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Copper particles decorated boron carbon nitride, an efficient catalyst for methyl orange oxidation under sonication and sunlight irradiation

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ABSTRACT

A simple and efficient method has been developed for synthesis of zerovalent copper decorated boron-carbon-nitrogen hybrid layers (Cu-BCN) and its application as a highly effective and reusable catalyst for wet oxidation of methyl orange (MO) under sonication and direct sunlight irradiation. Structural, chemical and morphological properties of as-prepared hybrid structures were thoroughly investigated. The catalytic performance of Cu-BCN studied with MO dye showed enhanced degradation efficiency with ultrasound as compared to direct sunlight irradiation. The effects of various experimental parameters like pH, catalyst loading, dye concentration, scavenger and enhancer on the efficiency of Cu-BCN in degrading MO dye solution under ultrasound irradiation were systematically studied. Experimental results suggested that the degradation efficiency enhances with increase of Cu-BCN dosage, whereas it decreases with increasing dye concentration, solution pH and radical scavenger. The role of Cu in the catalytic performance of Cu-BCN was studied with Cu particles (without BCN support) and BCN (without Cu particles). This proved that degradation of dye is only due to the synergistic effect of Cu and BCN in the hybrid material. The mechanism of MO degradation by Cu-BCN has been elucidated through kinetics of degradation process by calculating the rate constant. It is proposed that the radical formation and LSPR effect are responsible for the photo and sonocatalytic activity of Cu-BCN.

1. Introduction

Modern dyes are typically made resistant towards water, sunlight, detergents and other basic chemicals thus making them essentially more difficult to treat. Azo dyes, which constitute more than 50% of the global dye production (700,000 ton per year), are used in textile, pharmaceuticals and paper printing industries and about 15% of them are discharged into the effluent streams [1–3]. The discharged complex aromatic-conjugated azo dyes give intense colour to the water and are poisonous, carcinogenic and teratogenic to human beings and causes series of environmental issues to various life forms [3–5]. Therefore, removal of such pollutants becomes a major concern in wastewater effluent treatment before discharging to receiving water. Non-destructive methods of ultrafiltration, reverse osmosis, adsorption on activated carbon, coagulation by chemical inert, etc are expensive and cause secondary pollution which requires additional arrangement to remove the byproducts [6,7]. Hence, the advanced oxidation technologies such as photocatalysis, sonocatalysis, microwave degradation, Fenton's chemistry and gamma irradiation have been applied for complete removal of dye pollutants in waste water treatment [8]. An advanced oxidation process (AOP) is defined as a process that involves formation of highly reactive free radicals, such as $^{\bullet}OH$, $^{\bullet}O_2^-$, and $^{\bullet}O_2H$ and their subsequent reactions which can completely destroy the various organic pollutants present in waste water [9,10].

In recent years, zerovalent metals like zero-valent iron (ZVI) and copper have drawn considerable attention towards the treatment of pollutants and dyes [11–13]. Zhou et al. [11] have reported Fenton-like iron catalyst for degradation of azo dyes in aqueous solutions. In all these cases, the degradation reaction of azo-dyes is found to occur on the surface of metal. However, metal nanoparticles tend to aggregate, agglomerate which may result in loss of surface reactivity. Very few attempts were made to improve the surface area and catalytic activity of the nanoparticles. Li et al. [14] stabilized iron particles over double walled carbon nanotube and mixed metal oxide flakes where high dispersion and strong

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interaction between iron and carbon materials enhanced the catalytic activity of Fe based catalyst system for dye degradation. Xiong et al. [15] reported Cu decorated graphene, in which copper acts as an electron relay and thereby passes the excited electron from RGO sheets to adsorbed oxygen, thus leading to continuous generation of reactive oxygen species for the degradation of RhB.

Presently, two-dimensional nanosheets containing boron (B), nitrogen (N) and carbon (C) have shown tremendous potential in applications ranging from electronics to catalysis [16,17]. Several groups have reported that doping with carbon and oxygen within layered h-BN structures tend to modify the adsorption and emission properties of these materials. Our group has recently synthesized h-BNC and BCN structures showing high catalytic activity for oxygen reduction reaction and dye degradation under UV irradiation [18,19]. In this work, for the first time BCN has been used as a support material to disperse/encapsulate Cu nanoparticles via thermal treatment involving glycine, copper nitrate and B_2O_3. The degradation efficiency of the as-prepared Cu-BCN has increased manifold under ultrasound conditions as compared to uncapped Cu particles. Kinetics of the degradation process has also been studied by calculating the rate constant.

2. Experimental section

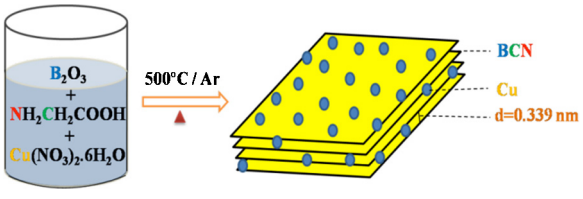
2.1. Experimental

The Cu-BCN catalyst was prepared via simple solution combustion technique in which boron trioxide (source of boron), glycine (source of carbon and nitrogen) and copper nitrate (source of copper) were taken in the ratio of 1:2:2. The mixture was dissolved in 10 ml deionised water and sonicated for 30 min. The resultant solution was then heated in a tubular furnace to 500 °C for 2 h with a heat rate of 2° per minute in an argon atmosphere. During combustion, reaction mixer reaches very high temperature (>1000 °C) which is a desired condition for formation of the Cu-BCN structure as shown in Scheme 1. The prepared product was washed with water to remove the residual B_2O_3 and dried at 80 °C in a vacuum oven.

