Synthesis and Characterization of Photocatalytic $\text{TiO}_2\text{-ZnFe}_2\text{O}_4$ Nanoparticles

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A new coprecipitation/hydrolysis synthesis route is used to create a $\text{TiO}_2\text{-ZnFe}_2\text{O}_4$ nanocomposite that is directed towards extending the photoresponse of TiO_2 from UV to visible wavelengths ($> 400\text{ nm}$). The effect of TiO_2 's accelerated anatase-rutile phase transformation due to the presence of the coupled ZnFe_2O_4 narrow-bandgap semiconductor is evaluated. The transformation's dependence on pH, calcinations temperature, particle size, and ZnFe_2O_4 concentration has been analyzed using XRD, SEM, and UV-visible spectrometry. The requirements for retaining the highly photoactive anatase phase present in a ZnFe_2O_4 nanocomposite are outlined. The visible-light-activated photocatalytic activity of the $\text{TiO}_2\text{-ZnFe}_2\text{O}_4$ nanocomposites has been compared to an Aldrich TiO_2 reference catalyst, using a solar-simulated photoreactor for the degradation of phenol.

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1. INTRODUCTION

The wide-bandgap semiconductor TiO_2 has become the dominant UV-activated photocatalyst in the field of air and water detoxification because of its high stability, low cost, high oxidation potential, and chemically favorable properties. The demand for visible-light-activated photocatalytic systems is increasing rapidly; however, currently, the efficiency and availability of photocatalysts that can be activated effectively by the solar spectrum and particularly indoor lighting are severely limited. Environmental pollution on a global scale is proposed to be the greatest problem that chemical scientists will face in the 21st century, and an increasing number of these scientists are looking for new photocatalytic systems for the solution. The vast majorities of current photocatalytic system use pure or modified TiO_2 with a metastable anatase crystal structure (3.2 eV bandgap), although two key shortcomings exist. The first shortcoming is low photocatalytic efficiencies that plague current photocatalysts due to undesired electron-hole pair (EHP) recombination, and the second is that TiO_2 utilizes only 3–5% of the solar spectrum and virtually none of the light commonly used for indoor illumination. Both of these spectral regions have applications needing active photocatalysts [1]. The push towards extending the photoresponse of TiO_2 to visible wavelengths is increasing exponentially every year, for both solar ($\lambda > \text{UV-A}$, 320 nm) and visible light applications

($> 400\text{ nm}$). The most successful techniques used thus far for the development of modified TiO_2 for visible-light photocatalysts are ion implantation methods using Cr or V ions [2], various synthesis techniques [3], and substitutional doping of nonmetals such as N ($\text{TiO}_{2-x}\text{N}_x$) [4, 5].

Recent efforts have also been sought to extend the photoresponse of TiO_2 through charge-transfer interactions with narrow-bandgap metal oxides such as the *n*-type ZnFe_2O_4 with a 1.9 eV bandgap. ZnFe_2O_4 , most prominently known for its magnetic properties, is a photocatalyst active for irradiation wavelengths shorter than 652 nm, although its photoactive lifetime is short due to the tendency of absorbing intermediate oxidation byproducts, thereby inhibiting it from oxidizing target organics [6]. Numerous publications in the past year have used sol-gel techniques [7, 8] to dope TiO_2 with ZnFe_2O_4 or Zn^{2+} and Fe^{3+} ions [9] for solar-light-irradiated photocatalytic studies. $\text{TiO}_2\text{-ZnFe}_2\text{O}_4$ alloys, on the other hand, are difficult to prepare because of the differences in preparation procedures (ZnFe_2O_4 is typically prepared through coprecipitation in alkaline solutions) and also the enhancement of TiO_2 's anatase to rutile transformation by the substitutional presence of Fe^{3+} ions. However, a complex colloidal chemistry method using surfactant capping has been reported for creating photoactive $\text{TiO}_2\text{-ZnFe}_2\text{O}_4$ nanocomposites that exhibit increased photocatalytic response to solar irradiation [10]. In this report, a simple coprecipitation/hydrolysis synthesis method is

used to create $\text{TiO}_2\text{--ZnFe}_2\text{O}_4$ alloys for the purpose of creating an inexpensive and nontoxic photocatalyst that is photoactive in response to wavelengths greater than 400 nm.

