Enhanced photocatalytic activity of calcined natural sphalerite under visible light irradiation

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Abstract

The photocatalytic activity of natural sphalerite (the main mineral ore of ZnS) is relatively low in the absence of sacrificial donors. Present work focuses on the improvement of the photocatalytic activity of a natural sphalerite obtained from Abunl deposit, Nigeria, via calcination at 600 °C, 700 °C and 800 °C. The raw and calcined natural sphalerite samples were characterized using X-ray diffraction (XRD), scanning electron microscopy (SEM), and specific surface area analysis. The activity of the raw and calcined samples was evaluated using photocatalytic decolorization of methyl orange (MO) as the model reaction. The kinetics of photocatalytic decolorization of MO on the raw and calcined natural sphalerite samples was fitted to the pseudo-first order approximation of the Langmuir–Hinshelwood model. The photocatalytic activity of the natural sphalerite was doubled upon calcination at 700 °C. The natural sphalerite calcined at 700 °C is also more active than the ones calcined at 600 °C and 800 °C due to the combined effects of chemical composition, crystallite size, specific surface area and oxygen vacancies.

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1. Introduction

Solar energy harvesting and conversion through semiconductor photocatalysis has a wide range of energy and environmental applications [1–3]. Visible light constitutes about 46% of the solar spectrum; whereas, ultraviolet light accounts for only about 5% of the solar spectrum [3]. The band gaps of the commonly used photocatalysts correspond to the UV region of the electromagnetic spectrum. Hence, they are capable of utilizing only a small portion of sunlight. For example, TiO2 has a wide band gap (3.0 eV for rutile and 3.15 eV for anatase) and can therefore absorb only a small portion of sunlight [1]. Therefore, development of visible light active photocatalysts capable of efficient utilization of solar energy is an area of considerable research interest. Coupling two or more semiconductors is one of the commonly employed techniques for extending the activity of high band gap photocatalysts into the visible region [4,5].

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Most composite semiconductors are often synthesized from expensive high purity chemicals. Synthesis of composite semiconductors may involve many steps and special conditions [4–6]. Hence, the cost of the synthesized composite semiconductors can be very high. On the other hand, naturally occurring mineral ores such as natural sphalerite [7–11] and vanadium bearing rutile [12] were found to behave like coupled semiconductors, exhibiting photocatalytic activity under visible light irradiation. Thus, natural sphalerite (obtained from a deposit in Hunan, China) was found to exhibit visible-light photocatalytic activity for bacterial inactivation and photoreductive degradation of methyl orange and carbon tetrachloride [7–11]. The photocatalytic activity of the natural sphalerite under visible light irradiation was mainly attributed to the substitution of transition metal ions for Zn$^{2+}$ and surface defects. The photocatalytic activity of the naturally occurring mineral ores is relatively low in the absence of sacrificial donors such as ascorbic acid [9,10] and hydrogen peroxide [12]. Addition of sacrificial donors may negatively affect the photocatalytic process through corrosion of equipment, contamination of the products, high cost of the sacrificial donors, separation and recycling of the sacrificial donors where possible, etc. Therefore, there is the need to employ other techniques for improving the photocatalytic activity of the naturally occurring mineral ores.

Photocatalytic activity of composite photocatalysts is strongly dependent on their chemical composition and surface properties [6,13–15]. The composition and properties of materials can be easily altered via calcination [5,13]. To the best of our knowledge, no attempt has been made to study the effects of chemical composition and surface properties of any natural sphalerite on its photocatalytic activity. Therefore, the aim of the present work was to investigate the effect of calcination temperature on the photocatalytic activity of a natural sphalerite, obtained from Abuni deposit, Nasarawa State, Nigeria with a view to improve its photocatalytic activity under visible light irradiation. Methyl orange (MO) is widely used as a model compound to investigate the photocatalytic activity of various photocatalysts [10,12]. Indeed, MO is highly stable to visible and near UV light, but can be decolorized in the presence of a photocatalyst [10]. Herein, MO is used as the model substrate for testing the photocatalytic activity of the raw and calcined natural sphalerite samples.

