A Novel Route for Synthesis and Characterization of Green Cu$_2$O/PVA Nano Composites

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ABSTRACT

A novel, simple, less time-consuming and cost-effective green method has been developed to synthesize Cu$_2$O nanoparticles and composite with poly vinyl alcohol relatively at low temperature in acidic pH. Cu$_2$O nanoparticles were prepared by reduction of Benedict's solution using agriculture wastes of Manihot esculenta leaves containing reducing sugars which act as reducing agent. The nanocomposite was prepared by addition of Cu$_2$O nanoparticles to the stirred solution of PVA. The solution was stirred for 0.5hour and dried at room temperature. The resulting Cu$_2$O nanoparticles and Cu$_2$O/PVA composite were characterized by X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM), UV-VIS absorption and Fourier-transform infrared (FTIR) spectroscopy.

Key words: Benedict's solution, Cu$_2$O nanoparticles, Manihot esculenta, Polyvinyl alcohol, Nano-composites
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INTRODUCTION

The study of nanocomposite materials is a fast growing area of research which generates many exciting new high-performance materials with novel properties. Nanocomposite materials significantly encompass a large variety of systems such as one-dimensional, two-dimensional, three-dimensional and amorphous materials made of distinctly dissimilar components and mixed at the nanometer scale.

Polymer nanocomposites, also presently known as nanostructured materials, are materials in which nanoscopic inorganic particles, typically 10–100 nm in atleast one dimension, are dispersed in an organic polymer matrix in order to dramatically improve the various properties of the polymer [1, 2]. Nanoparticles of metals and metal oxides embedded in polymer matrices have attracted more interest because of the unique properties displayed by these materials. Due to the nanometer size of these particles, their physicochemical characteristics differ significantly from those of molecular and bulk material [3, 4].

Poly(vinyl alcohol) is an important material in view of its large-scale applications, such as biomaterials, biosensors, electrochemical sensors, membranes with selective permittivity, viscous medium for controlling the crystallization process of salts, for controlled drug delivery or catalytic systems, etc. because it is a non-toxic, non-carcinogenic, biodegradable, biocompatible, water-soluble and non-expensive polymer. It could also be matrix for metal ions or salts in ecological composites [5, 6]. PVC can react with different organic or inorganic substances, via -OH groups from its macromolecular chain and three dimensional networks, which can absorb very high water content (up to 1800%).

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Cuprous oxide (Cu_2O) is a p-type semiconductor with a direct band gap of 2.1 eV. In recent years, Cu_2O nanostructures have been received more and more attention due to their applications in photo catalysis [7], lithium ion batteries [8], magnetic storage media [9], gas sensors [10], and conversion of CO to CO_2 [11]. Several methods have been developed for the preparation of cuprous oxide, including thermal reduction [12], sonochemical reduction [13], metal vapor synthesis [14] and chemical reduction [15]. Among all these methods mentioned above, the green method employing plant extracts have drawn much attention as a simple and viable alternative to chemical procedures and physical methods.

Green chemistry is the design, development and implementation of chemical products and processes to reduce or eliminate the use and generation of hazardous substance to human health and the environment. In synthesis of metal nanoparticles by reduction of the corresponding metal salt solutions, there are three areas of opportunity to engage in green chemistry: (i) choice of solvent (ii) the reducing agent employed and (iii) the capping agent used.

The Manihot esculenta leaves possesses biomolecules, such as carbohydrates [16], protein and crude fibres, which could be used as reductants to react with copper ions and as scaffolds to direct the formation of Cu_2O nanoparticles in solution. Synthesis of Cu_2O nanoparticles from plant extracts using green method was also reported in our previous work [17, 18].

The Cu_2O nanopaticles composites with Si [19], Au [20], Ag [21], polymer [22], carbon nanotubes [23] and metal oxide have been prepared by many authors and investigated for its commercial applications.

MATERIALS AND METHODS

Materials
All the chemicals including $CuSO_4.5H_2O$, sodium citrate, sodium carbonate, potassium thiocyanate, potassium ferrocyanide and polyvinyl alcohol (PVA) were of analytical grade and were used as received from Merck without further purification.