Methyl orange dye solutions were prepared by mixing dye powder (10 mg) with distilled water (1 L) and stirring the solution for 30 min to obtain the homogeneous solution. The prepared Cu-BCN (10 mg) was added to methyl orange (MO) solution (10 ml) following that solution was subjected to sunlight irradiation (12 pm–3 pm @ Karaikudi town (geographical location 10.07° North and 78.78° East) in March 2015, 30–35 °C) with constant stirring and ultrasound energy (250 W and 40 kHz). The change in color from orange to clear solution indicated the degradation of MO dye.

2.2. Characterization techniques

Structural analysis of Cu-BCN was performed with X-ray diffraction (XRD) patterns obtained from Bruker D8 Advance powder X-ray diffractometer with Cu Kα radiation. Bonding characteristics were analysed with Fourier transform infrared spectrum (FTIR) using a Bruker TENSOR 27 with spectral a resolution of 0.125 cm^{-1}. Raman spectrum was recorded using a high-resolution Renishaw Raman microscope having He-Ne laser of 1 mW at 514 nm as the source. The chemical environment of an element was predicted using X-ray photoelectron spectroscopy (XPS) with Sigma probe X-Ray Photoelectron Spectrometer (Thermo Scientific, a MULTILAB 2000 Base system with X-Ray, Auger and ISS attachment) with Al Kα as source of X-Rays. The surface morphology of synthesized material was observed using a scanning electron microscope (SEM) (Bruker, Tescan vega3) with an accelerating voltage between 0.3–30 kV using SE detector. Energy-Dispersive X-ray (EDX) for elemental analysis was obtained with an EDAX detector installed on the SEM and the elements were mapped with a Philips-Tecnai F20 field-emission transmission electron microscopy (FE-TEM) apparatus operated at 200 kV. The graphitic layered structure and selected area electron diffraction (SAED) pattern were acquired from a transmission electron microscope (TEM) (FEI make, model Tecnai 20 G2). The optical absorption of dye was measured from UV-VIS-NIR double beam spectrometer (Cary 500 scan, VARIAN) with wavelength range from 200 to 800 nm. TOC (Total organic carbon) was measured with spectroquant Pharo 300 MERCK (Germany) using MERCK TOC kit no: 1.14878.0001 with measuring range 5–80 mg/l. The amount of the Cu metal leached into solution during dye degradation was analyzed and determined by ICP-AES (Perkin Elmer OPTIMA 3000). The amount of light absorbed was measured directly from the UV–vis absorbance spectra (see Table S1).



Scheme1. Synthesis of Cu decorated BCN using glycine-nitrate combustion reaction.

3. Results and discussion

3.1. Characterization of the catalysts

Cu-BCN was synthesized via one step thermal decomposition of the mixture of boron oxide, glycine and cupric nitrate. Fig. 1 shows the XRD pattern of Cu-BCN (Fig. 1a). The pattern for Cu-BCN shows sharp intense peaks at angles of $2\Theta = 43.33°$, 50.53° and 74.16° which correspond to the lattice planes of Cu at (111), (200) and (220), respectively [20,21]. A broad low intensity peak at 26.23° corresponds to diffraction pattern of amorphous BCN structure. The residual B_2O_3 phase at 14.91° and 28.08° [22] can be easily removed with simple water washing (Fig. 1b). Thus, XRD confirms the formation of Cu stabilized amorphous BCN structures. The fingerprint analysis of prepared Cu-BCN was carried out with FTIR spectrum shown in Fig. 1(c). The bands at 776 cm^{-1} and 1372 cm^{-1} are attributed to sp^2 hybridized B—N—B bending (out of plane) and B—N stretching vibrations (in plane) of hexagonal boron nitride phase (h-BN) [17,18]. The peaks at 1064 and 1438 cm^{-1} are due to cubical B—C vibrations and C—C stretching vibrations and at 1643 cm^{-1} is ascribed to sp^2 hybridized C=N stretching vibrations [23]. The band for C—N stretching vibration is observed at 1206 cm^{-1} [24]. Thus, it is clear from the FTIR that formed amorphous BCN is the result of hybridization of B—C, C—N and h—BN bonds. Raman spectroscopy (Fig. 1d) was used to investigate the structural characteristics of as-prepared Cu-BCN. The broad peaks at 1340 and 1552 cm^{-1} correspond to the D and G bands of amorphous B—C—N compounds [18].

The convoluted XPS spectra of Cu-BCN shown in Fig. 2 give further information about the chemical environment of different elements present in the material composition. The survey spectrum confirms the presence of B, C, N, O and Cu in the prepared material. The convoluted C1s spectrum has peak values at 283.72, 284.88 and 286.2 eV corresponding to C—B, C—C and C=N bonding [16] and the B1s spectrum has peak values at 188.68 and 190.12 eV which are related to the B—C and B—N bonding [23,24]. Similarly, the N1 s spectrum is convoluted into two peaks centred at 398.37 and 399.76 eV which are assigned to N—B and N—C