2. Experimental

2.1. Materials

The natural sphalerite sample was obtained from a deposit in Abuni, Nasarawa State, Nigeria. The sphalerite sample was crushed into powder and then sieved to obtain fine powder with particle size below 106 µm. Analytical grade reagents were used in the work. Calcination of the natural sphalerite powders was conducted in Nabertherm C250 Electric furnace at 600 °C, 700 °C, and 800 °C for two hours each. The calcined natural sphalerite samples were abbreviated by S600, S700, and S800, corresponding to calcination temperatures of 600 °C, 700 °C, and 800 °C, respectively. The raw natural sphalerite is abbreviated by S0. The chemical composition of the natural sphalerite samples was determined using X-ray fluorescence (XRF) spectrometer (Panalytical, Minipal 4 model). The phases present in the samples were investigated using a powder X-ray diffractometer (Shimadzu, model 6000) with Cu Kα radiation (40 kV, 40 mA) at Bragg angles ranging from 10° to 80°. The morphology of the samples was analyzed using Phenom Pro-X desktop scanning electron microscope. The specific surface areas of the samples were measured using the Sear’s method [16].

2.2. Photocatalytic decolorization of MO

Photocatalytic decolorization of MO using the raw and the calcined natural sphalerite samples as photocatalysts was conducted at room temperature (30 ± 2 °C) with an initial concentration of MO solution of 10 mg l$^{-1}$ and a pH of 3.3. 500 W halogen lamp was used as the visible light source. Halogen lamp is often used as the source of visible light in photocatalytic experiments because less than 0.3% of the emitted light is ultraviolet [12]. 0.2 g of a photocatalyst was added to 200 ml MO solution and stirred for 60 min in the dark in order to establish absorption–desorption equilibrium, after which the suspension was exposed to visible light illumination. During the photocatalytic experiments, aliquots were withdrawn from the suspension at different intervals and filtered to completely remove the photocatalyst particles. The obtained filtrates were then analyzed for the residual concentration of MO using a UV–vis spectrophotometer. Percentage decolorization of MO was calculated using Eq. (1).

$$\text{Decolorization} = \frac{C_0 - C_t}{C_0} \times 100\%$$  \hspace{1cm} (1)

where $C_t$ is the concentration of MO remaining in the solution at irradiation time, $t$, and $C_0$ is the initial concentration of MO.

3. Results and discussion

3.1. Characterization of the raw and calcined natural sphalerite samples

The XRD patterns of the raw and calcined natural sphalerite samples are displayed in Fig. 1. The XRD pattern of the raw natural sphalerite (Fig. 1a) features prominent peaks at Bragg angles of 28.6°, 47.5°, and 56.2°, which can be well indexed to ZnS (ICPDS 77-2100). Also observed in the XRD pattern is a minor peak at Bragg angle of 26.6° due to the presence of quartz (α-SiO$_2$). The elemental composition of the natural sphalerite as determined by X-ray fluorescence (XRF) analysis is presented in Table 1. Zinc and sulfur are the main components of the natural sphalerite. The natural sphalerite also contains noticeable amounts of molybdenum, silicon, iron and silver. However, only ZnS and quartz peaks were observed in the diffractogram of the natural sphalerite. This can be attributed to amorphous nature of some of the impurities, their dispersion in the sphalerite matrix, and/or low concentration of some of the accessory minerals to the extent that cannot be detected by XRD technique. Similar results were reported by Mekatel et al. for Fe$_2$O$_3$ supported on natural Algerian clay [17].
Table 1 – Elemental Composition of the natural sphalerite.

<table>
<thead>
<tr>
<th>Element</th>
<th>Zn</th>
<th>S</th>
<th>Si</th>
<th>Ca</th>
<th>Mn</th>
<th>Fe</th>
<th>Ni</th>
<th>Cu</th>
<th>As</th>
<th>Y</th>
<th>Mo</th>
<th>Ag</th>
<th>La</th>
<th>Eu</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conc. (wt. %)</td>
<td>58.60</td>
<td>16.00</td>
<td>5.00</td>
<td>0.16</td>
<td>0.02</td>
<td>4.85</td>
<td>0.03</td>
<td>0.08</td>
<td>0.02</td>
<td>0.47</td>
<td>11.00</td>
<td>2.60</td>
<td>0.02</td>
<td>0.02</td>
</tr>
</tbody>
</table>

The XRD patterns of S700 and S800 shown in Fig. 1c and 1d reveal complete oxidation of ZnS to ZnO because ZnS peaks completely disappeared upon calcination at 700 °C. Therefore, ZnS in the natural sphalerite sample is completely oxidized to ZnO at 700 °C. The temperature required for the complete conversion of ZnS to ZnO is 700 °C for both pure ZnS [5] and natural sphalerite; hence, the impurities contained in natural sphalerite do not have much effect on the conversion temperature. S800 is more crystalline than S700 because the peaks of the latter are more intense and narrower than those of the former. Indeed, the XRD pattern of S700 is characterized by a broad background due to low crystallinity.