Preparation of Benedict's reagent
Benedict's reagent is prepared by dissolving 10 g of sodium citrate, 3.75 g of sodium carbonate and 6.25 g of potassium thiocyanate in 32mL of hot distilled water. Then it is mixed with 5mL of 8.38% (w/v) of $CuSO_4.5H_2O$ solution followed by the addition of 0.3mL of a 5% solution of potassium ferrocyanide and the mixture is stirred well using a mechanical stirrer. The resultant solution is then made up to 50mL by adding distilled water.

Preparation of Manihot esculenta leaf extract
About 20g of freshly, taxonomically authenticated healthy leaves of Manihot esculenta were collected, washed thoroughly with distilled water, cut into fine pieces and boiled with 100mL distilled water in Erlenmeyer flask for 8-10 min. The extract was cooled to room temperature and filtered through Whattman filter paper (No.42).

Preparation of Cu_2O Nanoparticles
In a typical experiment, 10mL of the Manihot esculenta leaf extract was added to 10 mL of a Benedict's solution. After 10 minutes a brick-red precipitate was obtained, indicating the formation of cuprous oxide nanoparticles. The precipitate was then washed with distilled water and dried at room temperature.

Preparation of Cu_2O /PVA nano-composite
PVA was dissolved using distilled water in a beaker under heating condition. Then Cu_2O nanoparticles were added into PVA solution with stirring and the stirring was continued for 0.5hour. The resultant product was cooled at room temperature and dried in a hot air oven to get Cu_2O/PVA nano-composite.

Characterization
Characterization of the as-prepared Cu_2O nanoparticles and Cu_2O/PVA nano-composite was carried out by different analytical techniques. UV-VIS spectra were measured using a TU-1901 model UV- VIS double beam spectrophotometer (Beijing Purkinje General Instrument Co., Lt, China). FTIR spectra were performed and recorded with a Fourier-transform infrared spectrophotometer Nicolet 870 between 4000 and 400 cm[1], with a resolution of 4 cm^{-1}. The morphologies and compositions were examined by Scanning Electron Microscopy (SEM), using a LEO

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1455 VP equipped with energy dispersive. X-Ray Diffraction (XRD) patterns were recorded with a Philips analytical X-ray diffractometer using CuKα radiation (λ= 1.5406 Å).

RESULTS AND DISCUSSION

The addition of Benedict's solution to the leaf extract containing carbohydrates (glucose) which have aldehyde groups causes the reduction of copper ions resulting in the formation of brick red precipitate of Cu_2O. The chemical reaction may be expressed in the following equation:

$$RCHO + 2Cu^{2+} + 2H_2O \longrightarrow RCOOH + Cu_2O + 4H^+$$
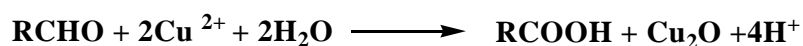
Therefore, we took advantage of the ready reactivity of solution with reducing sugars to innovate a facile method for the synthesis of Cu_2O nanoparticles.

Figure1 (a&b) shows the UV-Visible absorbance spectra of Cu_2O nanoparticles and Cu_2O/PVA nano-composite. The peak at 263 nm in Figure1 (a) is due to inter band transition of core electrons of copper and copper oxide [24]. The absorbance peak at 272 nm in fig.1 (b) shows that the absorption of Cu_2O in Cu_2O/PVA nano-composite was shifted from the original spectrum.
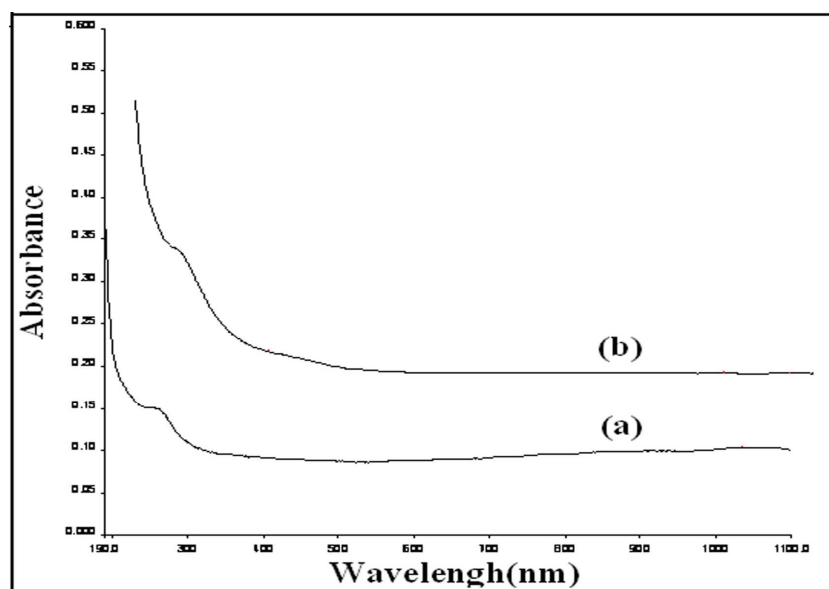

