Biological Synthesis of Cu$_2$O Nanoshells and its Optical Properties

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ABSTRACT

Using extract of fruits of pomegranate (Punica Granatum L.), the bulk amount of Cu$_2$O Nanoshells was synthesized rapidly with a very simple method. The as prepared sample was characterized by FESEM, TEM, UV-VIS spectroscopy and FTIR. The UV-VIS spectra and FTIR spectra confirmed the stability of Cu$_2$O nanoshells at room temperature even after longer time. Further the optical properties of Cu$_2$O nanoshells was investigated by using Photo Luminescence Spectra, which shows broad intense green luminescence. The fast growth of bulk amount of Cu$_2$O nanoshells was successfully achieved by optimizing the experimental conditions.

KEYWORDS: Cu$_2$O nanoparticles, Biological synthesis, nanoshells, Pomegranate extract, Cu2O nanoparticles

INTRODUCTION

From last decade, it is required to synthesize nanostructures with controlled manner and with simple method in bulk amount, so that it can be utilized in industry to fabricate optoelectronic devices in large scale. The P-type semiconductor material such as Copper oxide (Cu$_2$O) has gained profound interest due to its unique optical, magnetic and chemical properties [1-4]. The Cuprous oxide (Cu$_2$O) is p-type semiconductor material having direct bandgap of 2.2 eV. It is efficient solar light absorber and so provides the feasibility to build heterojunction solar cells with n-type materials such as TiO$_2$, ZnO etc.[5-6]. The biological applications such as antibacterial activity of Cu$_2$O nanoparticles was also demonstrated successfully [7-9]. Due to its electrical and optical properties Cu$_2$O can be utilized for various other applications like solar cells, gas sensing, magnetic resonance imaging (MRI) contrast agents, superconductor and battery applications (Lithium ion batteries) [10-15]. Recently, biosynthesis of nanoparticles has attracted attention because of the necessity to develop new clean, cost-effective and efficient synthesis techniques. The biosynthesis of Cu$_2$O nanoparticles has been carried out using brown algae (Bifurcaria bifurcate), Tridax procumbens leaf extract, Goose Berry (Phyllanthus Emblica) extract, Morganella psychrotolerans and extract of E-coli and via reverse micelles microemulsion [16-19].

In this paper the simple and fast method of biosynthesis of Cu$_2$O nanoshells has been discussed using extract of fruits of pomegranate (Punica Granatum L.). The optical properties of the Cu$_2$O nanoshells was investigated using UV-VIS spectra, FTIR spectra and Photoluminescence spectra. The as synthesized Cu$_2$O nanoshells would be potential candidate for using it for various industrial applications.
EXPERIMENTAL

The powder of Copper Sulphate (Cosmo Chem) was utilized as a precursor to synthesize Cu$_2$O nanoparticles. For the reduction of Cu$_2$O nanoparticles extract of pomegranate was used.

Preparation of extract

Fresh fruits of pomegranate were collected in Mortal and Pastel and crushed properly. After crushing the extract was filtered with help of Whatman’s filter paper No1 in beaker. The filtrate was then centrifuged at 5000 rpm for 2 min to remove any suspended material in the extract. Transparent and clean red colored extract was obtained. Extract was immediately used for the experiment.

Synthesis of Cu$_2$O nanoparticles

A 5% solution of Copper sulphate was prepared in deionized water, the solution was heated to 50 °C for completely dissolving the copper sulphate powder. After getting clear blue colored solution of CuSO$_4$, the 100 ml of extract was added in to it drop by drop in the 300 ml solution of copper sulphate (5%). Extract was added to the copper sulphate solution which was maintained at 50 °C using a hot plate. The extract was mixed with the copper sulphate solution using a magnetic stirrer. As soon as extract added drop by drop in to the CuSO$_4$ solution, the brown colored ppt was observed to form. The reaction was allowed to take place for 1 hr. at the same time the precipitate was allowed to settle down for one hour. After one-hour thick layer of copper brown color precipitate was settled at the bottom of the beaker.

