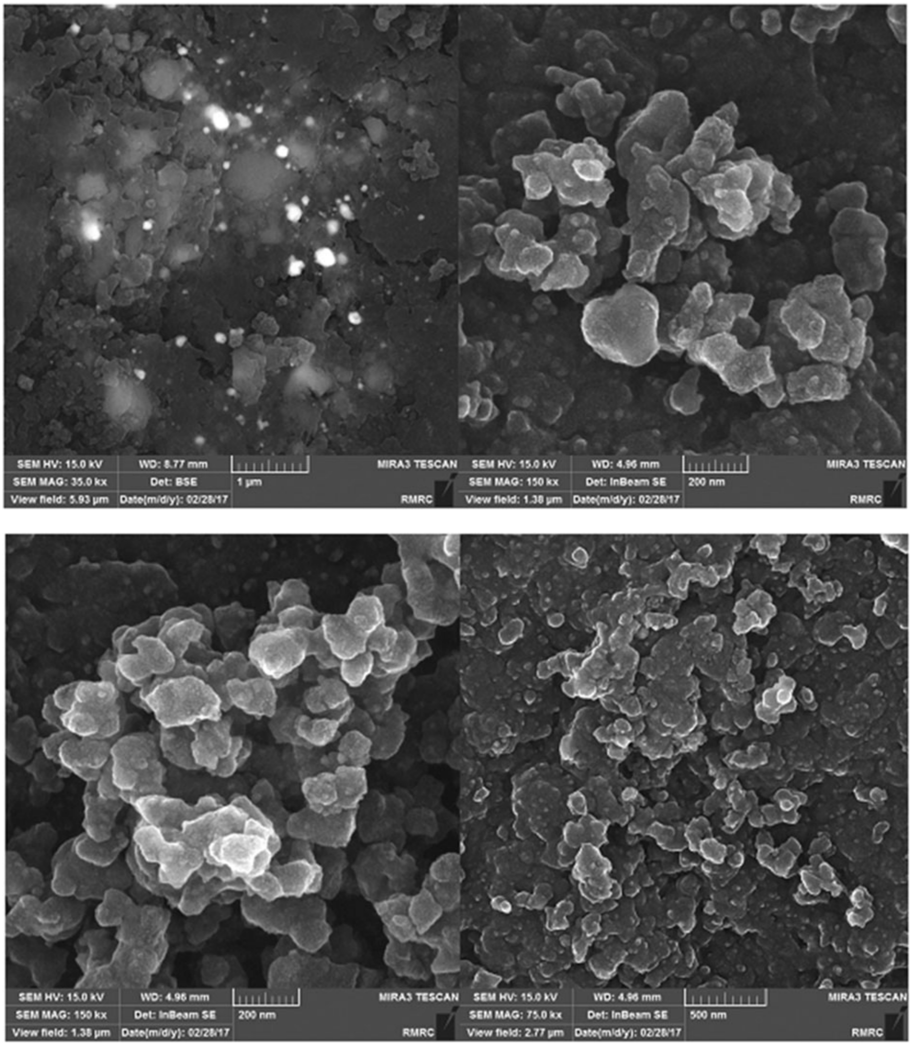


FIGURE 11 The FE-SEM images of recycled Pd/MnO_2 nanocomposite

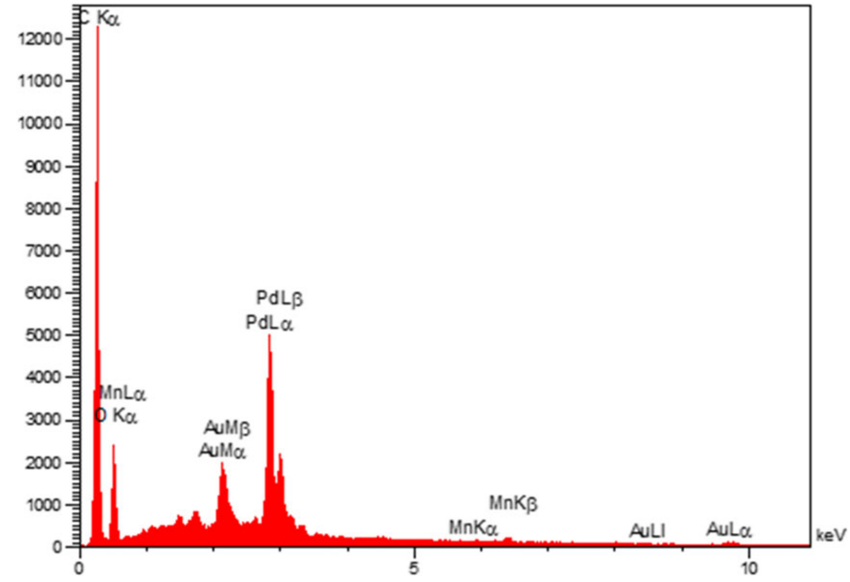


FIGURE 12 The EDS spectrum of recycled Pd/MnO_2 nanocomposite

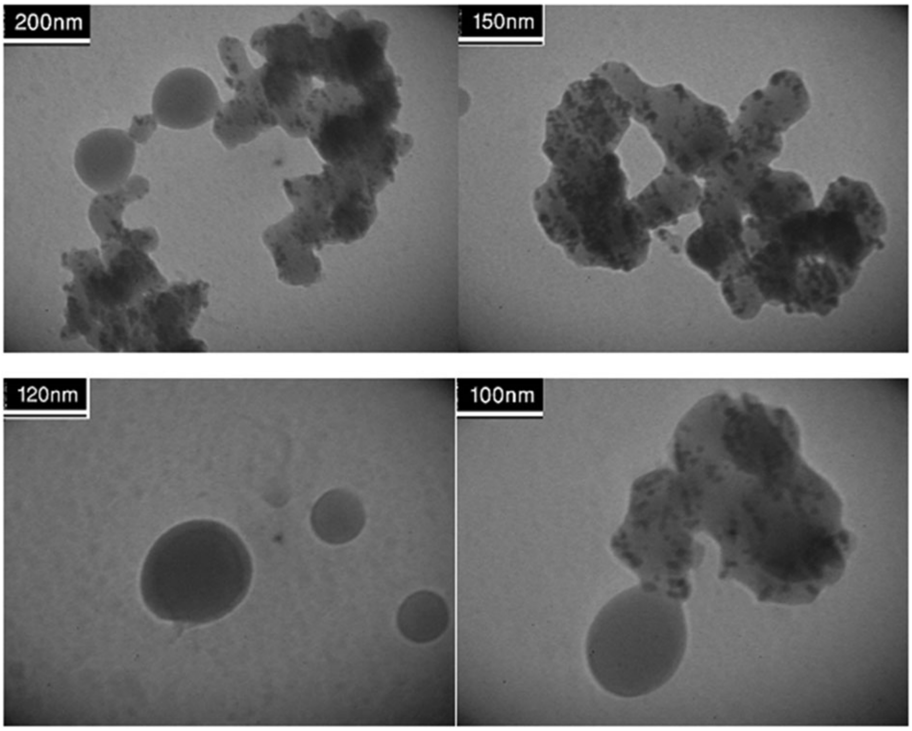


FIGURE 13 TEM images of recycled Pd/MnO_2 nanocomposite

reusability and catalytic activity with a slight decrease in yield. The FE-SEM, EDS and TEM analysis after the 5th recycle exhibited no obvious change in the size, shape and chemical composition of the reused Pd/MnO_2 nanocomposite (Figure 11–13).

3 | CONCLUSIONS

Pd/MnO_2 nanocomposite synthesized using *Solanum melongena* plant extract is a good catalyst for the synthesis of 5-aryl-1*H*-tetrazoles from aryl halides. The catalyst was characterized by FT-IR, FESEM, TEM, EDS and XRD. The experimental results suggest that the MnO_2 NPs play critical role in stabilizing the Pd NPs, which also prevent the Pd NPs from aggregating and leaching during the reactions. This synthetic method has the advantages of high yields, easy and simple preparation, the use of $K_4[Fe(CN)_6]$ as a non-toxic cyanide source, avoidance of the formation of dangerous and harmful hydrazoic acid, simple work-up procedure, simple preparation and availability of the MnO_2 as support.

In addition, the biosynthesized catalyst was stable and easily recycled and reused several times without remarkable loss in its catalytic activity.

4 | EXPERIMENTAL

4.1 | Instruments and reagents

All reagents used in the present work were purchased from Merck and Aldrich Chemical Companies without further purification. FT-IR (KBr) spectra were recorded using a Varian model 640 spectrophotometer. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker Avance DRX spectrometer at 400 and 100 MHz, respectively. Melting points were taken with a BUCHI 510 melting point apparatus that are uncorrected. A Philips model X'PertPro diffractometer X-ray diffraction equipped with a graphite monochromator crystal was used to perform X-ray diffraction (XRD) measurements ($\lambda = 1.5405$ Ao). The scanning rate was 2o/min in the 2θ range from 10 to 80^o. For investigation morphology and particle dispersion was used Scanning electron microscopy (SEM) (Cam scan MV2300). The chemical compositions of the prepared nanostructures were determined by EDS (energy dispersive X-ray spectroscopy) performed in SEM. The chemical analysis of prepared nanostructures was carried out by EDS (S3700 N). Transmission electron microscope (TEM) was used to identify the Ag/Feldspar shape and size using aPhilips-EM-2085 transmission electron microscope with an accelerating voltage of 100.0 kV.

