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Photoconductive network structured copper oxide for simultaneous photoelectrocatalytic degradation of antibiotic (tetracycline) and bacteria (*E. coli*)

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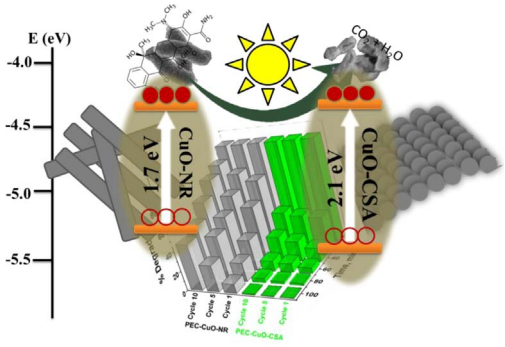
GRAPHICAL ABSTRACT



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ABSTRACT

As microbes develop resistance towards antibiotics, it is important to eliminate both from waste water streams simultaneously. Though photocatalysis is effective, complete removal can be achieved faster using photoelectrocatalysis (PEC) using photoconductive materials. Based on this idea, we have developed a network structured, high photoconductive copper oxide using solution combustion method. Various characterizations such as XRD, DRS, SEM, TEM, PL, XPS have been performed for a meticulous study of structural, optical, morphological and oxidation properties, respectively. CuO synthesized in this study possesses band gap of 2.1 eV, monoclinic structure, low recombination of charge carriers and shows much higher catalytic activity than copper oxide nano rods reported in the literature. Both antibiotics and bacteria have been simultaneously degraded via PEC. PEC exhibited a threefold higher rate of antibiotic degradation compared to photocatalysis. Reactive radical species such as electrons and superoxide radicals were illustrated to play a key role in accelerating the process of degradation. Notably, CuO-CSA was stable even after 10 cycles of reusability. A detailed mechanism of de-

Abbreviations: AB, antibiotic; hv, photon energy; h^+, hole; e^-, electron; I, intermediate; $O_2^{\cdot}$, superoxide radical; $OH^{\cdot}$, hydroxyl radical; EP, electrode potential; I_{light}, light; $C_{AB}0$, initial concentration of antibiotic; C_{AB}, concentration of antibiotic after time t; CuO, AB – adsorbed antibiotic on CuO surface; CuO, AB – h^+ and CuO – AB – e^- – electron and hole mediated adsorbed antibiotic species; CuO, I – adsorbed intermediate on CuO surface; A, B, C, kinetic parameters of photoelectrocatalysis; A′, B′, C′, kinetic parameters of electrocatalysis; A″, B″, C″, kinetic parameters of photocatalysis; L_{ij}, loop coefficient; λ_{ij}, segment coefficient; λ, pseudo first order rate coefficient of quasi – single molecular steps

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gradation PEC was developed and the cyclic network model was proposed for validation of the series of reactions. The degradation rate coefficients were obtained from this model. This work has important implications in the area of PEC for antibiotic and bacterial degradation.

1. Introduction

Untreated effluents from pharmaceutical industries, and hospitals leading to water, rivers and streams is an alarming environmental concern and causes water pollution [1,2]. Environmental Protection Agency (EPA) enumerates various hazardous pollutants [3,4]. Among various contaminants, antibiotics have a huge impact on our health by developing resistance among microorganisms [5,6]. This persistent increase of antibiotics in the ecosystem has led to an increase in specific or selective multidrug resistant bacteria [7]. In addition, the varying concentrations of selective antibiotics have triggered specific transcriptional processes in bacteria [8]. Similarly, the preferential adsorption of antibiotics had resulted in the increased concentration of antibiotics in the soil sediments near the treatment facilities [9].

Therefore, it becomes essential to develop reliable techniques to curtail the antibiotics pollution. RO combined with MBR (Membrane Bio Reactors) [10], ozonation, Fenton oxidation, sonolysis had resulted in better removal of antibiotics [11]. However, there are numerous technical barriers such as byproduct formations, safety hazards [12], high energy consumption [13], retrieval of Fe or reuse of Fe ion [14], huge power densities, acidic conditions [15], high cost, fouling of membranes and selective rejection of ionic species [16] that are associated with the aforementioned methods that impede their commercialization. Similarly, conventional UV photolysis is limited by the presence of aromatic rings, selective functional and photosensitive groups, radiation dosage, and contact time [17]. Therefore, unlike the waste water treatments of organics and heavy metals, special attention is necessary regarding bacteria, antibiotic and resistance developed bacterial decontamination from water.