Fig. 1 UV-Vis spectrum of (a) Cu₂O nanoparticles and (b) Cu₂O/PVA nano-composite. .

Figure 2(a&b) shows FT-IR spectrum of Cu_2O nanoparticles and Cu_2O/PVA nano-composite. In Figure 2(a) the peak at 3374 cm^{-1} is the characteristic band of hydrogen bonded -OH groups present in the aqueous phase. The peaks at 1610 cm^{-1}(asymmetric) and1442 cm^{-1}(symmetric) indicate the presence of (-COO-) carboxylate ions, responsible for the formation of Cu_2O nanoparticles. The peak at 621 cm^{-1} indicates the vibration of Cu (I)-O in Cu_2O nanoparticles [25]. Figure 2(b) represents the O–H stretching vibration of PVA at 3442 cm^{-1} and Cu (I)-O vibration at 623 cm^{-1} in the prepared Cu_2O/PVA nano-composite. This shows the presence of Cu_2O particles in PVA network.
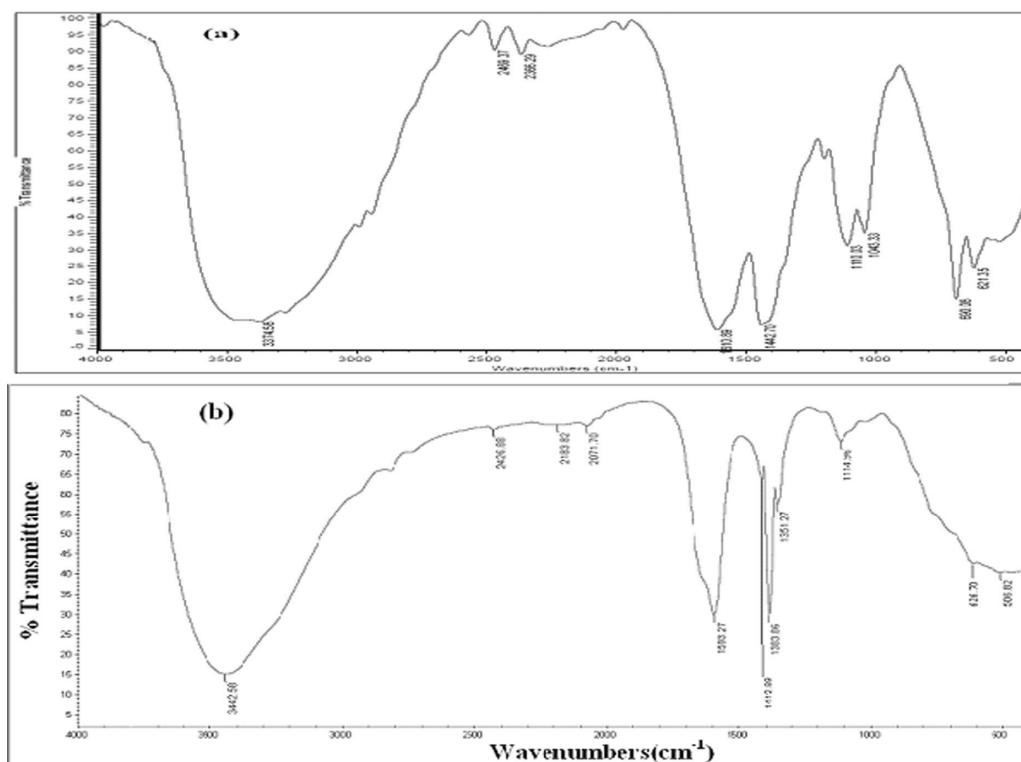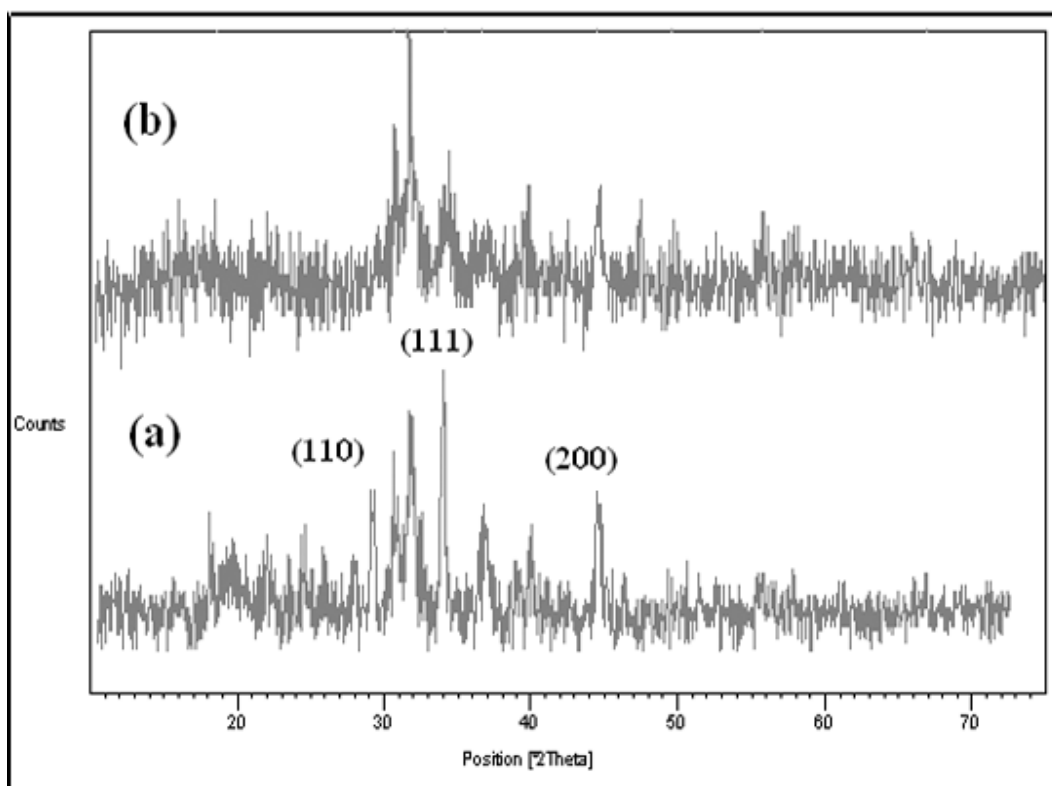
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Fig.2 FT-IR spectrum of (a) Cu₂O nanoparticles and (b) Cu₂O/PVA nano-composite.

Fig.3 XRD pattern of (a) Cu₂O nanoparticles and (b) Cu₂O/PVA nano-composite.

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Figure 3(a&b) shows X-ray diffractogram spectra for synthesized Cu_2O nanoparticles and Cu_2O/PVA nano-composite respectively. In fig.3a the peak positions are in good agreement with those for Cu_2O powder obtained from the International Center of Diffraction Data card (JCPDS file no. 05-0667) conforming the formation of Cu_2O nanoparticles. The peaks with 2 θ values of 29.26°, 36.19° and 43.59° correspond to the crystal planes of 110, 111 and 200 of crystalline Cu_2O, respectively. The crystallite size can be estimated using Scherrer's formula

$D = K\lambda/\beta\cos\theta$ where K is the constant which is to be 0.94, λ is the wavelength of X-ray, β and θ are the half width of the peak and the Bragg angle respectively. Using the equation, the crystallite size is found to be in the range of 50-80 nm. On comparison with Figures 3a and 3b, the peaks shown in Cu_2O nanoparticles are shifted in the Cu_2O/PVA nano-composite. This also shows the distribution of Cu_2O nanoparticles in the PVA network.

