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Biosynthesis, characterization and catalytic activity of Cu/RGO/Fe_3O_4 for direct cyanation of aldehydes with $K_4[Fe(CN)_6]$

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HIGHLIGHTS

- Green synthesis of Cu/RGO/Fe_3O_4 nanocomposite using *Euphorbia bungei Boiss* leaf extract.
- Cyanation of aldehydes with $K_4[Fe(CN)_6]$.
- Characterization of catalyst by XRD, FESEM, EDS, elemental mapping and UV–Vis.
- The catalyst can be recovered and reused for further catalytic reactions with almost no loss in activity.

GRAPHICAL ABSTRACT

$$\mathrm{ArCHO} \xrightarrow[\mathrm{K_4Fe(CN)_6,\ H_2O,\ 100\ ^oC}]{\mathrm{Cu/RGO/Fe_3O_4}} \mathrm{ArCN}$$

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ABSTRACT

This work reports the green synthesis of the Cu/reduced graphene oxide/Fe_3O_4 (Cu/RGO/Fe_3O_4) nanocomposite as a new catalytic system for cyanation of aldehydes to nitriles. This nanocomposite catalytic system was synthesized by aqueous extract of leaves of *Euphorbia bungei Boiss* as a reducing and stabilizing agent. Various substituted aryl nitrile were prepared under optimized conditions and providing moderate to excellent yields. In this process the catalyst exhibited a strong magnet response and could be easily separated by an external magnet and reused with no loss of catalytic activity.

1. Introduction

Nitriles are a valuable class of organic materials and the importance of these compounds comes from their widely utilized in chemical transformation, agrochemicals, biologically active compounds, pigments, dyes, herbicides and heterocycles [1].

The synthesis of aromatic nitriles is notable, because they can readily transformed to a series of functional groups such as aldehydes, amides, amines, amidines, tetrazoles, or other carboxy variants [2]. Some groups have developed synthetic methods for synthesis of aryl nitriles. However, these methods associated with using toxic cyanide sources such as trimethylsilyl, alkali-metal cyanides or acetone cyanohydrins [3–5].

Recently developed reports for synthesis of aryl nitriles involving some drawbacks such as limited substrate scope, harsh reaction conditions, low yields, formation of heavy metal waste, and the use of metal cyanides as cyanide source, that limiting their applications [6–11]. Such constraints should be removed to further develop the efficiency and utility of aryl nitrile synthesis. Therefore, the need for improved synthetic methods that reduce or eliminate such limitations of reaction is essential.

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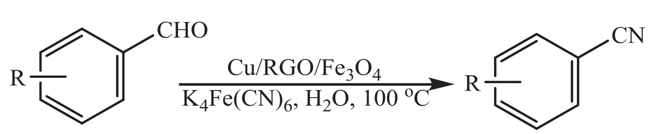
$K_4Fe(CN)_6$ is a cyanide source that is nontoxic, not explosive or flammable and also, it is a very useful and efficient reagent. For this reason, it is well-known as a good candidate for cyanation and synthesis of aryl nitriles [12–15].

Despite the enormous amount of reports about syntheses of aryl nitriles using $K_4Fe(CN)_6$ in the presence of homogeneous catalysts and various ligands such as N,N′ dimethylethylenediamine (DMEDA) and ethylenediamine [6,16–25], heterogeneous catalysts have received more attention. Therefore, synthesis of aryl nitriles in the presence of heterogeneous catalysts under ligand-free conditions has become more active research area. Nevertheless, the high cost of preparation of heterogeneous catalysts makes it not suited for large-scale synthesis.

In recent years, due to a higher available catalytic surface, heterogeneous catalysts are more and more used in the form of NPs [15]. There are several methods for the synthesis of metal nanoparticles (NPs). Unlike chemical and physical methods, biological synthesis by using bacteria, fungi, yeast as well as plants does not require the usage of hazardous chemicals, large amounts of energy, high temperature or pressure. Biological methods do not generate hazardous waste and the products usually do not need purification. For that reason, the biological methods are classified as green chemistry and are named as the green synthesis methods [26–32]. Therefore, the use of plants extract in the synthesis of metal NPs has economical and environmental benefits.

The *Euphorbia* genus from the family of *Euphorbiaceae* (spurge family) includes many species as both shrubs and trees in a large part of the world especially, Mediterranean, Middle East and South Africa [33,34]. Plants of the *Euphorbia* are often characterized by a unique profile of phenolics and flavonoids often accumulated in relatively complex mixtures based on the variety of those functional groups which effectively determine the bioactivity properties such as antioxidant, antimicrobial, anticancer and antifungi [33]. A chemical literature survey of *E. bungei Boiss* revealed the presence of various range of phytochemicals especially antioxidant phenolics such as flavonoid sulphates, flavone C- and O-glucosides, flavonol 3-O-monoglycosides, Rutin, Quercetin, Kaempferol and Myricetin and also jatrophanes and related macrocyclic diterpenoids [34]. Therefore, following the survey on reported literatures about the plant, it can be used as a suitable selection for the synthesis of nanoparticles using its potent antioxidants as naturally originated bioreductants.

