

Short Communication

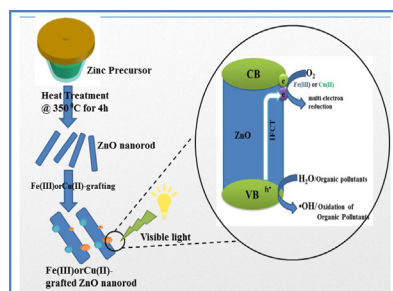
Synthesis of iron and copper cluster-grafted zinc oxide nanorod with enhanced visible-light-induced photocatalytic activity

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HIGHLIGHTS

- Thermal decomposition cum impregnation of Fe(III)-Cu(II) over ZnO.
- Visible light photocatalytic degradation of RhB, 4-NP and Paracetamol.
- Fe(III)-grafted ZnO nanorod showed profound activity over Cu(II) and pure ZnO.
- Role of Fe(III) in activity enhancement with detailed photocatalytic mechanism.

GRAPHICAL ABSTRACT



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ABSTRACT

Design of visible-light-responsive photocatalyst employing simple and cost-effective method is of great importance from commercial point of view. Herein, we report the synthesis of visible-light-sensitive ubiquitous nanoclusters of Fe³⁺/Cu²⁺-grafted ZnO nanorod using impregnation technique, which showed excellent photocatalytic activity towards the decomposition of Rhodamine B (RhB), 4-nitrophenol (4-NP) and paracetamol in aqueous suspension under atmospheric oxygen. Fe-grafted ZnO nanorod exhibited pronounced effect for the degradation of the above-mentioned pollutants compared to pure ZnO and Cu-grafted ZnO nanorod. The better activity could be due to the more positive redox potential of surface grafted Fe³⁺ species resulting in the generation of more hydroxyl radicals thereby, leading to higher photodegradation rate.

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1. Introduction

In recent years, the problem of water contamination caused by textile and pharmaceutical industries has become a serious environmental issue [1], which could be globally tackled by looking for an economical method for detoxification of such contaminants. In this regard, semiconductor-based photocatalysis has received increasing interest owing to its environmental benignancy and

cost-effect [1–3]. Among various semiconducting materials, TiO₂ has been known to have excellent photocatalytic activity and considered as benchmark material in the arena of photocatalysis [4,5]. Alternatively, Zinc oxide has also been used as a photocatalyst owing to its non-toxic nature, availability and stability [6]. The mechanistic principle of ZnO is similar to that of TiO₂ for degradation of organic pollutants, therefore, it has perceived a suitable alternative in the field of environmental remediation [7,8]. Recently, efforts have been made to modify ZnO by doping and deposition of metals in order to expand the spectral response to longer wavelength with an aim to enhance the photocatalytic activity in the visible region [7]. Despite above achievements, the

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quantum efficiency of most modified ZnO still remains unsatisfactory for practical applications because the impurity state created by metals reduces the reduction power of electrons and also acts as recombination center [9,10]. It has been well established that anion-doping creates isolated states above the valence band of semiconductor which lowers the oxidative power and mobility of the holes and thus curtails the photocatalytic activity [11,12]. Therefore, it is highly desirable to explore ZnO without altering its valence band state that leads to an efficient photocatalyst from vantage point of practical application.

Recently, increasing attention has been devoted to the surface modification of semiconductive oxides with Cu(II) or Fe(III), which showed excellent photocatalytic activity towards the decomposition of organic pollutants through a well-known interfacial charge transfer (IFCT) mechanism [13–15]. According to this mechanism, electrons can be directly moved to the surface grafted $\text{Fe}^{3+}/\text{Cu}^{2+}$ clusters upon irradiation and simultaneously holes present in the VB of catalyst could lead to complete oxidation of organic pollutants. These systems not only consume the photogenerated electron via the reduction process of the grafted metallic ions, taking benefit of the deep valence band holes for the oxidation reactions, but also increase the spectral sensitivity from UV to visible light region of the solar spectrum. Hashimoto and co-workers have first developed the visible-light-sensitive photocatalyst by grafting Fe(III) and Cu(II) on the surface of TiO_2 and evaluated their photocatalytic activity through the degradation of gaseous pollutants [16–18]. Later on, TiO_2 has also been modified by anchoring nanocluster of Fe^{3+} for degradation of liquid phase organic pollutants under visible light source [19,20]. The above results prompted us to develop visible light responsive photocatalyst by surface grafting of ubiquitous clusters using impregnation technique. In the present work, surface modified ZnO nanorod grafted with Fe(III)/Cu(II) has been synthesized using thermal decomposition of zinc acetate dihydrate followed by impregnation technique. The synthesized materials were characterized by standard techniques and their activity was tested by studying the degradation of a few selected priority organic pollutants in aqueous suspension under visible light source.

2. Experimental section

2.1. Materials and characterization

The relevant information such as details of materials used, preparation of ZnO nanorod, instrumentation used for the characterization of catalysts, procedure involved in testing of photocatalytic activity and quantification of hydroxyl radicals are provided in the [Supporting information](#).

