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ZnO/γ-Fe_2O_3 charge transfer interface in zinc-iron oxide hollow cages towards efficient photodegradation of industrial dyes and methanol electrooxidation

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ABSTRACT

Zinc-iron oxide hollow cages have been successfully synthesized in the form of thin films using a facile and template free electrochemical technique. The material has been structurally established using X-ray diffraction, transmission electron microscopy, field emission scanning electron microscopy, X-ray photoelectron spectroscopy, electron paramagnetic resonance spectroscopy and UV–Vis spectroscopy. The photocatalytic performance of the material has been explored by investigating the photodegradation of three widely used industrial dyes viz. Methylene Blue, Rose Bengal, and Solochrome Black-T. The synergistic integration between ZnO/γ-Fe_2O_3 caused effective charge transfer mechanism and made the material an excellent photocatalyst as well as an electrode for the electrooxidation of methanol.

1. Introduction

In 1955, Markham first showed the photocatalytic degradation of organic compounds using various metal oxides such as ZnO, Sb_2O_3, and TiO_2. Later on, Bard et al. and several other groups made significant contribution to the photodegradation properties of metal oxides and studied the effect of noble metals on the metal oxide semiconductors, which act as co-catalyst [1,2]. Even though many groups argued on the efficiency of these semiconductor metal oxide photocatalysts in terms of nature of the oxidative agents ($OH^{\cdot}$ vs hole, generated under illumination); study of semiconductor metal oxide based photocatalysis has always been fascinating to the scientists. In 1984, Sherpon et al. for the first time came up with encouraging solution by attaining enhanced photocatalytic efficiency by coupling two semiconductors viz. CdS and TiO_2, resulting in the formation of a multi-component heterostructure [3–5]. Recently, surface functionalized metal-oxide heterostructures have been found to exhibit enhanced photocatalysis and gas sensing property [6]. In order to carry out effective photocatalysis by generating $^{\cdot}OH$ radicals, the valance band must be sufficiently positive (with respect to NHE) with adequate concentration of holes; as we are considering a composite system constituting two n-type semiconductors (ZnO/γ-Fe_2O_3) [7]. Therefore, in this study, we have chosen ZnO which is one of the most popular photocatalyst owing to its high thermal stability, position of defect levels and photosensitivity [8–12]. However, with ZnO, the major drawback is high charge recombination rate and lack of effective absorption in visible light region due to its wide band gap (Eg = 3.2 eV) [13,14]. Thus, in order to reduce recombination and improve carrier generation, ZnO can be coupled with a comparatively narrow band gap semiconductor, as in our case, γ-Fe_2O_3, which facilitates electron-hole transfer thereby reducing recombination of carrier in the ZnO/γ-Fe_2O_3 heterostructure. Moreover, ZnO films can easily get dissolved in low pH medium and they also suffers from photocorrosion on prolong exposure to light. On the other hand, γ-Fe_2O_3 is not only a thermodynamically stable material, but also highly resistant to photocorrosion [15]. Thus, on coupling ZnO with γ-Fe_2O_3, resistance to both photocorrosion and chemical corrosion of the synthesized heterostructured catalyst can be achieved, which, however, is not achievable with ZnO alone [16–17]. The absorption onset of γ-Fe_2O_3 falls within 600–750 nm; due to its band gap energy (E_g) 1.7–2.1 eV, making it a suitable candidate to combine with ZnO to harvest visible light to carry out photocatalysis. Recently, Wei et al. synthesised γ-Fe_2O_3/ZnO composites with different γ-Fe_2O_3 contents via

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aqueous solution route to evaluate the photocatalytic activity of the as-prepared composites towards the degradation of pentachlorophenol (PCP) in aqueous solution under UV–Vis light irradiation [18]. Jiang et al. reported spindle-like mesoporous γ-Fe_2O_3/ZnO core-shell heterostructures by seed-mediated strategy with the help of post-annealing treatment [19]. Scneider et al. fabricated ZnO/γ-Fe_2O_3 heterostructures based on the hydrolysis of $FeCl_3$ in the presence of ZnO nanoparticles which also came out as a good photocatalyst [20]. Furthermore, metal oxide semiconductors and modified metal oxide semiconductors are also famous for their applications as electrodes for electrooxidation and electrochemical sensing of several organic and organometallic compounds [21–25]. In this field also, ZnO is one of the most studied materials, however, the use of ZnO/γ-Fe_2O_3 heterostructure for the electrooxidation of methanol, which is known to have toxic effects, is quite unexplored to the best of our knowledge.

Here we are reporting a facile route for the synthesis of thin films of ZnO/γ-Fe_2O_3 heterostructure via an *in situ* electrodeposition technique from the precursor solutions $ZnSO_4$ and Mohr's Salt, followed by post annealing treatment. These films were found to show excellent photocatalytic properties towards the degradation of three dyes, viz. Rose Bengal (RB), Methylene Blue (MB) and Solochrome Black T (SBT). The photocatalytic activities of ZnO/γ-Fe_2O_3 nanocomposite were systematically explored by monitoring the lowering of intensities of the specific absorption peak of aqueous dye solutions. The deposited material was also found to exhibit significant electrocatalytic activities towards methanol oxidation reaction. The electrocatalytic activities were measured by studying the current-voltage and chronoamperometric properties of methanol in phosphate buffer solution.

