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NrGO wrapped Cu-ZrO_2 as a multifunctional visible-light-sensitive catalyst for advanced oxidation of pollutants and CO_2 reduction.

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A R T I C L E I N F O

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A B S T R A C T

Construction of tailor made photocatalyst is the need to achieve high visible light assimilation and charge carrier separation. In this path, combination of catalytic active element (Cu), defect rich metal oxide (ZrO_2) and photoactive (NrGO) is an effective strategy. Herein, NrGO wrapped Cu-ZrO_2 was prepared by modified Hummers-thermal annealing-hydrothermal approach. The synergism between Cu, Zr and NrGO was studied using transient photocurrent, EIS and TEM images. Consequently, O_3/NrGO@Cu-ZrO_2-10/Vis synergistic system has achieved superior photocatalytic ozonation-catalytic ozonation than individual photocatalysis and ozonation. Further, the advanced oxidation process was optimized and the catalyst was efficiently used for the reduction of CO_2 into useful products. Tolerance of O_3/NrGO@Cu-ZrO_2-10/Vis system against rhodamine B, hydroquinone, bisphenol A and p-cresol has been investigated. A plausible mechanism was proposed based on ESR studies, BODIPY fluoresence method, band gap and Mott-Schottky data. This research provides an idea of multifunctional catalyst for advanced oxidation of contaminants and CO_2 reduction.

1. Introduction

Currently, combination of ozonation with catalysis would effectively solve environmental pollution issue due to effluents [1–3]. On the other hand, there are constant efforts made by the researchers to find efficient strategies for the photoreduction of CO_2 in order to overcome the drawbacks of conventional CO_2 mitigation methods [4]. Ozone has strong oxidizing power that can be efficiently tapped for the separation of photostimulated charge-carriers thereby improving the overall photocatalysis [5]. Also, decomposition of ozone into reactive oxygen species would improve the degradation capacity by symbiotic effect between catalytic-ozonation and photocatalytic degradation [6,7]. However, our focus in the present research is the fabrication of a multifunctional catalyst that could achieve degradation of effluents in a synergistic mode, as well to reduce carbon dioxide into value added products. Many materials like titania [8], bismuth based [9], carbon based [10] and tungstic oxide [11] were explored as conventional photocatalytic materials, but they could not stimulate ozonation process and CO_2 reduction. Thus, success behind the photocatalytic ozonation-catalytic ozonation (POz-COz) and CO_2 reduction is the

Abbreviations: AO, ammonium oxalate; BODIPY, 1,3,5,7-tetramethyl-8-phenyl-4,4-difluoroboradiazaindacene; BQ, benzoquinone; Coz, catalytic ozonation; Cu-ZrO_2, copper doped ZrO_2; DMPO, 5,5-dimethyl-1-pyrroline N-oxide; E_{fb}, flat band potential; GO, graphene oxide; ITO, indium tin oxide; 4-NP, 4-nitrophenol; NrGO, nitrogen doped graphene oxide; PC, photocurrent; PL, photoluminescene; POz, photocatalytic ozonation; POz-Coz, photocatalytic ozonation-catalytic ozonation; PVP, polyvinylpyroolidine; rGO, reduced graphene oxide; RhB, rhodamine B dye; SP, sodium persulfate; TBA, tertiary butyl alcohol.

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