2. EXPERIMENTAL METHOD

A coprecipitation/hydrolysis synthesis method was used for the formation of $\text{TiO}_2\text{--}(X)\text{ZnFe}_2\text{O}_4$ nanocomposites with X (mole fraction) values of 0.01, 0.05, 0.1, 0.15, and 0.2. All chemicals used were purchased from Sigma Aldrich and were of 99.9% purity or higher. ZnFe_2O_4 was first precipitated using the respective quantity of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ precursors in a solution of $\text{C}_3\text{H}_7\text{OH}$ (isopropyl alcohol) heated at 65°C and stirred for 30 minutes. To coprecipitate the nitrate precursor, the pH of the aqueous solution was raised to 6.5 by slowly adding a 3.5 M NH_4OH solution using $\text{C}_3\text{H}_7\text{OH}$ as the solvent. Approximately 10 g of deionized H_2O was next added dropwise to the solution in addition to the H_2O already existing from the added NH_4OH and the solution was left stirring for 45 minutes. A separately prepared solution of $\text{Ti}(\text{OBU})_4$ and $\text{C}_3\text{H}_7\text{OH}$ was mixed in a ratio of 1 : 2 by weight and added dropwise to the coprecipitated ZnFe_2O_4 solution for a controlled hydrolysis with $\text{H}_2\text{O} : \text{Ti}(\text{OBU})_4$ ratios of 50, 25, 15, 5 : 1. The final solution was kept stirring at 65°C for 90 minutes, filtered, dried at 100°C and 220°C , respectively. Thus prepared $\text{TiO}_2\text{--ZnFe}_2\text{O}_4$ nanoparticles have been calcined in a flowing air atmosphere at various temperatures for 3 hours.

The UV-Vis and visible-light photoactivity of the nanocomposites were determined using photoreactor consisting of a 1000 W ($340 < \lambda < 680\text{ nm}$) metal halide lamp, reflector, and borosilicate reaction vessel. For visible-light photoactivity experiments, a thin-film UV cutoff filter provided by Edmund Optics was inserted on the glass lens of the metal halide lamp to completely remove irradiation with wavelengths shorter than 400 nm. Phenol was used as the organic test degradant since it absorbs wavelengths around 265 nm and therefore will not be susceptible to photolysis. Experimental reaction conditions for all studies consisted of 40 ppm phenol, 1100 g of deionized H_2O , 1 g/L catalyst loading, magnetic stirring, and 1.5 L/min of air injected through a sparger to perform the role of electron scavenging. The degradation of phenol was evaluated by centrifuging the retrieved samples and measuring the intensity of phenol's absorption peak (268 nm) relative to its initial intensity (C/C_0) by UV-Vis spectroscopy with an Ocean Optics fiber optic spectrometer.

3. RESULTS AND DISCUSSION

3.1. X-ray diffraction

To confirm the multiphase synthesis of $\text{TiO}_2\text{--}(X)\text{ZnFe}_2\text{O}_4$ nanocomposites, alloys were formed using a high concentration ($X = 0.2$) of ZnFe_2O_4 . XRD measurements revealed the formations of anatase and rutile TiO_2 , as well as ZnFe_2O_4 and traces of ZnTiO_3 and ZnO . Although a low calcination

FIGURE 1: XRD spectra of $\text{TiO}_2\text{--}(0.2)\text{ZnFe}_2\text{O}_4$ calcined at 400°C for various h values.

temperature of 400°C was used, the anatase-to-rutile transformation was nearly complete due to the inherent substitution of Fe^{3+} for Ti^{4+} ions, thereby creating oxygen vacancies that promote the formation of rutile throughout the bulk of the nanoparticles [11]. The considerable amount of Fe^{3+} ions needed to realize such a low temperature anatase-rutile transformation may also explain the formation of ZnTiO_3 and ZnO as an incomplete formation of ZnFe_2O_4 due to the absence of available Fe. Figure 1 shows the XRD spectra of the $\text{TiO}_2\text{--}(0.2)\text{ZnFe}_2\text{O}_4$ nanocomposites using various h values ($h = \text{H}_2\text{O}/\text{Ti}[\text{OBU}]_4$), since this ratio effects the hydrolysis of TiO_2 and therefore the photoactivity of the nanocomposite.

Based on the previous experiment, as well as others conducted on pure hydrolyzed TiO_2 [12], it was decided to use h values of 25 for the remainder of the nanocomposites. This ratio provides the optimal tradeoff between hydrolysis homogeneity, anatase content, and photocatalytic activity. $\text{TiO}_2\text{--}(X)\text{ZnFe}_2\text{O}_4$ nanocomposites were next synthesized using X values of 0.01, 0.05, 0.1, and 0.15 to determine the maximum concentration of ZnFe_2O_4 that can be coupled with TiO_2 while still maintaining an anatase crystal structure which is predicted to be needed for the redox reactions derived from a charge-transfer phenomenon. The XRD spectra of the $\text{TiO}_2\text{--}X\%\text{ZnFe}_2\text{O}_4$ nanocomposites are shown in Figure 2.

