Journal of Colloid and Interface Science 506 (2017) 471–477

Contents lists available at ScienceDirect

Journal of Colloid and Interface Science

journal homepage: www.elsevier.com/locate/jcis

Regular Article

Green synthesis of copper nanoparticles using *Plantago asiatica* leaf extract and their application for the cyanation of aldehydes using $K_4Fe(CN)_6$

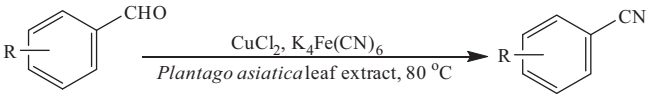
Mahmoud Nasrollahzadeh [a,b,*], Seyedeh Samaneh Momeni [c], S. Mohammad Sajadi [d]

[a] Department of Chemistry, Faculty of Science, University of Qom, PO Box 37185-359, Qom, Iran
[b] Center of Environmental Researches, University of Qom, Qom, Iran
[c] Department of Chemistry, Science and Research Branch, Islamic Azad University, Tehran, Iran
[d] Department of Petroleum Geoscience, Faculty of Science, Soran University, PO Box 624, Soran, Kurdistan Regional Government, Iraq

HIGHLIGHTS

- Green synthesis of the Cu NPs using aqueous extract of the leaves of *Plantago asiatica*.
- Cu NPs was characterized by FT-IR, UV–Vis, TEM, X-ray diffraction.
- Cu NPs exhibited good catalytic activity in cyanation of aldehydes in the extract as a green solvent.
- This catalyst could be easily recovered and reused several times.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 1 May 2017
Revised 15 July 2017
Accepted 18 July 2017
Available online 20 July 2017

Keywords:
Aryl nitrile
Aldehyde
Cyanation
Green synthesis
Plantago asiatica

ABSTRACT

Copper nanoparticles (Cu NPs) were synthesized via a green method by using of *Plantago asiatica* leaf extract as natural solvent and reaction biomedia under environmentally benign reaction conditions. It was observed that use of *Plantago asiatica* leaf extract makes a simple, eco-friendly and cost effective method for the preparation of the Cu NPs and can reduce copper ions into Cu(0) within 5 min of reaction time without using any stabilizer or surfactant agent. The progress of the reaction was monitored using UV–Visible spectroscopy. Polyphenolics could be adsorbed on the surface of Cu NPs, possibly by interaction through π-electrons interaction in the absence of other strong ligating agents. The catalytic activity of the Cu NPs was evaluated by cyanation of aldehydes in the extract as a green solvent. This method provided several advantages such as cleaner easy work-up, shorter reaction time and higher yield. Cu NPs were characterized by FT-IR, UV–Vis, TEM, X-ray diffraction and the synthesized products were characterized by FT-IR and ^{1}H NMR.

1. Introduction

Synthesis of nitriles has been a subject of intense investigation because of their broad application in the preparation organic compounds such as aldehydes, amines, amides, carboxylic acids, nitrogen-containing heterocycles and in industry for the synthesis of herbicides, pharmaceuticals, agrochemicals and dyes [1,2].

There are several methods for the synthesis of aryl nitriles using toxic inorganic or organic cyanide sources such as trimethylsilyl cyanide, alkali-metal cyanides and acetone cyanohydrin [3–7]. However, these methods suffer from different drawbacks such as employing expensive, moisture sensitive and reagents and catalysts, long reaction times, poor yield of products, tedious

* Corresponding author at: Department of Chemistry, Faculty of Science, University of Qom, PO Box 37185-359, Qom, Iran.
E-mail address: mahmoudnasr81@gmail.com (M. Nasrollahzadeh).

http://dx.doi.org/10.1016/j.jcis.2017.07.072
0021-9797/

Fig. 1. Geographical image of Haji Omran by Google Earth and Image of *Plantago asiatica* plant.

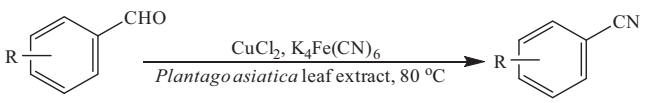
work-ups, formation of side products and heavy metal waste and harsh reaction conditions [8–11].

