Optik 161 (2018) 204–216

Contents lists available at ScienceDirect

Optik

journal homepage: www.elsevier.de/ijleo

Original research article

Photo-Fenton degradation of nano-structured La doped CuO nanoparticles synthesized by combustion technique

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ARTICLE INFO

Article history:
Received 9 January 2018
Accepted 30 January 2018

Keywords:
Combustion synthesis
CuO
Lanthanum
Photocatalyst

ABSTRACT

In the development of nano structured materials, metal oxide nanoparticles are extensively pursued because of their promising applications due to their effective physio-chemical properties. In the midst of these fascinating metal oxides, copper oxide nanoparticles have received substantial acquaintance because of the exclusive electrical, optical, structural and catalytic chattels. The CuO nanoparticles owns supercilious physical and chemical properties which are reliant on the variation of the particle or crystallite size. A cost effective and time saving combustion synthesis was used to synthesize lanthanum doped copper oxide nanoparticles in order to investigate their structural, morphological and optical properties. The as-prepared nanoparticles were characterized by XRD, FT-IR, UV–vis, TEM and Raman spectroscopy. The crystallite size of the nanoparticles was determined by X-ray diffraction technique. By using FTIR, the fingerprint regions of vibrational bands of CuO were interpreted in the range of 300–600 cm^{-1}. The morphology of the agglomerated CuO nanoparticles was obtained from TEM. The UV-spectral analysis reveal the optical property and hence the optical band gap was found using Kubelka-Munk plot and the Raman spectroscopy was taken in the range of 200–1350 cm^{-1} to determine the microstructural nature of CuO nanoparticles. From the overall results, the effect of dopants on the CuO nanoparticles were studied and the photocatalytic characteristics of the synthesized samples were studied for degradation of Methylene Blue dye which was superintended by UV–vis spectrophotometric studies in the regular interval of time.

1. Introduction

At the present time, scientists are striving to unravel the dispute of the hygienic water crisis in the world which is growing out as a major issue with the swelling population rate. Owing to urbanization, the demand for hygienic water has mounted stupendously because of the contamination of the water reservoirs. Severe environmental issues have been caused due to the presence of various pollutants, for instance NO_2, CO_2, SO_2, organic dyes, gasoline and hydrocarbons generated from the industrial wastes [1]. Dyes are the major pollutants in various industries as they are used in the process of adding color to the

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https://doi.org/10.1016/j.ijleo.2018.01.125
0030-4026/

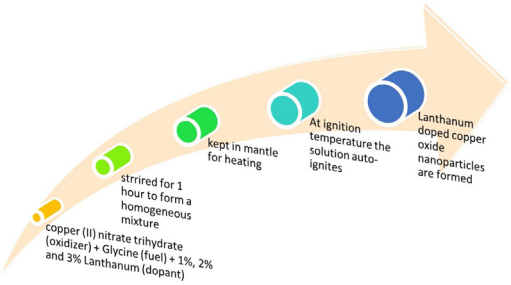

Fig. 1. Synthesis of CuO Nanoparticles procedure chart.

product which end up as toxic and are dangerous for micro-organisms and all living beings. Thus removal of dye from waste water is an astonishing challenge now a days. As a result, the evolution of nanotechnology and the tremendous advancement in nano materials paved a way to shrink these issues. The nano materials possess incomparable structural, morphological, electronic, optical and mechanical properties which were also a boon because they have large surface to volume ratio, special electronic properties, high chemical reactivity, increased activity and unique optical properties [2–6] when compared to their bulk. This facilitated the manufacturing of highly efficient devices, semiconductors, sensors, cells, photocatalyst etc., [7–9]. Out of this huge lot of nano materials, the transitional metal oxides [10] have attracted much consideration due to their vast illuminating properties. Among the known diversities of metal oxides, copper oxide nanoparticles hold unique physicochemical properties such as high reactive surface morphology, high surface to volume ratio, remarkable thermal stability, active sites and smaller particle size [11,12]. The copper oxide NPs are of monoclinic structure, a p-type semiconductor [13] with a narrow band gap 1.2 eV for bulk and is used for photoconductive, photothermal and photocatalytic applications [14–17]. A superior procedure, Advanced Oxidation Process (AOP's) reduces the concentration of toxicity in water from ppm to ppb range. So the photocatalytic technique in treatment of water was selected over other techniques such as quick oxidation, non-formation of polycyclic products etc., [18]. When the copper oxide is doped with rare earth elements they tend to possess a narrow band gap which lies in the visible region leading to a higher optical activity.

For the past few decades, numerous routes have been used in the synthesis of the metal oxides such as co-precipitation [19], sol-gel [20], hydrothermal, combustion synthesis, solvothermal [21,22], spray pyrolysis [23], sonochemical, wet-chemical [24], chemical reduction [25] and thermal decomposition of precursors. Among the known variety of synthesis, a rapid, time and cost effective combustion synthesis [26] process was selected to fabricate nanoparticles. Different parameters such as choice of fuels, oxidizer-fuel ratio, pH level play a vital role in the properties of the synthesized nanoparticles. In the present investigation we have induced trivalent La^{3+} ions in nominal percentages with the copper oxide nanoparticles and have reported the changes in structural [27], optical [28], morphological [29] and photocatalytic activity that are formed as a result of doping.

2. Experimental section

2.1. Chemicals

The AR graded Merck chemicals, copper (II) nitrate trihydrate $Cu(NO_3)_2{\cdot}3H_2O$, glycine $C_2H_5NO_2$ and lanthanum nitrate hexahydrate $La(NO_3)_3{\cdot}6H_2O$ were used without further purification for the synthesis of lanthanum doped copper oxide nanoparticles.

2.2. Synthesis of CuO nanoparticles

In general, salts such as nitrates, metal sulfates and carbonates can be used as an oxidants and glycine, urea, sucrose are used as a fuel. copper (II) nitrate trihydrate ($Cu(NO_3)_2{\cdot}3H_2O$) is an oxidizer and glycine ($C_2H_5NO_2$) is a fuel. As seen in Fig. 1, they are taken under a stoichiometric composition of redox mixture thus keeping the O/F ratio to unity, which was then dissolved in double distilled water. The lanthanum dopants were added in a mole percentage of 1, 2 and 3 in nitrate form with the solution which was then stirred at a constant speed for 1 h in a flat bottomed flask to form a homogenous mixture. The mixture was then heated using a mantle and when the solution reaches ignition temperature it auto-ignites with rapid propulsion of gases in large volume to form fine powder. The as-prepared powder was ground well and characterized to study its properties.

2.3. Photocatalytic activity

The degradation of the Methylene Blue (MB) dye in an aqueous solution under the visible light irradiation [30] with a 125 W mercury lamp as a light source. 50 mg of photo-catalyst was dispersed in 50 ml of 10 mg/l of MB aqueous solution. The suspension was magnetically stirred in dark conditions for 30 min to confirm desorption-adsorption equilibrium of MB