Quite recently, we reported the green synthesis of a Cu/RGO/Fe_3O_4 nanocomposite using *Euphorbia wallichii* leaf extract and its application as a recyclable and heterogeneous catalyst for the reduction of 4-nitrophenol and Rhodamine B [35]. In continuation of our efforts to develop environmentally friendly synthetic methodologies [15,35–37], we report the procedure for the direct cyanation of aldehydes using $K_4Fe(CN)_6$ in the presence of catalytic amounts of Cu/RGO/Fe_3O_4 nanocomposite under ligand-free conditions (Scheme 1). Cu/RGO/Fe_3O_4 nanocomposite was prepared using *Euphorbia bungei Boiss* leaf extract and characterized using the X-ray diffraction analysis (XRD), field emission scanning electron microscope (FESEM), energy-dispersive X-ray spectroscopy (EDS), elemental mapping, fourier-transform infrared (FT-IR) spectroscopy and UV–Vis.

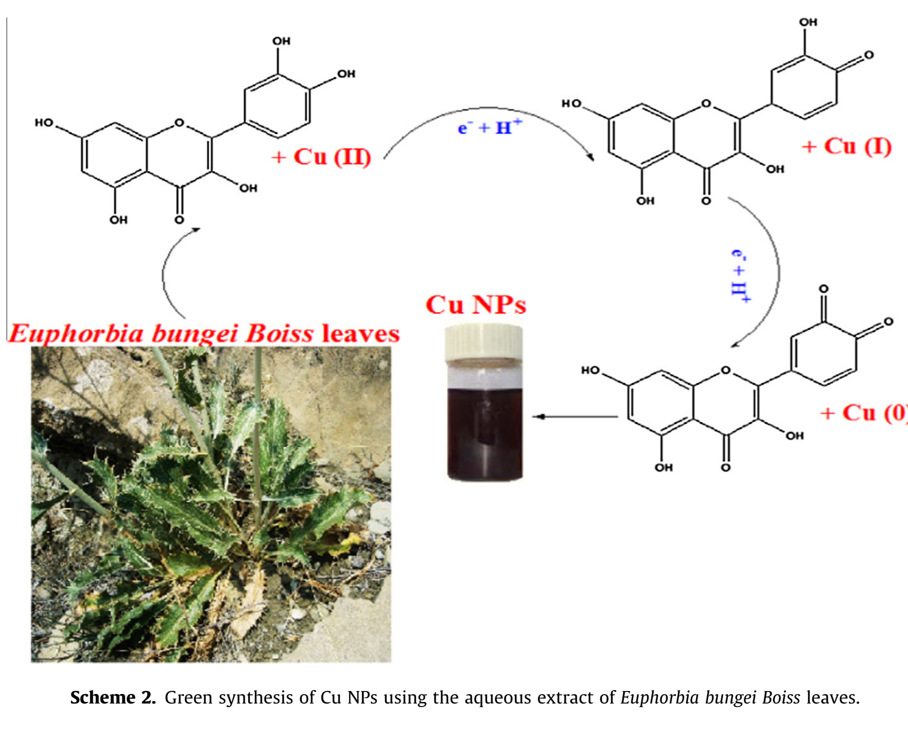


Scheme 1. Cyanation of aldehydes in water.

2. Experimental

2.1. Instruments and reagents

High-purity chemical reagents were purchased from the Merck and Aldrich chemical companies. All materials were of commercial reagent grade. FT-IR spectra were recorded on a Nicolet 370 FT/IR spectrometer (Thermo Nicolet, USA) using pressed KBr pellets. Melting points were determined in open capillaries using a BUCHI 510 melting point apparatus and are uncorrected. UV–Vis spectral analysis was recorded on a double-beam spectrophotometer (Hitachi, U-2900) to ensure the formation of nanoparticles. Morphology and particle dispersion was investigated by scanning electron microscopy (SEM) (Cam scan MV2300). The chemical composition of the prepared nanostructures was measured by EDS (Energy Dispersive X-ray Spectroscopy) performed in SEM. ^1H NMR and ^{13}C



Scheme 2. Green synthesis of Cu NPs using the aqueous extract of *Euphorbia bungei Boiss* leaves.