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Synthesis of Cu_2O/Ag nanocomposite and their catalytic application for the one pot synthesis of substituted pyrroles

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ABSTRACT

The present protocol reports a facile and efficient method of preparation for Cu_2O/Ag nanocomposite (NPs) using ethylene glycol under microwave irradiation within a short duration of time. The synthesized Cu_2O/Ag NPs well characterized by XRD, FEG-SEM, EDS and NH_3-TPD, ICP-AES techniques. Futher, the catalytic application of Cu_2O/Ag NPs for the synthesis of substituted pyrroles *via* multicomponent reaction (MCRs) by using an aldehyde, amine, 1,3-diketone and nitromethane at room temperature. The catalytic system provide good yields of products for a wide range of substrates. Also catalyst shows excellent catalytic recyclability without much loss of its activity.

1. Introduction

The developments in nanoscience and nanotechnology due to their distinctive properties than that of the bulk of the compounds have a wider range of applications in the different fields and which also open up the new scope for nano metal oxide applications. The metal oxide nanomaterials have wider applications in water splitting, solar cells, supercapacitors, lithium ion batteries, fuel cells and catalysis [1,2]. Nowadays, the synthesis of size and shape selective nanomaterisls have great importance due to their unique features [3]. The synthesis and application of Cu_2O/Ag NPs are in demand and have broad range of applications as immunosensors, photocatalytic degradation of organic pollutants, antibacterials and Raman scattering technology [4–7]. There are various methods have been reported for the synthesis of Cu_2O/Ag composites as electron beam irradiation method, thermal decomposition, photocatalytic method, electrodeposition, hydrothermal, in situ solution synthesis, wet chemical reduction [8–14] *etc*.

Multicomponent reaction (MCRs) is reactions in which three or more molecules react together to give the desired product in a one pot system. The MCRs have the advantage in terms of green chemistry and economic point of view because efficient, cost effective and less generation waste products as compared with the traditional methods. Due to fast and simple experimental procedure of MCRs useful for the synthesis of many heterocyclic compounds. MCRs catalysed by various catalysts for the synthesis of heterocyclic compounds such as pyrroles, pyridines, pyrazolyl-pyrazolone methanes, 1,4-dihydropyridine, Propargylamines, *N*-sulfonylacrylamidines, benzoxanthenones [15–21] *etc*.

Pyrroles and its derivatives are the important moities in the various biologically active compounds such as alkaloids, porphyrins, bile pigments, coenzymes, and pharmaceutical compounds [22–24]. The traditional methods for the synthesis of pyrroles and its derivetaives, which includes Hantzsch, Knorr and Paal-Knorr synthesis [25–27]. Recently, pyrroles synthesis catalysed by various metals and metal oxides has taken considerable attention [28]. The various catalytic systems were used for the synthesis of pyrroles including $NiFe_2O_4$, $CoFe_2O_4$, Fe-MIL-101, $FeCl_3$, Silica gel supported tungstic acid, Amberlyst-15 and ionic liquids [29–35]. Also, the synthesis of pyrroles done by using various methods depending upon the available starting precursors [36–40]. These methods have one or more limitation such as expensive catalyst, longer reaction time, high reaction temperature, non-easily availability of starting materials, use of solvents, difficulty in recovery of the catalyst. To overcome these limitations there is still need to develop the green protocol, which works under the mild reaction conditions.

Herein, we have reported a simple and covenient method for the synthesis of various Cu_2O/Ag NPs using ethylene glycol under microwave irradiation and well characterized by using FEG-SEM, XRD, EDS and NH_3-TPD, ICP-AES. Further, the catalytic application of Cu_2O/Ag NPs for the one pot synthesis of pyrroles at room

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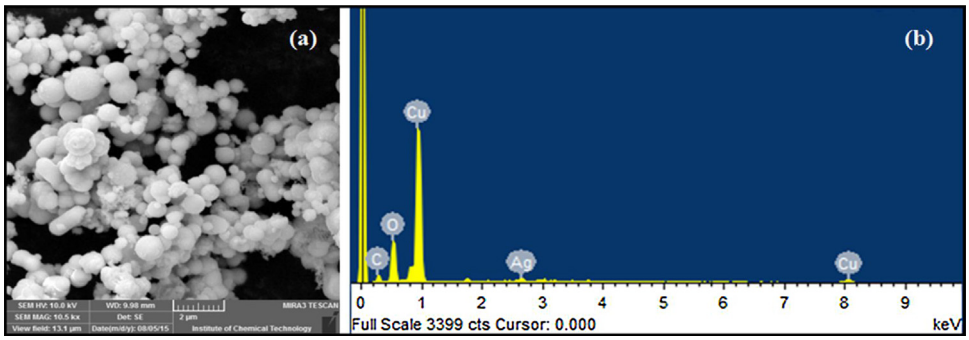

Fig. 1. (a) FEG-SEM and (b) EDS images of Cu_2O/Ag-(A) NPs.

temperature using aldehyde, amine, 1,4-dicarbonyl compound and nitromethane *via* MCRs.

2. Experimental

2.1. Chemicals and reagents

All chemicals and reagents of A. R. grade were purchased from SD Fine Chemicals Ltd., Mumbai, India and used without further purification.