4.2 | Preparation of the *Solanum melongena* plant extract

20 g of dried powdered of *Solanum melongena* plant and 150 mL double distillated water well mixed on magnetic heating stirrer at 80 °C for 30 min and then the mixture was centrifuged in 7000 rpm and filtered. Finally, the green extract was kept at refrigerator to use further.

4.3 | Biogenic synthesis of Pd NPs using *Solanum melongena* plant extract

10 ml of extract was added dropwise to 50 mL of 0.005 M $PdCl_2$ solution at 80 °C. Bio-reduction process to form the nano-palladium (Pd^o) finished around 4 min as solution color changed to dark brown and monitored by UV–Vis spectroscopy. Then the colored solution centrifuged at 7000 rpm for 45 min to completely separation.

4.4 | Preparation of MnO_2 nanoparticles

MnO_2 nanoparticles were prepared according to the literature.[65]

4.5 | Green synthesis of the Pd/MnO_2 nanocomposite using aqueous extract of *Solanum melongena* plant

In a 250 ml flask, 50 mL of the aqueous extract of *Solanum melongena* plant was added to the MnO_2 NPs (1.0 g) and magnetically stirred for 15 min at 80 °C. Then, 0.1 g of $PdCl_2$ dissolved in 10 mL of water by hydrochloric acid (37%) gradually added to the above mixture under the continuous stirring and heated for 3 hr. The formed Pd/MnO_2 nanocomposite was then centrifuged, washed with ethanol and dries in an oven and then characterized.

4.6 | General procedure for the synthesis of 5-substituted 1*H*-tetrazoles

The synthesis of tetrazole derivative are follow by typical procedure. A mixture of aryl halide (1.0 mmol), $K_4[Fe(CN)_6]$ (0.22 mmol), sodium carbonate (1.0 mmol) and 0.05 g Pd/MnO_2 nanocomposite was stirred in 7 mL DMF at 120 °C. Then, to the benzonitrile generated *in situ* (as indicated by TLC), then was added NaN_3 (1.5 mmol) and the mixture magnetically stirred at 120 °C for appropriate time. The reaction progress was monitored by TLC till completion. The catalyst was removed by filtration, the reaction mixture was acidified by 20 mL of HCl (4.0 M) and the solution diluted with 25 ml ethyl acetate and stirred vigorously. The organic layer was separated, and the aqueous layer was extracted with ethyl acetate twice. The combined organic layers were concentrated to give a crude product. All products are pure enough for IR and NMR spectroscopic analysis. However, the products were further purified by recrystallization from aqueous ethanol.

ACKNOWLEDGEMENTS

We gratefully acknowledge from the Iranian Nano Council and University of Qom for the support of this work.

ORCID

Mahmoud Nasrollahzadeh http://orcid.org/0000-0002-4539-3544

S. Mohammad Sajadi http://orcid.org/0000-0001-8284-5178

REFERENCES

[1] N. P. Butler, A. R. Katritzky, C. W. Rees, E. F. Scriven (Eds), *Comprehensive Heterocyclic Chemistry*, Pergamon, Oxford, UK **1996** 4.

[2] G. A. Patani, E. J. LaVoie, *Chem. Rev.* **1996**, *96*, 3147.

[3] R. J. Herr, *Bioorg. Med. Chem.* **2002**, *10*, 3379.

[4] S. J. Wittenberger, *Org. Prep. Proced. Int.* **1994**, *26*, 499.

[5] D. Moderhack, *J. Prakt. Chem.* **1998**, *340*, 687.

[6] V. Novakova, J. Roh, P. Gela, J. Kunes, P. Zimcik, *Chem. Commun.* **2012**, *48*, 4326.

[7] G. Steinhauser, T. M. Klapötke, *Angew. Chem. Int. Ed.* **2008**, *47*, 3330.

[8] T. Fendt, N. Fischer, T. M. Klapötke, J. Stierstorfer, *Inorg. Chem.* **2011**, *50*, 1447.

