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Quaternary magnetic BiOCl/g-C_3N_4/Cu_2O/Fe_3O_4 nano-junction for visible light and solar powered degradation of sulfamethoxazole from aqueous environment

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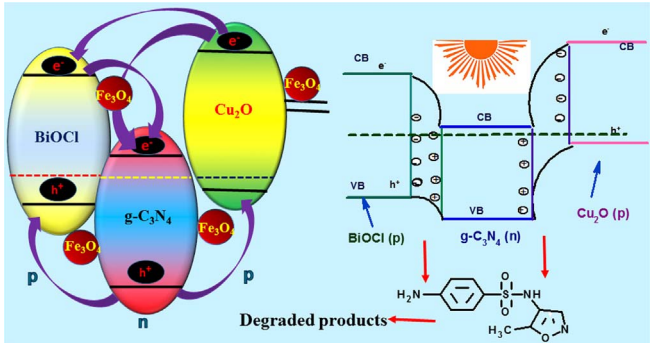
GRAPHICAL ABSTRACT



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ABSTRACT

Novel magnetic quaternary BiOCl/g-C_3N_4/Cu_2O/Fe_3O_4 (BGC-F) nano-heterojunction with excellent photocatalytic activity was prepared by facile co-precipitation method. The visible photodegradation activity of the junction was analyzed for sulfamethoxazole (SME) as target pollutant. BGC-F with a dosage of 0.2 g L^{-1} exhibits high photocatalytic activity with 99.5% of SME (100 μM) degraded in 60 min under visible (Xe) lamp and 92.1% in 120 min under natural sunlight. The activity of quaternary junction was found to be 7.2, 6.8 and 4.2-fold higher as compared to C_3N_4/BiOCl/Fe_3O_4, Cu_2O/BiOCl/Fe_3O_4 and Cu_2O/BiOCl/C_3N_4 junctions respectively. Formation of an effective p-n-p junction (BiOCl-C_3N_4-Cu_2O) leads to shifting of energy bands and rising of an in-built electric field and charge separation. The effect of parameters as pH, catalysts loading amount, NO_3^- and HCO_3^- have been studied. The $^{\cdot}O_2^-$ and $^{\cdot}OH$ was found to be major reactive species identified by scavenging experiments and the band gap structure analysis The results for mineralization were analyzed in terms of Liquid chromatography-mass spectroscopy (LC-MS), total organic carbon (TOC) removal and chemical oxygen demand (COD). 41.6% of TOC was removed in 3 h experiment under Xe lamp exposure. The drug degradation was also confirmed by testing activity on *E. coli* and cyto-toxicity on human peripheral blood lymphocytes (PBL). Only 2.1 mm zone of inhibition was observed for *E. coli* in case of exposure to SME degraded products while for pure SME it was 18.1 mm hinting complete mineralization. In addition 99% cell viability was observed for PBL cells

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treated with degraded products of SME. Furthermore, BGC-F exhibited good reusability after magnetic separation and regeneration, rendering it a promising multi-functional catalyst with active use of advanced oxidation processes for treating pharmaceutical waste water.

1. Introduction

Innovations in visible assisted photo-degradation of noxious organic pollutants is being considerably needed for practical environmental detoxification [1,2]. The insolent industrialization has led to discharge of untreated wastes from textile, pharmaceuticals, pesticides and cosmetics industries with deteriorating threats to flora and fauna [3–5]. Antibiotics are widely used for disease prevention in humans and animals and are one of most important part of pharmaceutical industry. However when they are released into aquatic environment, they become threat to aquatic life and environment because they eventually increase the drug resistance in pathogens [6]. Sulfamethoxazole (SME) is a broad spectrum antibiotic and used for both human as well as in animals to treat variety of infectious diseases [7–9]. SME has been documented to survive in the aquatic environment which comes from excretory waste as well as from pharmaceutical effluent [9,10]. Among various organic pollutants, antibiotics are challenging to remove via traditional methods as biological, chemical and adsorption. Many methods have been utilized for SME removal from real and simulated waste water systems like ozonation [11,12], adsorption [13], flocculation [14], membrane separation [15], biological treatment [16], electrolysis [17] and coagulation [18].

SME which is polar has been frequently detected in surface water as well as in drinking water in a concentration range of 60–150 ng L^{-1} and 10–12 ng L^{-1} respectively [19,20]. Thus mineralization of SME from water is indispensable to screen human and ecological health from its adverse effects. SME belongs to sulphonamides which can be bio-degraded but the process is to slow to be used for practical treatment. Other techniques are also not successful in removal of SME because of its low concentration in water and bio-refractory property. In addition many techniques are highly costly, slow and may not lead to complete mineralization for low concentration persistent pollutants. Advanced oxidation processes (heterogenous photocatalysis) have proven to be an efficient technique because of high degradation, greener approach, cost-effectiveness, lower toxicity, and ease of performance [2].