The ppt was filtered and washed several times using DI water. The as prepared brown color ppt was layered on the glass substrate using Dr. Blade method. After drying it for 24 hours the sample was used for further characterizations. The sample was first characterized by X-ray diffractometer (XRD) (Shimadzu 6000) with Cu K$_\alpha$ radiation (λ=0.154 nm) and UV-VIS spectrometer. A field emission scanning electron microscope (FE-SEM) (JEOL JSM-6500F SEM) operating at 10 kV accelerating voltage was used for morphological studies of the products. To analyze the chemical composition, JEOL JEM-2010 transmission electron microscope (TEM) (200 kV), equipped with an energy-dispersive spectrometer (EDS) have been used. The photoluminescence property of the sample has also been explored.

RESULTS AND DISCUSSION

The as prepared samples were taken for further characterization. The Figure 1 depicts FESEM images of the sample. FESEM images clearly show the uniform morphology of Copper oxide nanoshells. The bunch of nanoshells is formed with the diameter ranging from 5 nm to 20 nm. The shape of nanoshells is irregular.
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**Fig. 1:** FESEM images of as prepared samples.

Figure 2 shows TEM and HRTEM images of Cu$_2$O nanoshells. The nanoshell is nearly of the size of 5 nm. From the HRTEM image the spacing between the fringes was calculated. The measured d-spacing (0.25 nm) confirmed the Cu$_2$O nanoshell structure.

**Fig. 2:** TEM and HRTEM image of Cu$_2$O nanoshells

**UV-VIS Spectra**

To monitor the synthesis of Cu$_2$O nanoshells, UV-visible absorption spectrum of Cu$_2$O samples was recorded after 48 hrs after synthesizing it. The above spectrum has one peak centered at 375 nm as shown in Figure 3. This obtained peak confirmed the stability of Cu$_2$O nanoshells at room temperature for longer time. It was observed that UV-visible absorption spectrum was showing same peak at 375 nm after even 2 months.
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**FTIR Spectra**

Figure 4 depicts FTIR spectrum of Cu$_2$O nanoshells synthesized by using fruits of pomegranate extract. In the above Figure the absorption peaks are located at 3336 cm$^{-1}$, 2920-2990 cm$^{-1}$, 1632 cm$^{-1}$ and 660 cm$^{-1}$. The 3336 cm$^{-1}$ peak is attributed to band of hydrogen bonded OH groups present in the aqueous extract. The peaks at 2920-2990 cm$^{-1}$ are indicating asymmetric and symmetric C-H stretching. The 1632 cm$^{-1}$ peak is attributed to the presence of (-COO-) carboxylate ions, responsible for stabilizing the Cu$_2$O nanoshells. The peak at 618 cm$^{-1}$ is assigned to Cu (I)-O vibration of Cu$_2$O nanoshells.

**Photo Luminescence Spectra**

To investigate about information related to excitons and transitions associated with excitons for Cu$_2$O nanoshells, Photoluminescence (PL) study was essential part of characterization. Figure 5 shows photoluminescence spectrum of Cu$_2$O Nanoshells. A broad intense green luminescence having peak at 538 nm (2.3 eV) is observed as shown in Figure 5. The green fluorescence is attributed to band to band transition of copper-oxide and also due to the transition between the donor level to the valance band, which in turn also depends upon the morphology of the nanoparticles [20].
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**Fig. 5:** Steady state room temperature photoluminescence (PL) spectra of the Cu$_2$O nanoshells.

The morphology of copper oxide nanoshells may have a strong effect on the optical properties and so it can be useful as a suitable material as visible light emitting material for fabrication of photo-electronic devices.

**CONCLUSION**

The simple, low cost, biosynthesis method was optimized for synthesis of Cu$_2$O nanoshells at room temperature using extract of fruits of pomegranate (*Punica Granatum* L.). The FESEM and TEM images confirmed the shell morphology of the Cu$_2$O nanoparticles. The stability and long ageing period of Cu$_2$O nanoshell was investigated using UV-VIS spectra. The FTIR spectra indicated the asymmetric and symmetric C-H stretching and presence of (-COO-) carboxylate ions, which was responsible for stabilizing the Cu$_2$O nanoshells. Photoluminescence (PL) study shows a broad intense green luminescence. Thus simple biological synthesis method of highly stable bulk amount of Cu$_2$O nanoshells having strong green emission may raise the chances of using this material for optoelectronic devices like fluorescent bio-labeling, photoelectrochemical devices and Light Emitting Diodes (LEDs) etc.

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