The average crystallite sizes of the raw and calcined natural sphalerite samples were estimated using the Debye–Scherrer formula. The computed average crystallite sizes are listed in Table 2. When natural sphalerite was calcined at 600 °C, the crystallite size increases from 28 to 43 nm. However, upon calcination at 700 °C, the crystallite size decreases to 19 nm due to complete conversion of ZnS to ZnO. Calcination at 800 °C resulted in much larger crystallite size of 53 nm. The specific surface areas of the raw and calcined natural sphalerite samples are also presented in Table 2. The specific surface area decreased upon calcination at 600 °C, and then suddenly increased when calcination was performed at 700 °C. Further increase in the calcination temperature to 800 °C resulted in lower specific surface area. As seen in Table 2, S700 has the

Fig. 2 – SEM images of (a) S0, and (b) S700.

Fig. 1 – XRD patterns of (a) S0, (b) S600, (c) S700, and (d) S800.

In addition to characteristic peaks of ZnS and quartz, the XRD pattern of S600 displayed in Fig. 1b features a set of peaks at Bragg angles of 31.7°, 34.5°, 36.3°, 47.6°, 56.5°, 62.7°, 68.1°, and 69.3°. The latter set of peaks can be attributed to the hexagonal wurtzite structure of ZnO (JCPDS 36-1451). Hence, S600 is mostly composed of crystalline ZnO and ZnS. The peak at 35.3° in the diffractograms of S600, S700, and S800 is attributed to magnetite (Fe3O4). The XRD patterns of S700 and S800 are devoid of ZnS peaks. The diffractograms of S700 and S800 are dominated by peaks due to ZnO. It has been reported by Zhao et al. [5] that conversion of pure ZnS to ZnO is a stepwise oxidation process and complete conversion of ZnS to ZnO occurs at 700 °C and above according to Eq. (2):

\[
2\text{ZnS} + 3\text{O}_2 \rightarrow 2\text{ZnO} + 2\text{SO}_2
\]  

(2)
highest specific surface area and lowest crystallite size in the series.

The SEM images of S0 and S700 are displayed in Fig. 2. The surface of S0 is characterized by irregularly shaped particles with a wide range of particle size ranging from submicron to over 10 μm. On the other hand, the surface of S700 is composed of submicron clusters of grains with some interparticle voids, which may account for the high specific surface area of S700. Chemical transformation of ZnS to ZnO at 700 °C is mainly responsible for the observed drastic changes in the morphology of S0 and S700.

3.2. Photocatalytic decolorization of MO

The results of photocatalytic decolorization of MO using the raw and the calcined natural sphalerite samples in an irradiation period of one hour are shown in Fig. 3a. Generally, the observed decolorization of MO on naturally occurring ores is relatively low [9,12]. The percentage photocatalytic decolorization of MO on the raw natural sphalerite is only 9.5% after one hour of visible light irradiation with a 500 W halogen lamp. The photocatalytic activity of the calcined natural sphalerite samples increases with increase in the calcination temperature up to 700 °C, and then decreases upon calcination at 800 °C. After two hours of visible light irradiation with a 500 W halogen lamp, Li et al. [9] observed only 4.09% decolorization of MO using natural sphalerite obtained from Hunan, China as the photocatalyst.

The kinetics of photocatalytic processes often obeys pseudo-first order approximation of the Langmuir–Hinshelwood model, \( \ln(C_0/C) = k_{app}t \), where \( k_{app} \) is the apparent rate constant, which can be used to compare the photocatalytic activity of a series of photocatalysts because it permits evaluation of photocatalytic activity independent of the concentration of the substrate remaining in the solution and adsorption in the dark step of photocatalysis [15]. The plots of \( \ln(C_0/C) \) as a function of irradiation times are shown in Fig. 4. The derived values of the apparent rate constants are presented in Table 3. The high values of the regression coefficients (\( R^2 \)) show that the photocatalytic decolorization of MO follows pseudo-first order kinetics. As seen in Table 3, the apparent kinetic rate constant over S700 is twice higher than that over S0. Indeed, S700 also exhibits the highest photocatalytic activity among the calcined natural sphalerite samples.

