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Novel combination of zero-valent Cu and Ag nanoparticles @ cellulose acetate nanocomposite for the reduction of 4-nitro phenol

Farman Ullah Khan[a,b,c], Asimullah[c], Sher Bahadar Khan[a,b,*], Tahseen Kamal[a,b], Abdullah M. Asiri[a,b], Ihsan Ullah Khan[d], Kalsoom Akhtar[e]

[a] *Center of Excellence for Advanced Materials Research (CEAMR), King Abdulaziz University, Jeddah 21589, Saudi Arabia*
[b] *Chemistry Department, Faculty of Science, King Abdulaziz University, Jeddah 21589, Saudi Arabia*
[c] *Department of Chemistry, University of Science and Technology, Bannu-28100, KPK, Pakistan*
[d] *Department of Fundamental and Applied Sciences, University Technology Petronas, Perak, Malaysia*
[e] *Division of Nano Sciences and Department of Chemistry, Ewha Womans University, Seoul, Republic of Korea*

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ABSTRACT

A very simple and low-cost procedure has been adopted to synthesize efficient copper (Cu), silver (Ag) and copper-silver (Cu-Ag) mixed nanoparticles on the surface of pure cellulose acetate (CA) and cellulose acetate-copper oxide nanocomposite (CA-CuO). All nanoparticles loaded onto CA and CA-CuO presented excellent catalytic ability, but Cu-Ag nanoparticles loaded onto CA-CuO (Cu^0-Ag^0/CA-CuO) exhibited outstanding catalytic efficiency to convert 4-nitrophenol (4-NP) into 4-aminophenol (4-AP) in the presence of $NaBH_4$. Additionally, the Cu^0-Ag^0/CA-CuO can be easily recovered by removing the sheet from the reaction media, and can be recycled several times, maintaining high catalytic ability for four cycles.

1. Introduction

Nitrophenols and their derivatives are the most stubborn pollutants in industrial wastewaters. The United States Environmental Protection Agency regards nitrophenols and their derivatives as priority pollutants due to their perilous nature [1,2]. Keeping in view the hazardous nature of toxic compounds and the need for pollution diminishment, a study concerning the catalytic reduction of 4-NP is necessary. Many approaches have been acclaimed to eliminate 4-NP from aquatic environments, including electrochemical treatment, adsorption, and microbial degradation [3,4] but the usual treatment procedures have some major limitations, including limited degradation efficiency, slow degradation rate, high costs and strict conditions. These limitations restrict their large scale applications [5–7].

To assess the activity of noble metallic nanoparticles, the catalytic reduction of 4-NP using borohydride ions (BH_4^-) in the presence of a metal catalyst has become a commonly-used reaction [8–19]. Although the reaction is thermodynamically feasible, kinetically it is not achievable in the absence of a catalyst because of a high kinetic barrier between the equally-repelling negative ions of 4-nitrophenoxide and $BH^-{}_4$ [20]. According to traditional theory, the electrons are transferred from BH_4^- to 4-NP through adsorption of reactant molecules onto the metallic nanoparticle surface during catalytic reduction of 4-NP by metallic nanoparticles. Metallic nanoparticles then transmit and pass electrons to complete the oxidation-reduction reaction, thus contributing to overcoming the kinetic barrier of the reaction [21].

Numerous metal catalysts, such as palladium and gold, have been used for the reduction of aromatic nitro compounds and have shown high catalytic efficiency. This catalyst is generally loaded onto various supporting matrices. Of the various polymers and their derivatives, cellulose acetate (CA), derived from natural cellulose fibres by esterification, has attracted the attention of researchers as a new class of carbohydrate polymer, due to its size, convenient

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* Corresponding author at: Center of Excellence for Advanced Materials Research (CEAMR), King Abdulaziz University, Jeddah, Saudi Arabia.
E-mail address: sbkhan@kau.edu.sa (S.B. Khan).

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morphology, easy surface chemistry, elevated surface area, greater environmental sustainability and moderately low cost. Moreover, due to rich hydroxyl and carboxylate groups on the surface of CA, different surface alterations and various reactions have been carried out with CA [22].

We have therefore designed a highly active bimetallic Cu-Ag nanocatalyst loaded onto CA-CuO nanocomposite. CA-CuO nanocomposite was used as a supporting matrix to take advantage of low-cost CA and the catalytic properties of metallic nanoparticles in order to transform 4-NP into 4-aminophenol (4-AP) using sodium borohydride ($NaBH_4$).

2. Experimental section

2.1. Chemical and solvents

All chemicals, reagents and solutions used in the experiment were of analytical grade, and were used without further distillation or purification. Copper sulphate ($CuSO_4$), silver nitrate ($AgNO_3$), acetone, $NaBH_4$ and 4-NP were provided by Sigma Aldrich. All solutions used in the current study were prepared with deionised water.

2.2. Synthesis of CuO nanomaterials

CuO nanomaterial was prepared by simple hydrothermal method. Copper salt was dissolved in water to prepare 0.1 M aqueous copper salt solution and then 5% wt of carbon black was added into aqueous copper salt solution. After well dispersion of carbon black in aqueous solution, 0.5 M NaOH solution was drop wise added till pH of the solution reached around 10. This highly basic solution was kept 60 °C for overnight and then the prepared CuO was washed several times with deionised water to remove impurities [23,24].