The morphologies of the synthesized Cu_2O nanoparticles and the resultant Cu_2O/PVA nano-composite were characterized by scanning electron microscopy. The SEM image (Figure 4a) show that shapes of the Cu_2O nanoparticles appeared like cubic and hexagonal with rough surfaces. The SEM image of Cu_2O/PVA nano-composite (Figure 4b) shows that the particle has core-shell structure and their surface is covered with PVA film. From this image it is observed that polyvinyl alcohol has irregular shaped Cu_2O particles dispersed in its composites.
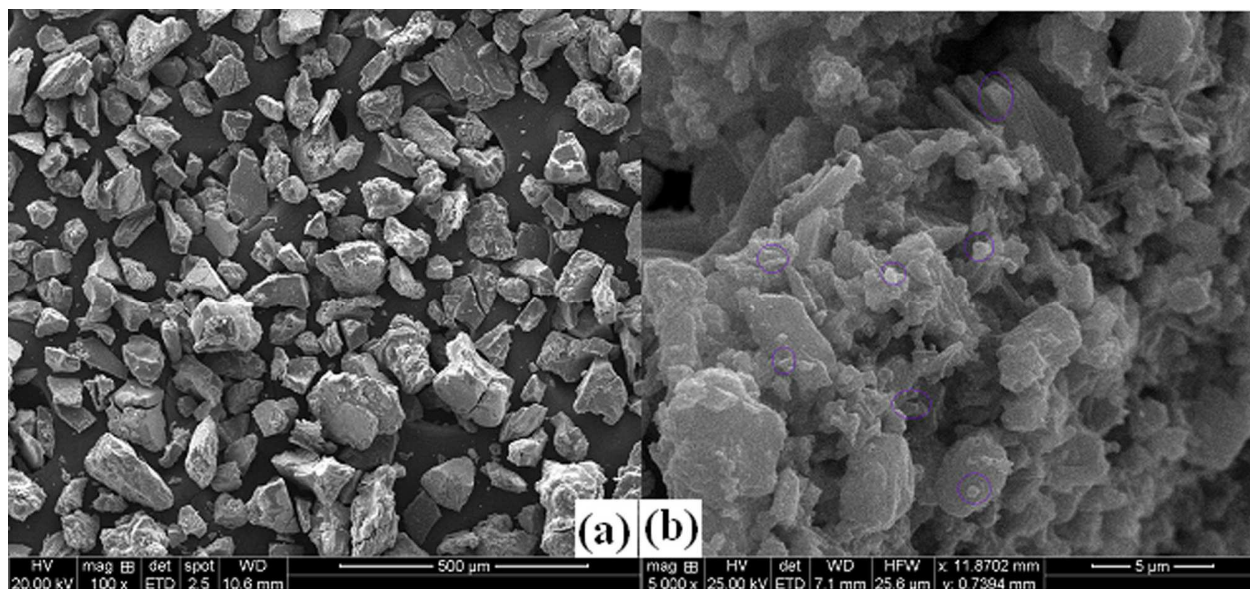

Fig. 4 SEM micrographs of (a) Cu_2O nanoparticles and (b) Cu_2O/PVA nano-composite

CONCLUSION

A rapid, eco-friendly synthesis process for Cu_2O nanoparticles using reducing sugars extracted from Manihot esculenta leaf has been demonstrated. The reduction of cuprous ions and stabilization of the Cu_2O nanoparticles is thought to occur through the participation of reducing sugars. From the morphological studies, it was noticed that Cu_2O particles were dispersed in PVA matrix. The distribution of Cu_2O particles in Cu_2O/PVA nano-composite was confirmed by scanning electron microscopy. Accordingly, it was revealed that PVA composite with Cu_2O nanoparticles, which could be prepared by simple green method.

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