3. Results and discussion

Fig. 1a shows the XRD spectra of pure ZnO nanorod and Cu(II)/Fe(III)-grafted ZnO nanorod. In all cases, similar distinct peaks were found showing wurtzite structure of ZnO. No peak corresponding to Fe_2O_3 , CuO or Fe/Cu-containing phases were detected, indicating the successful dispersion of Cu(II) and Fe(III) on the surface of ZnO nanorod. The results suggest that the graft of Cu/Fe are present in the form of amorphous Cu(II) or Fe(III) oxide nanocluster on the surface of ZnO which is again confirmed by TEM and EPR measurements.

UV–Vis diffuse reflectance spectra of pure and Cu(II)/Fe(III)-grafted ZnO are shown in **Fig. 1b**. It could be seen from the figure that pure ZnO nanorod showed an absorption onset at 393 nm which infers to the band to band transition characteristics of pure ZnO. The surface grafted ZnO with Fe(III) showed an absorption

band in the region from 450 to 550 nm attributed to the interfacial charge transfer (IFCT) from the valence band of ZnO to Fe(III) [14]. It is pertinent to mention here that this optical absorption is responsible for driving the degradation reaction more efficiently under visible light source [13]. The band gap energies of the prepared samples were calculated from the Tauc plot shown in **Fig. S2** [plot of $(ah\nu)^2$ vs photon energy ($h\nu$)] and the details are provided in [Supporting information](#).

The morphology and structure of pure and Fe(III)-grafted ZnO nanorod were examined by SEM and TEM analyses and the results are depicted in **Figs. S3(a,b)** and **2(a,b)**, respectively. It could be seen from the **Fig. S3(a,b)** that both the samples (pure as well as Fe-grafted ZnO) are found to have rod-like morphology with lower agglomeration. **Fig. 2(a,b)** shows the TEM image of pure and Fe-grafted ZnO nanorod. **Fig. 2a** clearly indicates the sample being in uniform nanorod shape with a diameter of ~15–20 nm, whereas in the case of Fe-grafted ZnO (**Fig. 2b**), nanocluster of Fe(III) could be clearly seen on the surface of ZnO nanorod, indicating the successful grafting of Fe on the surface of the catalyst. The existence of elements such as Fe, Zn and O in Fe-grafted ZnO nanorod was confirmed by acquiring energy dispersive spectra (EDS) attached to SEM as depicted in **Fig. S3c**. In addition, the existence of Cu on the surface of ZnO was further confirmed by the reaction of ammonia with Cu-grafted ZnO in a separate experiment. In this reaction, impregnated Cu-grafted ZnO (heated at 120 °C) produces a typical blue tetraamminecopper(II) complex, while the Cu-grafted ZnO calcined at 500 °C does not show any color upon addition of ammonia as shown in **Fig. S3d**. These results infer that the chemical nature of Cu(II) was found to change after calcination, perhaps migrated from the surface to the bulk on heating at 500 °C.

To further provide conclusive evidence for the existence of clusters of Cu(II) and Fe(III) on the surface ZnO nanorod, EPR measurements were carried out at room temperature and the results are depicted in **Fig. S4(a,b)**. It is well known that Cu(II) contains unpaired electrons in their outer shell which contributes to the EPR signal as presented in **Fig. S4a**. This signal gives the information about the presence of Cu(II) on the surface of ZnO nanorod. In the case of Fe(III) as shown in **Fig. S4b**, a signal at g value of 4.29 implies the characteristic feature of a high spin Fe^{3+} located in a strongly distorted rhombic environment [20], which is well supported by TEM results where small clusters of Fe(III) appear on the surface of the ZnO nanorod. It is obvious from the results that the single isolated Cu(II) and Fe(III) surface sites are present on the surface of ZnO nanorod.

The photocatalytic performance of pure and Fe(III)/Cu(II)-grafted ZnO nanorod was evaluated by studying the degradation of Rhodamine B (RhB), 4-nitrophenol (4-NP) and paracetamol under visible light irradiation in aqueous suspension. **Fig. S5(a,b)** shows the time-dependent UV–Vis absorption spectra of 4-NP and RhB in the presence of Fe-grafted ZnO nanorod on irradiation in aqueous suspension in the presence of visible light. The absorption intensity of 4-NP and RhB decreases with the increase of irradiation time as observed by the decrease in their characteristics $\lambda_{\text{max}} = 405$ nm and 553 nm, respectively. Control irradiation experiments in the absence of catalyst with both pollutants indicate negligible loss, manifesting the role of catalyst for efficient degradation of the pollutants. **Fig. 3(a,b)** shows the change in concentration of 4-NP and RhB as a function of time on irradiation in aqueous suspension in the presence of different samples. The results indicate that the enhanced photocatalytic activity was observed in the case of Fe(III)-grafted ZnO nanorod as compared to pure and Cu(II)-grafted ZnO nanorod for degradation of both pollutants under investigation. The results reveal that around 68.6 and 93.2% degradation of 4-NP and RhB were achieved after 240 and 120 min of illumination time in the presence of Fe-grafted ZnO. In the case of RhB, when irradiation was carried out with pure ZnO some

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