2.3. Preparation of CA-CuO

To prepare the desired CA nanocomposite, 2 g of CA was weighed and then placed in a beaker. To uniformly distribute the metal oxide nanomaterial in the CA polymer, the polymer was solvated using pure acetone (99% purity) for complete dissolution of the cellulose polymer and then metal oxide nanomaterials (CuO) were added to the solution based on their calculated weight (0.1 g). The solution was stirred with a magnetic stirrer to produce a uniform mixture at ambient temperature. After homogeneous scattering of the nanomaterial in CA, the prepared nanocomposite was then subjected to preparation for thin films. The uniform mixture was spread by glass rod on a glass plate and was left to dry. After drying, the film was removed and stored in a plastic bag prior to further studies.

2.4. Uptake of metal ions by CA and CA-CuO

Aqueous solutions of $CuSO_4$, $AgNO_3$, and a 1:1 mix solution of $CuSO_4$ and $AgNO_3$ were prepared by dissolving in double distilled water. The solutions were mechanically shaken until complete dissolution occurred. CA and CA-CuO films were then dipped in the solution and after 5 h, CA and CA-CuO films were collected that had been loaded with copper and silver metal ions. The films were dried and then subjected to nanoparticle synthesis.

2.5. Preparation of CA and CA-CuO nanoparticles

CA and CA-CuO metal-loaded films were placed in a freshly prepared $NaBH_4$ solution, and Ag^0/CA, Cu^0/CA, Cu^0-Ag^0/CA, Ag^0/CA-CuO, Cu^0/CA-CuO and Cu^0-Ag^0/CA-CuO nanoparticles were prepared by reducing Cu^{2+}, Ag^+ and Cu^{2+}-Ag^+ ions adsorbed by CA and CA-CuO in $NaBH_4$. Over the course of the reaction, the thin film turned brown in color, indicating the formation of nanoparticles.

2.6. Catalytic reduction of 4-NP

The prepared films of Ag^0/CA, Cu^0/CA, Cu^0-Ag^0/CA, Ag^0/CA-CuO, Cu^0/CA-CuO and Cu^0-Ag^0/CA-CuO were evaluated for suitability in the catalytic reduction of 4-NP to 4-AP with $NaBH_4$, which is considered to be a model reaction for the determination of the catalytic performance of metal and metal oxide nanoparticles [25]. The reaction rate could be regarded as being independent of the concentration of $NaBH_4$, as an excess amount of $NaBH_4$ was used as a reducing agent [26]. Typically, aqueous 4-NP (100.0 mL, 0.15 mmol) and aqueous $NaBH_4$ (100.0 mL, 15.0 mmol) were transferred to a sealed quartz cuvette for immediate UV–vis measurement in the range of 200–800 nm at an interval of 1 min. The absorption of 4-NP was observed at 325 nm, and the unreacted 4-NP exhibited a significant characteristic absorption band at approximately 400 nm, which was associated with the concentration of 4-NP ions. Finally, the absorption of the product 4-AP was observed at 317 nm.

2.7. Characterisation

Analysis of CA-CuO nanoparticles was achieved via X-ray diffraction (XRD) using an ARL X'TRA X-ray diffractometer with a Cu Kα radiation ($\lambda = 0.154$ nm) source. Fourier transformed infrared (FT-IR) spectra of CA-CuO nanoparticles were recorded using a Thermo scientific FT-IR spectrometer. The morphology of CA-CuO nanoparticles was studied using a field emission-scanning electron microscope (FESEM), JEOL (JSM-7600F, Japan). Energy dispersive X-ray spectrometry (EDS) of CA-CuO nanoparticles was performed for elemental analysis by the Oxford-EDS system. The catalytic reduction of phenols was measured using a UV-3300 spectrophotometer.

3. Results and discussion

The cellulose layer is a biopolymer that is not only with a good biocompatibility, but also has a large number of hydroxyl groups, which take part in the stabilization of metal nanoparticles [27]. The multifunctional biopolymer plays dual characters of dispersing stable copper oxide nanomaterial into an aqueous solution and providing functional groups to bind metal ions and metal nanoparticles [28,29]. Thus, the hydroxyl groups that are preferential reactive sites are in electrostatic conjunction with copper sulphate and silver nitrate, followed by the reduction of these metals ions to produce Cu^0 and Ag^0 on the surface of CA and CA-CuO (Scheme 1). Cu^0, Ag^0 and Ag^0-Cu^0 were grown on CA and CA-CuO and the whole process i.e synthesis of CA-CuO nanocomposite, adsorption of Cu, Ag and Cu-Ag metal ions, conversion of metal ions into nanoparticles, and catalytic reduction of nitrophenols into aminophenols using nanoparticles is shown in schematic illustration (Scheme 1).

In first step, CuO was mixed with CA and prepared CA-CuO nanocomposite film. 2 g CA was dissolved in acetone followed by incorporation of 0.1 g CuO nanomaterials. Stirring was continued to ensure the complete and uniform dispersion of the CuO nanomaterial in the CA-acetone solution. At the end of this step, the prepared solution was poured on the glass and kept for drying which resulted in the formation of CA-CuO composite film. Separately for the preparation of CA film, 2 g CA was dissolved in acetone, cast on the glass and dried. In 2nd step, pure CA and CA-CuO nanocomposite films were inserted into each metal ion solution individually and the color of the films turned blue, dark red and bluish red due to Cu, Ag and Cu-Ag ions adsorption. CA and CA-CuO films were dipped in either $AgNO_3$, $CuSO_4$, or combined $AgNO_3$ and $CuSO_4$ aqueous solution. Metal ions from corresponding aqueous