[9] M. Gobel, K. Karaghiosoff, T. M. Klapotke, D. G. Piercey, J. Stierstorfer, *J. Am. Chem. Soc.* **2010**, *132*, 17216.

[10] R. Wang, Y. Guo, Z. Zeng, J. M. Shreeve, *Chem. Commun.* **2009**, *19*, 2697.

[11] S. J. Wittenberger, B. G. Donner, *J. Org. Chem.* **1993**, *58*, 4139.

[12] V. Rama, K. Kanagaraj, K. Pitchumani, *Org. Prep. Proced. Int.* **2011**, *76*(21), 9090.

[13] V. Aureggi, G. Sedelmeier, *Angew. Chem. Int. Ed.* **2007**, *46*, 8440.

[14] K. Sisido, K. Nabika, T. Isida, S. Kozima, *J. Organomet. Chem.* **1971**, *33*, 337.

[15] J. V. Duncia, M. E. Pierce, J. B. Santella, *J. Org. Chem.* **1991**, *56*, 2395.

[16] G. Garipova, A. Gautier, S. R. Piettre, *Tetrahedron* **2005**, *61*, 4755.

[17] E. Ettenhuber, K. Ruhlmann, *Chem. Ber.* **1968**, *101*, 743.

[18] T. Jin, F. Kitahara, S. Kamijo, Y. Yamamoto, *Tetrahedron Lett.* **2008**, *49*, 2824.

[19] J. Bonnamour, C. Bolm, *Chem. – Eur. J.* **2009**, *15*, 4543.

[20] D. Cantillo, B. Gutmann, C. O. Kappe, *J. Am. Chem. Soc.* **2011**, *133*, 4465.

[21] Z. P. Demko, K. B. Sharpless, *J. Org. Chem.* **2001**, *66*, 7945.

[22] M. Nasrollahzadeh, Y. Bayat, D. Habibi, S. Moshaee, *Tetrahedron Lett.* **2009**, *50*, 4435.

[23] P. Mani, C. Sharma, S. Kumar, S. Kumar Awasthi, *J. Mol. Catal. A: Chem.* **2014**, *392*, 150.

[24] G. A. Meshram, S. S. Deshpande, P. A. Wagh, V. A. Vala, *Tetrahedron Lett.* **2014**, *55*, 3557.

[25] J. He, B. Li, F. Chen, Z. Xu, G. Yin, *J. Mol. Catal. A: Chem.* **2009**, *304*, 135.

[26] B. Yakambram, A. Jaya Shree, L. Srinivasula Reddy, T. Satyanarayana, P. Naveen, R. Bandichhor, *Tetrahedron Lett.* **2014**, *59*, 445.

[27] B. Sreedhar, A. S. Kumar, D. Yada, *Tetrahedron Lett.* **2011**, *52*, 3565.

[28] P. Sivaguru, K. Bhuvaneswari, R. Ramkumar, A. Lalitha, *Tetrahedron Lett.* **2014**, *55*, 5683.

[29] D. Amantini, R. Beleggia, F. Fringuelli, F. Pizzo, L. Vaccaro, *J. Org. Chem.* **2004**, *69*(8), 2896.

[30] R. Kant, V. Singh, A. Agarwal, *C. R. Chim.* **2016**, *19*, 306.

[31] M. Tajbakhsh, H. Alinezhad, M. Nasrollahzadeh, T. A. Kamali, *Monatsh. Chem.* **2016**, *147*, 2135.

[32] Y. Zhu, Y. Ren, C. Cai, *Theor. Chim. Acta* **2009**, *92*, 171.

[33] A. Kleemann, J. Engel, B. Kutscher, D. Reichert, *Pharmaceutical Substances: Syntheses, Patents, Applications of the most relevant APIs*, 4th ed., Georg Thieme, Stuttgart **2001**.

[34] R. C. Larock, *Comprehensive Organic Transformations: A Guide to Functional Group Preparations*, Wiley-VCH, Weinheim, Germany **1989** 819.

[35] K. Zheng, P. Yu, S. Chen, F. Chen, J. Cheng, *Chin. J. Chem.* **2013**, *31*, 449.

[36] S. Zheng, C. Yu, Z. Shen, *Org. Lett.* **2012**, *14*, 3644.

[37] S.-L. Zhang, L. Huang, *Org. Biomol. Chem.* **2015**, *13*, 9963.

[38] P. Y. Yeung, C. M. So, C. P. Lau, F. Y. Kwong, *Org. Lett.* **2011**, *13*, 648.

[39] P. Y. Yeung, C. P. Tsang, F. Y. Kwong, *Tetrahedron Lett.* **2011**, *52*, 7038.

