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Tinospora cordifolia mediated facile green synthesis of cupric oxide nanoparticles and their photocatalytic, antioxidant and antibacterial properties

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ABSTRACT

The study reports a facile method for the green synthesis of copper oxide nanoparticles (CuO Nps) by a solution combustion method using *Tinospora cordifolia* water extract. The Nps were characterized by XRD, SEM, TEM and UV–visible studies. XRD data indicates the formation of pure monoclinic crystallite structures of CuO Nps. SEM images show that the particles have sponge like structure with large surface area and the average crystallite sizes were found to be ~6–8 nm. These observations were confirmed by TEM analysis. Photocatalytic activity studies of CuO Nps reveal that they act as very good catalyst for the effective degradation of methylene blue (MB) in the presence of UV and Sun light. Also, the degradation of MB was found to be pH dependent. The Nps found to inhibit the activity of 1,1-Diphenyl-2-picrylhydrazyl (DPPH) free radicals effectively. CuO Nps exhibit significant bactericidal activity against *Klebsiella aerogenes*, *Pseudomonas aeruginosa*, *Escherichia coli* and *Staphylococcus aureus*. The study reveals a simple, ecofriendly and robust method for the synthesis of multifunctional CuO nanoparticle employing under-utilized medicinal plants.

1. Introduction

Industrial dyestuff contain one of the largest groups of organic compounds that lead to discoloration of water and cause great loss of aquatic life. The elimination of these colors and other organic materials is a priority for ensuring a safe and clean environment [1]. Advanced oxidation processes (AOPs) have been used during the last decade to degrade dyes in aqueous media without the formation of harmful by-products [2]. AOPs are based on the generation of very reactive species such as hydroxyl radicals ($OH^{\bullet}$) that oxidize a broad range of pollutants quickly. Irradiation sources have a vital role in enhancing the activity of catalysts, and UV radiation sources are widely used but they are also expensive and polluting [3]. CuO is one of the most important catalysts used to eliminate industrial effluents in the environment. Earlier studies indicate that the catalytic reaction is apparently a structure sensitive process and the oxygen surface lattice of

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CuO is involved in the reaction [4]. Catalytic reactivity of CuO nanostructures depends on the shape and the exposed crystal planes. Hence the architectural shape-controlled synthesis of CuO structures may be helpful for designing novel structures with preferred improved performance [5].

In the last few years, synthesis of metal oxide nanostructures with desired architecture has received significant attention due to their unique properties and applications [6,7]. Among metal oxides, cupric oxide (CuO) is a p-type semiconductor with a bandgap of 1.2 eV [8]. The synthesis and application of CuO Nps are of practical and fundamental importance. CuO is used in numerous applications like gas sensors [9], solar energy conversion [10], electrode material in lithium ion batteries [11], as field emitter [12] and as a heterogeneous catalyst [13]. Due to the versatile properties and diverse applications, various kinds of CuO nanostructures e.g. nanorods, nanosheets, and nanodendrites as well as honeycomb-like, urchin-like and dumbbell-like structures [14–17]. They have been synthesized using a variety of fabrication techniques including the chemical bath method, sol–gel method, gas phase oxidation, micro-emulsion, and many other techniques [18–21]. Recently, there have been several attempts to synthesize functional materials through greener approaches for achieving materials with variety of properties. Also, these methods avoid the extensive use of hazardous chemicals for the synthesis. Additionally, solution combustion synthesis is one of the best and easy methods for the synthesis approach towards the uniform mixing with combustible fuel. This is an exothermic reaction between oxidizing and reducing agents. Usually metal nitrates are used because of their unique solubility to form homogeneous solution. Metal nitrates act as oxidizer agents and fuel acts as reducing agents for the synthesis of CuO nano crystals [22,23].

In this paper, we report the green synthesis of CuO Nps via solution combustion synthesis using *Tinospora cordifolia* leaf extract of water for the first time. *T. cordifolia* commonly named as "Guduchi" in Sanskrit belongs to the family Menispermaceae. It is a genetically diverse, deciduous climbing shrub with greenish yellow typical flowers found at higher altitude [24,25]. It mainly contains alkaloids, diterpenoid lactones, glycosides, steroids, sesquiterpenoid, phenolics, aliphatic compounds and polysaccharides [26,27]. *T. cordifolia* leaf extract is extensively used in various herbal preparations which have anti-periodic, anti-spasmodic, anti-microbial, anti-osteoporotic, anti-inflammatory, anti-arthritic, anti-allergic and anti-diabetic properties [28]. Various components present in leaves of *T. cordifolia* (Fig. 1) are antioxidants and may act as good fuels for the preparation of Nps. Therefore, this study attempts to exploit *T. cordifolia* extract as fuel for the synthesis of CuO Nps. The procedure involves a self-sustained reaction in homogeneous solution of Copper nitrate and *T. cordifolia* extract.

2. Materials and methods

T. cordifolia leaves were sourced from Tumkur University Campus, Tumkur, Karnataka, India. The plant material was shade dried and powdered into 100 mesh size and stored at room temperature in an airtight container.

Fig. 1. Leaves of *Tinospora cordifolia*.

2.1. Preparation of the extract

The coarsely powdered plant material was mixed with water (1:10 proportion) and extracted at 100 °C with a reflux arrangement for 5 h. The extract was filtered and centrifuged to eliminate any un-dissolved material. It was then concentrated, dried using roto evaporator and stored in airtight bottles at 4 °C.

2.2. Synthesis of nanoparticles

CuO Nps were prepared by eco-friendly green combustion route using *T. cordifolia* plant leaf extract as fuel [29,30]. The Copper nitrate trihydrate was procured from Sigma-Aldrich (AR) and used without further purification. Exactly 1.205 g of $Cu(NO_3)_2 \cdot 3H_2O$ was dissolved with 0.2 g of *T. cordifolia* leaf extract in 10 ml of distilled water. The mixture was kept in a pre-heated muffle furnace at 400 ± 10 °C and subjected for combustion. The reaction was completed within 5 min. A fine black colored material was obtained. The synthesis of Nps was repeated with different concentrations of the plant extract such as 0.3, 0.4, and 0.5 g keeping copper nitrate concentration constant at 1.205 g. The obtained product was stored in airtight container until further use.

2.3. Structural and morphological studies

Optical properties of CuO Nps were measured using an UV–visible spectrophotometer (Thermo Scientific Evolution – 220). The sample was sonicated for uniform dispersion and the aqueous component was subsequently analyzed at room temperature for optical band gap (E_g) determination. The morphology of the Nps was assessed by Scanning Electron Microscopy (Hitachi – 7000 Table top) and TEM (TECNAIF-30). Phase purity and grain size were determined by using X-ray diffraction analysis using Shimadzu – 7000 with monochromatized Cu-Kα radiation. All experiments were performed in triplicates and the data