Recently, visible light driven heterogeneous photocatalysis has attracted research community owing to its green and low cost facets in the various fields such as environmental remediation, splitting of H_2O to hydrogen, CO_2 conversion to fuels etc. [21,22]. The heterostructure of different materials such as bismuth oxyhalide (BiOX, X = Cl, Br, I)), transition metal oxides (MO, M = Zn, Ti, Cu, Fe, Mn) have been extensively investigated [23,24]. BiOCl with indirect band gap 3.2–3.6 eV, has been studied by many researchers owing to its good biocompatibility, double layered structure and high chemical stability [25]. However, wide energy band gap limits its use for large practical applications as it performs in UV region.

The p-type semiconductor Cu_2O with properties such as excellent visible light response owing to its direct band gap 2.0–2.4 eV, natural abundance and non-toxic nature make it a propitious material for photocatalysis [26]. When Cu_2O undergoes photo-illumination the excited e^-/h^+ pairs are not efficiently separated leading to fast recombination rate which limits its photo activity and this hitch needs to be improved [27].

Recently, graphitic carbon nitride (g-C_3N_4) a metal free polymeric photocatalysts has been extensively used because of its unique merits like low band gap, inertness to chemical and thermal attacks, 2-D structure, eco-friendly nature and abundance of its precursor material [28,29]. g-C_3N_4 has a high degree of condensation and with a heptazine ring structure it shows good physicochemical properties and a medium range band gap [30]. Thus it has been used in heterogeneous catalysis, pollutant degradation, oxygen reduction reactions and water splitting [31,32]. However, it also suffers from low quantum yield because of high charge recombination rate of its photogenerated e^-/h^+ pairs, which might hinder the overall photo activity [33].

Furthermore, the popular photocatalysts suffer from drawbacks as ease of separation, lower visible absorption, low surface area and high recombination [34]. This limitation is mainly associated with single-component photocatalysts which can be overcome by fabricating the heterojunction which not only improves the photo-activity but also decreases the e^-/h^+ pair charge recombination rate significantly [35,36]. Recently various novel carbon nitride based heterojunctions as g-C_3N_4/$CuCr_2O_4$ [37], BiOBr/Iron oxides [38], coal char/g-C_3N_4/RGO [39], g-C_3N_4/Fe_3O_4/Ag/Ag_2SO_3 [40], g-C_3N_4/Fe_3O_4/AgI/Bi_2S_3 [41], BiOBr/BiOI/Fe_3O_4 [42] have been utilized for photodegradation of aquatic pollutants. Since current waste water treatment technologies and materials are insufficient in degradation of pharamaceuticals as SME, it is important to design responsive materials which can utilize the existing advanced oxidation processes in a rational manner. Hence a systematic experimental study has been made in this laboratory scale work to utilize quaternary nano-photocatalyst BiOCl/g-C_3N_4/Cu_2O/

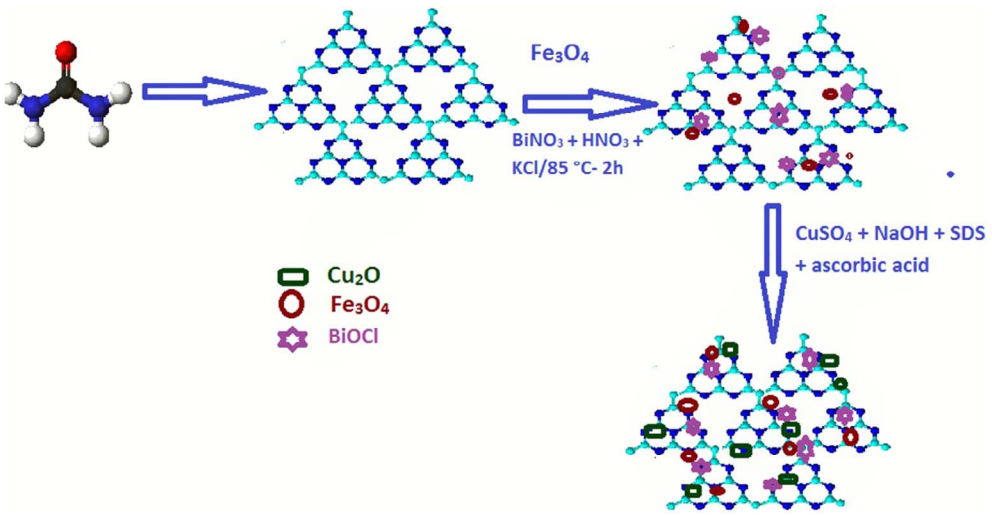

Fig. 1. Synthesis scheme for BGC-F.