Photocatalytic activity is often rationalized in terms of the chemical and surface properties as well as the ability of a photocatalyst to absorb incident light energy to generate electrons and holes. The specific surface area of natural sphalerite calcined at 700 °C is larger than those of the raw and other calcined natural sphalerite samples (Table 1). Photocatalysis is a heterogeneous process; hence, larger specific surface area improves photocatalytic activity [18,19]. Usually, photocatalytic activity decreases as the calcination temperature is increased due to increase in the grain size and decrease in the specific surface area of the photocatalyst. Although S700 and S800 have similar chemical composition, the photocatalytic activity remarkably decreased when the calcination temperature of natural sphalerite was increased from 700 °C to 800 °C due to significant decrease in the specific surface area caused by increase in grain size. Similar observations were reported in the literature [14,18-20]. Thus, the photocatalytic activity of ZnFe2O4 calcined at 500 °C is higher than that of ZnFe2O4 samples calcined at 600 °C, 700 °C, 800 °C and 900 °C [20].

<table>
<thead>
<tr>
<th>Sample</th>
<th>( k_{app} ) (min(^{-1} ))</th>
<th>( R^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>S0</td>
<td>0.0017</td>
<td>0.983</td>
</tr>
<tr>
<td>S600</td>
<td>0.0029</td>
<td>0.999</td>
</tr>
<tr>
<td>S700</td>
<td>0.0036</td>
<td>0.999</td>
</tr>
<tr>
<td>S800</td>
<td>0.0030</td>
<td>0.973</td>
</tr>
</tbody>
</table>
The observed differences in the photocatalytic activity of S0, S600, and S700 can be attributed to the combined effects specific surface area, which decreases upon calcinations at 600 °C and then increases when the calcination temperature was raised to 700 °C, and incomplete and complete chemical conversion of ZnS to ZnO at 600 °C and 700 °C, respectively. As reported in Table 2, the specific surface area of S0 is higher than that of S600; however, the photocatalytic activity of S600 is much higher than that of S0. Obviously, the higher photocatalytic activity of S600 is caused by the conversion of the ZnS in natural sphalerite to ZnO. ZnO–ZnS composites are often more effective photocatalysts than pure ZnO or ZnS due to the shift of their band gaps to lower energies and more efficient separation of the photogenerated electron–hole pairs [4,6].

Elsewhere, ZnO was found to display higher activity than pure ZnS and ZnS–ZnO composites for the photocatalytic decolorization of MO under UV irradiation thanks to the oxygen vacancies in ZnO, and more efficient separation of the electron–hole pairs [5]. As apparent in Fig. 1, calcination of natural sphalerite involves substitution of sulfur with oxygen in the crystal lattice. Since the atomic radius of sulfur (100 pm) is larger than that of oxygen (60 pm), lattice distortion occurs during calcination which results in oxygen vacancies [21]. The oxygen defects are the active sites of ZnO that can entrap photogenerated electrons thereby allowing efficient separation of the photogenerated electrons and holes [22]. Although S700 and S800 have the same chemical composition as shown by their XRD patterns, S700 will have more oxygen defects than S800 because the number of oxygen vacancies decreases with increase in calcination temperature [23]. In this work, S700 exhibits the highest photocatalytic activity which can be attributed to the presence of oxygen vacancies in the lattice (Table 2), and more oxygen defects which will promote more efficient separation of photogenerated electrons and holes [22].

Neither ZnS nor ZnO is photocatalytically active under visible light irradiation due to their high band gap, the observed activity of the raw and calcined natural sphalerite samples under visible light irradiation is indeed mainly attributed to the presence of accessory minerals and surface defects as extensively discussed in previous reports [7,8]. More detailed experimental work on the effects of impurities on the photocatalytic activity of raw and calcined natural sphalerite samples is needed in order to fully optimize their compositions for more efficient application of these materials as visible light responsive photocatalysts. Detailed investigation of the role of oxygen vacancies on the separation of charge carriers in the raw and calcined natural sphalerite samples may also provide useful data for gaining deeper understanding of the mechanism of the photocatalytic activity of the materials.

4. Conclusions

Percentage decolorization of MO on the natural sphalerite is only 9.5% after one hour of visible light irradiation. The photocatalytic activity of the natural sphalerite was doubled upon calcination at 700 °C. The natural sphalerite calcined at 700 °C is more active than the one calcined at 600 °C, due to higher crystallite size and lower specific surface area of the latter, as well as incomplete conversion of ZnS to ZnO at 600 °C. Complete conversion of ZnS to ZnO was achieved at 700 °C. The natural sphalerite calcined at 700 °C and 800 °C have similar chemical composition. However, the natural sphalerite calcined at 700 °C is more photocatalytically active than the one calcined at 800 °C, because the former has lower crystallite size, higher specific surface and more oxygen vacancies which will promote more efficient separation of photogenerated electrons and holes. Hence, 700 °C is the best calcination temperature for enhancing the photocatalytic activity of the natural sphalerite.

Conflict of interest

The authors declare no conflicts of interest.

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