Figure 2 shows the effect of ZnFe_2O_4 alloying concentration on the anatase-to-rutile transformation. For a calcination temperature of 450°C , X values of 0.01, 0.05, 0.1, 0.15, and 0.2 correspond to respective anatase mass fractions of 100, 100, 72.7, 54.1, and 47.2%, as calculated by the equation

$$X_A = \frac{1}{1 + 1.26 \cdot (I_A/I_R)} \cdot 100, \quad (1)$$

X_A is the mass fraction of anatase, I_A and I_R are the X-ray integrated intensities of the (101) reflection of anatase and rutile phases, respectively. It should be noted that this equation only takes into consideration the percent of anatase and

FIGURE 2: XRD spectra of $\text{TiO}_2-(X) \text{ZnFe}_2\text{O}_4$ calcined at 450°C .

rutile in the formed TiO_2 and not of the entire nanocomposite.

3.2. UV-visible spectroscopy

An Oriel Instruments spectrometer with an integrating sphere has been used for UV-Vis spectrometry measurements used to analyze the redshifts in the absorption regions as a function of ZnFe_2O_4 alloying concentration. The nanoparticles have been deposited on the glass slides by spin-coating technique at 3000 rpm. The UV-Vis transmittance measurements were taken and converted into absorption readings. Figure 3 represents the UV-Vis absorption spectra for $\text{TiO}_2-(X) \text{ZnFe}_2\text{O}_4$ nanocomposites with $X = 0.01, 0.05, 0.1, 0.15$, and 0.2 . It can be seen that the redshift of the absorption edge is roughly proportional to the ZnFe_2O_4 alloying concentration. The absorption bands were smooth for low alloying concentrations ($X < 0.15$), however small shoulders appeared for higher ZnFe_2O_4 concentrations as often seen in the absorption bands of doped photocatalysts.

3.3. Photocatalytic studies

The photocatalytic activity of the samples in response to UV-Vis and visible-light irradiation was determined using phenol degradation over a 105-minute time period, with samples withdrawn every 15 minutes. The UV photoactivity of the $\text{TiO}_2-(X) \text{ZnFe}_2\text{O}_4$ nanocomposites was found to decrease in rough proportion to the increasing concentration of ZnFe_2O_4 . The visible-light photoactivity (shown in Figure 4), however, was characterized by a bell curve, with the maximum degradation being achieved with X equal to 0.10 . For comparison with the nanocomposite materials, pure ZnFe_2O_4 prepared by the hydrolysis and coprecipitation method has been plotted in this figure. Figure 5 shows a breakdown of the photocatalytic activity of $\text{TiO}_2-(X) \text{ZnFe}_2\text{O}_4$ nanoparticles from various degradation experiments.

FIGURE 3: UV-Vis absorbance spectra of $\text{TiO}_2-(X) \text{ZnFe}_2\text{O}_4$ nanocomposites. FIGURE 4: Visible-light-activated photocatalytic degradation rates for $\text{TiO}_2(X) \text{ZnFe}_2\text{O}_4$ nanocomposites.

The decreasing photoactivity for the catalysts for X values more than 0.1 when irradiated by UV light is attributed to the increasing formation of the rutile phase with ZnFe_2O_4 concentrations as well as possible defects in the TiO_2 lattice, in addition to enhanced electron-hole pair (EHP) recombination. The increased photoactivity for X values of 0.01 to 0.10 may be associated with the role ZnFe_2O_4 substituted or surface-stabilized anatase TiO_2 serves in extending the photoresponse of the catalyst to short-wavelength visible irradiation and effectively transferring charge carriers to particles capable of the appropriate redox reactions.

FIGURE 5: Breakdown of the degradation characteristics for $\text{TiO}_2-(\text{X})\text{ZnFe}_2\text{O}_4$ nanocomposites irradiated by UV, and UV-Vis, and visible light.

The photoactivity that characterizes the nanocomposite photocatalysts using visible-light irradiation is not directly (or at least completely) linked to ZnFe_2O_4 . The reason for this conclusion is that the consistent degradation rates characteristic of the $\text{TiO}_2-(\text{X})\text{ZnFe}_2\text{O}_4$ nanocomposites are dissimilar to the degradation rates for ZnFe_2O_4 which were found in prior experiments to cease after short durations using both UV and visible-light irradiations. It can also be concluded from the poor visible-light photocatalytic activity of nanocomposites with X equal to 0.15 and 0.20 that anatase TiO_2 plays a critical role in the visible-light photocatalysis of $\text{TiO}_2-\text{ZnFe}_2\text{O}_4$ alloys. Although the ZnFe_2O_4 concentration increases, thereby allowing more charge carriers in response to enhanced visible-light absorption, it is thought that the high rutile concentrations impede the overall reaction.

4. CONCLUSION

$\text{TiO}_2\text{ZnFe}_2\text{O}_4$ nanocomposites were synthesized, and their photocatalytic activity in response to UV, UV-Vis (solar), and visible light was determined. It was concluded that the narrow-bandgap semiconductor ZnFe_2O_4 can be effectively coupled with TiO_2 for visible-light ($> 400\text{ nm}$)-activated photocatalysis. This study shows the potential of inexpensive and nontoxic photocatalysts for indoor visible-light applications.

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