[40] G. Yan, C. Kuang, Y. Zhang, J. Wang, *Org. Lett.* **2010**, *12*, 1052.

[41] H. Khojasteh, M. Salavati-Niasari, M.-P. Mazhari, M. Hamadanian, *RSC Adv.* **2016**, *6*, 78043.

[42] H. Khojasteh, M. Salavati-Niasari, A. Abbasi, F. Azizi, M. Enhessari, *J. Mater. Sci.: Mater. Electron.* **2016**, *27*(2), 1261.

[43] M. Salavati-Niasari, M. Esmaeili-Zare, M. Gholami-Daghian, *Adv. Powder Technol.* **2014**, *25*(3), 879.

[44] H. Safajou, H. Khojasteh, M. Salavati-Niasari, S. Mortazavi-Derazkola, *J. Colloid Interface Sci.* **2017**, *498*, 423.

[45] M. Nasrollahzadeh, S. M. Sajadi, A. Rostami-Vartooni, M. Alizadeh, *J. Colloid Interface Sci.* **2016**, *466*, 360.

[46] P. Singh, Y.-J. Kim, D. Zhang, D.-C. Yang, *Trends Biotechnol.* **2016**, *34*, 588.

[47] A. J. Kora, L. Rastogi, *Ind. Crop Prod.* **2016**, *81*, 1.

[48] S. M. Alshehri, T. Almuqati, N. Almuqati, E. Al-Farraj, N. Alhokbany, T. Ahamad, *Carbohydr. Polym.* **2016**, *151*, 135.

[49] Z. Wang, C. Xu, G. Gao, X. Li, *RSC Adv.* **2014**, *4*, 13644.

[50] F. S. Sangsefidi, M. Salavati-Niasari, S. Varshoy, M. Shabani-Nooshabadi, *Int. J. Hydrogen Energy* **2013**, *42*(47), 28473.

[51] M. Ghiyasiyan-Arani, M. Salavati-Niasari, *J. Phys. Chem. C* **2018**, *122*(29), 16498.

[52] A. Karthikeyan, V. Shanthi, A. Nagasathaya, *Int. J. Green Pharm.* **2009**, *3*, 78.

[53] K. T. Augusti, *Indian J. Exp. Biol.* **1996**, *34*(3), 634.

[54] S. Karthikumar, K. Vigneswari, K. Jegatheesan, *Sci. Res. Essays* **2007**, *2*(4), 101.

[55] M. Ashrafudoulla, S. F. Bellah, F. Alam, S. S. Faisal, M. A. H. Kafi, F. Fuad, *J. Med. Plants Stud.* **2016**, *4*(1), 35.

[56] Available at: http://www.jardinage.eu/article/planter-des-aubergines-645.

[57] H. Wang, Z. Lu, D. Qian, Y. Li, W. Zhang, *Nanotechnology* **2007**, *18*, 115616.

[58] D. Jaganyi, M. Altaf, I. Wekesa, *Appl. Nanosci.* **2013**, *3*(4), 329.

[59] C. Tao, B. Wang, L. Sun, J. Yi, D. Shi, J. Wang, W. Liu, *J. Chem. Res.* **2016**, *41*, 25.

[60] K. Ishihara, M. Kawashima, T. Matsumoto, T. Shioiri, M. Matsug, *Synthesis* **2018**, *50*, 1293.

[61] B. Mitra, S. Mukherjee, G. C. Pariyar, P. Ghosh, *Tetrahedron Lett.* **2018**, *59*, 1385.

[62] A. Coca, E. Turek, *Tetrahedron Lett.* **2014**, *55*(16), 2718.

[63] S. K. Prajapti, A. Nagarsenkar, B. N. Babu, *Tetrahedron Lett.* **2014**, *55*(24), 3507.

[64] M. Alterman, A. Hallberg, *J. Org. Chem.* **2000**, *65*, 7984.

[65] S. Naghdi, M. Sajjadi, M. Nasrollahzadeh, K. Y. Rhee, S. M. Sajadi, B. Jaleh, *J. Taiwan Inst. Chem. Eng.* **2018**, *86*, 158.

How to cite this article: Nasrollahzadeh M, Ghorbannezhad F, Sajadi SM. Biosynthesis of Pd/MnO_2 nanocomposite using *Solanum melongena* plant extract and its application for the one-pot synthesis of 5-substituted 1*H*-tetrazoles from aryl halides. *Appl Organometal Chem*. 2018; e4698. https://doi.org/10.1002/aoc.4698