Recently, heterogeneous catalysis in conjunction with advanced oxidation processes such as semiconductor photocatalysis has emerged as a promising technique [18]. Photocatalysis needs nanomaterials to produce reactive species such as electron, holes, hydroxyl and superoxide radicals for degrading chemical contaminants [19–22]. Many metal, non-metal, metal oxide and perovskite based photocatalysts have been employed for antibiotic degradation. However, these studies showed that better photoactivity and efficiency of antibiotic catalysis can be achieved only after surface modification by other semiconductors or incorporating noble metals and metal dopants [23–26].

Despite efficient light utilization, recent research has focused on modifications of photocatalysis for better sustainability to increase the rate of the reactions. Photoelectrocatalysis (PEC) has been considered as one of such emerging modifications [27–29]. PEC is the application of electric bias to a photocatalytic electrode or electrolyte consisting of photocatalysts that exhibits remarkable enhancement in the degradation rates due to the synergism between electrocatalysis and photocatalysis [30,31]. Similarly, fabrication of nanomaterials for various properties such as size, morphology and structure are predominantly governed by the synthesis route [18]. Therefore, the choice of method in synthesizing nanomaterials plays a crucial role in determining the photoactivity. Among several routes of synthesis [20], solution combustion method is easier, quick and economically viable [32,33]. The challenge of effective PEC involves developing a nanomaterial with low band gap and high conductivity. This study presents the degradation of tetracycline (antibiotic) by conventional photocatalysis and enhanced PEC methods. Copper oxide nanoparticles were synthesized using solution combustion technique. The efficacy of combustion synthesized catalyst was compared with copper oxide nanorods synthesized using hydrothermal method. All the catalysts were characterized for various properties using XRD, DRS, PL, SEM, TEM and photoconductivity.

The mechanistic aspect of PEC was developed by cyclic network model involving series of reactions. The kinetic model development is depend on the kind of photocatalysis operation (batch or continuous) [34–36]. Different kinetic models such as power law, Langmuir Hinshelwood (LH) models have been developed for degradation of phenols, dyes and antibiotics for batch operations with insignificant mass transfer resistance [34,35,37]. However, recently, the photoelectrocatalytic degradation kinetics of phenols was studied in micro channel reactors considering mass transfer resistance, due to diffusion dominance at such length scales of the reactor [36]. In photocatalysis or PEC, the kinetics can be proposed by elementary reaction with the possible intermediates. Instead of considering usual power law or LH kinetic models, rigorous network models were proposed and validated successfully with the experimental findings [30,38]. In the present study, the reaction pathways have been proposed with the help of scavenger experiments to understand the role of reaction intermediates in PEC and a detailed network model was developed. This is the first study to explore the degradation of antibiotics with PEC and also explore the simultaneous bacterial inactivation and antibiotic degradation.

2. Experimental

2.1. Materials

Copper nitrate trihydrate (≥98%), sodium hydroxide (≥99.5%), glycine (≥99%), urea (99%) and ascorbic acid (≥97%) were purchased from Merck (India). Tetracycline (≥96%) was procured from Sigma Aldrich (USA). Millipore water was used for all the synthesis.

2.2. Catalyst synthesis

2.2.1. Combustion synthesis of copper oxide nanoparticles

Copper oxide was synthesized using solution combustion method [39]. Stoichiometric quantities of copper nitrate as oxidizer and ascorbic acid as reducer were taken for combustion synthesis. Initially, 3.03 g and 1.10 g copper nitrate trihydrate and ascorbic acid were dissolved in a separate beaker with 15 mL of D.I. water, respectively. Both the solutions were mixed and sonicated for 10 min. The mixed solution was kept in muffle furnace maintained at 400 °C for 20 min. Later, when the mixture was introduced into preheated furnace, the solution started boiling and has undergone a rapid combustion (with sparks) forming copper oxide nanoparticles. After 20 min, a very less dense fluffy black powdered copper oxide nanoparticles were obtained (Video 1 of the solution combustion process can be found in the electronic supplementary information (ESI)). Similarly, copper oxide nanoparticles were also synthesized using various fuels such as glycine and urea by solution combustion method. Various fuels were chosen to understand the effect of amine, acid and amino acid mediated combustion of metal precursors. The nanoparticles synthesized using ascorbic acid, glycine and urea as fuels are denoted as CuO-CSA, CuO-CSG and CuO-CSU respectively.