2.2. Preparation of Cu_2O/Ag NPs

Copper nitrate trihydrate (187 mg) was dissolved in 4 mL ethylene glycol. With this solution 6 mL of 0.01 M $AgNO_3$ solution was added and irradiated under the microwave at 600 W for 4 min which gives red to black precipitate which indicates the formation of Cu_2O/Ag NPs which is designated as Cu_2O/Ag-(A). The precipitate was separated by centrifugation at 8000 rpm for 10 min. The precipitate was washed with 20 mL distilled water and then with 20 mL of ethanol and dried in an oven at 80 °C for 1 h.

Similarly, above same procedure was followed only change in the volume of 4 mL of 0.01 M $AgNO_3$ and 8 mL of 0.01 M $AgNO_3$ for the synthesis of Cu_2O/Ag NPs which is designated as Cu_2O/Ag-(B) and Cu_2O/Ag-(C) respectively.

2.3. Characterization of Cu_2O/Ag NPs

The prepared Cu_2O/Ag NPs were characterized using various analytical techniques such as FEG-SEM by Tescan MIRA 3. The energy dispersive X-ray spectrum (EDS) was recorded by using INCA x-act Oxford instrument (Model 51-ADD0007), XRD analysis was done by using Shimadzu XRD-6100, acidity by NH_3-TPD by using thermo scientific TPDRO 1100, elemental composition was done by using ICP-AES (Spectro Analytic Instruments GmbH, Germany).

2.4. General procedure for synthesis of substituted pyrroles by one pot synthesis

In a reaction vial, aldehyde (1 mmol), amine (1 mmol), 1,3-diketone (1 mmol), 1 mL of nitromethane and catalyst Cu_2O/Ag NPs (5 mg) were added. The reaction mixture was stirred at room temperature for 15 h. The progress of the reaction was monitored by TLC. Upon the completion of reaction, the catalyst was separated by centrifugation. The reaction mixture was extracted in the ethylacetate and concentrated under the vacuum. The products were purified by chromatograpgy. All the products are well known and reported in the literarure and characterized using GC–MS and compared with authentic samples.

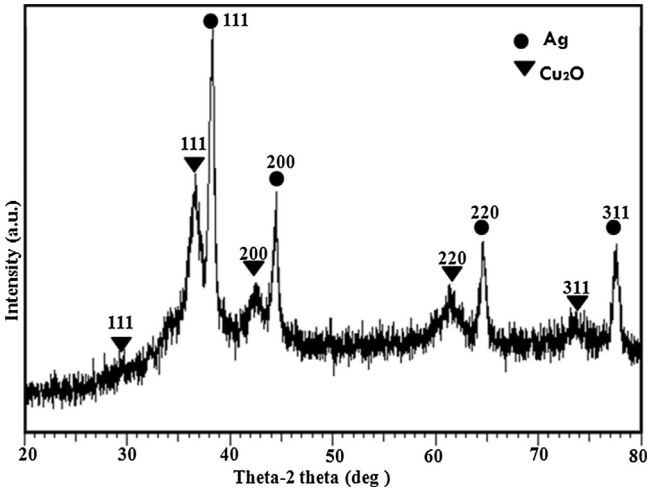

Fig. 2. XRD Pattern for Cu_2O/Ag-(A) NPs.

3. Results and discussion

3.1. Characterization of Cu_2O/Ag NPs

The morphology of the synthesized Cu_2O/Ag-(A) NPs was observed using an FEG-SEM. The Fig. 1a which indicates the particles are in the spherical shape and in nano range. The elemental spectrum, which indicates the presence of copper, oxygen and silver, which confirm the pure form of Cu_2O/Ag NPs with absence of any other impurites (Fig. 1b). The morphology of Cu_2O/Ag-(B) and Cu_2O/Ag-(C) are appers to be in the spherical shape (ESI, Fig. S1).

X-ray diffraction analysis of Cu_2O/Ag-(A) was performed with an X-ray wavelength of Cu Kα radiation at λ = 1.5405 Å with the scanning rate of 2°/min from 20° to 80° for Cu_2O/Ag NPs (Fig. 2). Peaks corresponding to both Cu_2O and Ag were observed in the XRD pattern. The lattice planes of (111) (200) (220) and (311) were corresponding to the FCC lattice of silver (JCPDS: 04-0783) [41] and (111) (200) (220) and (311) were corresponding to the FCC structure of Cu_2O (JCPDS: 05-0667) [42]. Similarly, XRD of Cu_2O/Ag-(B) and Cu_2O/Ag-(C) analysed which are matches with the standard (ESI, Fig. S1).

The acidity of prepared Cu_2O/Ag-(A) NPs were calculated by using TPDRO 1100 thermo scientific. Before analysis of sample, sample is pretreated with helium gas at 200 °C for 2 h to remove moisture and other impurities on the surface of the catalyst and then cooled to room temperature. Then the sample was saturated with pure NH_3 and then NH_3-TPD started from room temperature up to 1000 °C with the temperature ramp of 10 °C/min with helium gas as the carrier gas. The amount of NH_3 desorbed was 22110 μmol/g which indicates the high acidity of the catalyst

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