2. Experimental section

2.1. Materials

Commercially available zinc sulphate heptahydrate ($ZnSO_4 \cdot 7H_2O$), ammonium iron (II) sulphate or Mohr's Salt [$(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$], methanol (anhydrous, 99.8%), potassium hydrogen phosphate (K_2HPO_4) and potassium dihydrogen phosphate (KH_2PO_4) were procured from Sigma-Aldrich. Methylene Blue (MB), Rose Bengal (RB) and Solochrome Black-T (SBT) were purchased from Merck. All chemicals were of analytical grade and used without further purification.

2.2. Synthesis of ZnO/γ-Fe_2O_3 hollow cages

For the *in situ* synthesis of thin films of ZnO/γ-Fe_2O_3 heterostructures, we have chosen a modified galvanic route. In this case, 100 ml of working electrolytic solution was prepared by directly dissolving requisite amount (by weight) of zinc sulphate heptahydrate and Mohr's salt in 100 ml of Millipore water (18 MΩ) so that the final concentration of $ZnSO_4$ and Mohr's salt in the working solution becomes 0.01 M and 0.004 M, respectively. The pH of the working solution was c.a. 6.5. The fluorine doped tin oxide (FTO) coated glass substrates were used as the working electrode for the cathodic deposition of the desired material. The FTO coated glass substrates were first subjected to ultrasonication in acetone medium followed by boiling in anhydrous methanol for proper cleaning. The cleaned FTO substrates along with a metallic Zn rod (>99% purity) were then immersed in beaker containing the working solution by proper clipping and connected externally by a conducting wire. The distance between the FTO glass and Zn rod was maintained as 2 cm and the active area of the FTO substrate that was immersed into the working solution was fixed to be 2.5×2.5 cm^2. Here, FTO substrate acts as the cathode and the Zn rod acts as a sacrificial anode. The schematic of the system has been provided as Scheme 1. On short circuiting the FTO substrate with Zn rod, oxidation of Zn takes place at the metal-electrolyte interface (as E^o_{ox} of the system $Zn \rightarrow Zn^{2+} + 2e$ is +0.76 V), resulting in Zn^{2+} ions which migrate to the solution. The electrons that were released on the Zn surface instantly migrate to the FTO substrate through the external conducting wire and make FTO as the electron rich or cathode. The Fe^{2+} and Zn^{2+} ions present in the solution will then migrate to the FTO cathode and on the vicinity of the cathode, they will react with the OH^- ions available in the aqueous medium to form the corresponding metal hydroxides viz. $Fe(OH)_2$ and $Zn(OH)_2$. The almost equal ionic mobility of Fe^{2+} ($\mu^*_{eff} = 9.93 \times 10^9$ m^2 S^{-1} V^{-1}) and Zn^{2+} ($\mu^*_{eff} = 7.65 \times 10^9$ m^2 S^{-1} V^{-1}) helps in co-deposition of the respective metal hydroxides in nearly 1:1 ratio. So, on the cathode surface, a film containing both iron and zinc hydroxides will be formed which is then converted to ZnO/γ-Fe_2O_3 heterostructure on post deposition annealing at 600 °C for 15 min in air. The deposition was carried out for 6 h at 27 °C. The following reactions are supposed to be involved in the system:

In solution:

$$Zn \rightarrow Zn^{2+} + 2e \quad E^o_{ox} = +0.76\ V \tag{1}$$

$$(NH_4)_2Fe(SO_4)_2 \rightarrow 2NH_4^+ + Fe^{2+} + 2SO_4^= \tag{2}$$

$$ZnSO_4 \rightarrow Zn^{2+} + SO_4^= \tag{3}$$

$$H_2O = H^+ + OH^- \tag{4}$$

At anode:

$$Zn \rightarrow Zn^{2+} + 2e^- \quad (E^o_{ox} = +0.76\ V) \tag{5}$$

On cathode surface [26]:

$$Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2 \tag{6}$$

$$3Fe(OH)_2 + 1/2O_2 \rightarrow Fe(OH)_2 + 2FeO(OH) + H_2O \quad [26] \tag{7}$$

$$Fe(OH)_2 + OH^- \rightarrow FeO(OH) + H_2O \quad [26] \tag{8}$$

$$Zn^{2+} + 2OH^- \rightarrow Zn(OH)_2 \tag{9}$$

On annealing:

$$Fe(OH)_2 + FeO(OH) + Zn(OH)_2 \rightarrow ZnO/\gamma\text{-}Fe_2O_3 \tag{10}$$

The presence of NH_4^+ ions in the solution helps to maintain the pH c. a. 6.5 and due to the nearly neutral pH, the working solution was almost clear, indicating negligible extent of chemical reactions among the constituents of the working solution.

2.3. Characterization

The phase purity and crystal structure of the deposited material was investigated using X-ray diffraction (XRD, Philips PANalytical X'PERT Pro, parallel beam geometry, Bragg-Brentano goniometer, source Co Kα, λ = 1.78897 Å) technique. To determine the spin state of iron (i.e. either Fe(II) and/or Fe(III)) electron paramagnetic resonance (EPR) spectroscopy was carried out using an EPR spectrometer (JEOL-JES FA200) with X-Band frequency: 8.75–9.65 GHz, Sensitivity: 7 × 109 spins/0.1 mT, Resolution: 2.35 μT. The morphology of the deposited films was examined by a field-emission scanning electron microscope (FESEM Carl Zeiss, Sigma). Transmission electron microscopy (TEM, JEM 2100) was further carried out to have an in depth idea about the crystal structure of the ZnO/γ-Fe_2O_3 heterostructure. The composition of the prepared material was analysed using X-ray photo-electron spectroscopy (XPS, PHI 5000 VersaProbeII, Japan) with micro-focused