Interestingly, recently, $K_4Fe(CN)_6$ was used as a very useful, efficient, inexpensive and non-toxic reagent for the synthesis of aryl nitriles [12–17]. It is cheaper than KCN and NaCN and used in the food industry for metal precipitation. There are many reports on the synthesis of aryl nitriles through cyanation of aryl halides using $K_4Fe(CN)_6$ as a cyanide source in the presence of palladium catalysts [18–24], while less expensive copper catalysts have less received attention. However, the high cost of palladium catalysts restricts their use in large-scale process. In addition, copper-catalyzed cyanation of aryl halides was carried out in the presence of organic ligands such 3,3′-(1,4-phenylene) bis-(2-imino-2,3-dihydrobenzo[*d*]-oxazol-5-ol) [25], *N,N′*-dimethylethylenediamine (DMEDA), [6,26] ethylenediamine, [14] 1,3-phenylene-bis-(1*H*)-tetrazole [27]. Therefore, there is an ever-growing need to develop and promote the green synthesis of aryl nitriles which are more environmentally friendly.

In the recent years, a lot of studies on the synthesis of aryl nitriles have been reported through cyanation of aryl halides using $K_4Fe(CN)_6$ in the presence of metal NPs [28–31]. However, there are very few examples in which aldehydes are used as start materials for the preparation of aryl nitriles. Thus, the development of a novel and efficient system for the preparation of aryl nitriles from aldehydes still remains an active research area.

In this paper, for the first time we studied the *in situ* preparation of Cu NPs using *Plantago asiatica* leaf extract (Fig. 1) as the biomaterial without addition of any other external reducing agent. Cu NPs exhibit highly efficient and recyclable catalytic activity for the direct cyanation of aldehydes using $K_4Fe(CN)_6$ in the presence of *Plantago asiatica* leaf extract as a green solvent (Scheme 1).

Plantago asiatica from the family of *Plantaginaceae*, is a perennial herb which geographically distributed in temperate regions of Asia, Australia, North Africa and North America [32,33]. The plant is a very valuable source of medicinal phytochemicals with numerous applications in folk medicine. The literature survey showed that the plant is a potent reducing source for the presence of bioactive phytochemicals and strong antioxidants such as polysaccharides, flavonoids, caffeic acid, glycoside esters, phenylethanoid glycosides, iridoid glucosides, triterpene acids, phenylethanoid glycosides, and other phenolic constituents with anti-inflammatory, antibacterial, antioxidant, analgesic and antiallergic activities [34–38]. Therefore, these properties caused to choose the plant as a valuable bioreducer source for green synthesis of nanoparticles without using any synthetic reductants and toxic chemicals.



Scheme 1. The new strategy for the cyanation of aldehydes.

2. Experimental

2.1. Plant materials

The plant of *Plantago asiatica* (2 kg) was collected in July 2016 in "Haji Omran" alpine region (at an elevation of 1705 m above sea level) at Kurdistan of Iraq (Fig. 1).

2.2. Preparation of Plantago asiatica leaf extract

50 g of dried powdered of the plant leaf extracted under thermal conditions at 80 °C for 30 min in 500 mL double distillated water and centrifuged at 7000 rpm. The obtained extract then filtered and kept in refrigerator for further use.

2.3. Investigation of the antioxidant activity of the plant using the DPPH method

DPPH radical scavenging activity was determined according to Xu et al. [39]. A 0.2 mM of DPPH radical solution in ethanol was prepared, and then 1 mL of this solution was mixed with 1 mL of plant extract dissolved in 100 mM Tris-HCl buffer (pH 7.4); the mixture was then shaken up vigorously and left for 30 min at room temperature in the dark. The absorbance was measured at 517 nm. Ascorbic acid (AA) used as positive controls. All values are presented as the mean ± SD (n = 3). This activity is given as percent DPPH radical scavenging and is calculated as:

$$\%\text{DPPH radical scavenging} = [1 - (\text{Ai} - \text{Aj})/\text{Ac}] \times 100$$

where Ai is the absorbance of mixture of 1 mL sample and 1 mL 0.2 mM DPPH; Aj is the absorbance of mixture of 1 mL sample and 1 mL ethanol and Ac is the absorbance of mixture of 1 mL 0.2 mM DPPH and 1 mL Tris-HCl buffer.

2.4. Preparation of Cu NPs using the aqueous extract of the leaves of Plantago asiatica

20 mL solution of $CuCl_2{\cdot}2H_2O$ 5 mM was mixed with 100 mL of the aqueous plant extract along with vigorous shaking at 80 °C until changing the color of the mixture to dark during 5 min as a signal for Cu nanoparticles formation (as monitored by UV–Vis technique). The colored mixture then centrifuged at 7000 rpm for