

Fabrication and Photocatalytic Properties of $\text{MgFe}_2\text{O}_4/\text{rGO}/\text{V}_2\text{O}_5$ Heterostructure Nanowires

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Abstract—Development of green clean energy has become one of promising challenge recently. One popular application of solar energy is photocatalysis, where semiconductors were used as photocatalyst to convert solar light into photoelectrons/holes. Photocatalysis technology has been widely applied for water splitting and degradation. Tetracycline (TC) is a sort of popular anthropogenic emissions in wasted water, which will caused seriously environmental pollution. A novel $\text{MgFe}_2\text{O}_4/\text{GO}/\text{V}_2\text{O}_5$ heterostructure has been successfully prepared by electrospinning method and high temperature chemical vapor deposition. The structure of samples was systematically characterized by XRD patterns and SEM images. The morphology of MgFe_2O_4 and $\text{MgFe}_2\text{O}_4/\text{GO}/\text{V}_2\text{O}_5$ was both uniform one-dimensional nanowires. The degradation ratios of TC by MgFe_2O_4 and $\text{MgFe}_2\text{O}_4/\text{rGO}/\text{V}_2\text{O}_5$ were 18% and 40%, respectively. The enhanced photocatalytic property of $\text{MgFe}_2\text{O}_4/\text{GO}/\text{V}_2\text{O}_5$ indicated that the GO and V_2O_5 played an important role in the separation of photogenerated holes and electrons. Therefore, $\text{MgFe}_2\text{O}_4/\text{rGO}/\text{V}_2\text{O}_5$ can be used efficient photocatalyst for sewage treatment in environment.

Keywords—heterostructure; $\text{MgFe}_2\text{O}_4/\text{rGO}/\text{V}_2\text{O}_5$; electrospinning; nanowires; photocatalytic property;

I. INTRODUCTION

The excessive use of fossil energy has resulted in a large number of toxic and greenhouse gas emissions, which increasingly caused serious global environmental problems.[1-4] Development of green clean energy became one of promising challenge today. Solar energy is a clean and environmental-friendly energy, which can satisfy the increasing demand of the world. Recently, one popular application of solar energy is photocatalysis, and the semiconductors used as photocatalyst convert solar light into photoelectrons/holes which are applied for water splitting and degradation. Therefore, design and fabrication of efficient semiconductor photocatalyst has attracted great attention in the field of photo-catalytic degradation of organic pollutants.[5-7]

The band gap width, microstructure and composited model of semiconductor take an important role in optimize the photocatalytic activities of photocatalyst, So many researchers have focused on the design and fabrication of novel semiconductor photocatalyst. MgFe_2O_4 is a kind of

spinel semiconductor, which has a cubic structure of normal spinel-type and soft magnetic property.[8] More importantly, the narrow band gap (1.9 eV) endows MgFe_2O_4 with the responding ability of visible lights. As well known, visible light in solar accounts for about 50%, so MgFe_2O_4 as a potential photocatalyst can efficiently utilize the solar energy. However, the practical efficiency of bare MgFe_2O_4 is not ideal, due to the significant recombination of photoelectrons and holes. As previous reports, fabrication of heterostructure is recognized as a feasible routes to remedy the recombination of photoelectrons and holes form bare semiconductor.[9-11] Vanadium pentoxide (V_2O_5) is a suitable semiconductor for photocatalyst, because of narrow bandgap energy (ca. 2.2 eV) and photodegrading activity of organic pollutants.[12]

Moreover, graphene oxide (GO) has raised concern in synthesis of composited materials due to its favorable solubility in water, which offers opportunity for loading GO on smooth substrates.[13] As the unique phase compared with graphene and graphene oxide, reduced graphene oxide (rGO) possesses excellent plasticity and electrical conductivity, which made rGO have potential application in fabrication of heterostructure photocatalyst. Therefore, Inspired by above discussion, it will be feasible to design novel heterostructure photocatalyst based on MgFe_2O_4 , rGO and V_2O_5 .

In this work, $\text{MgFe}_2\text{O}_4/\text{rGO}/\text{V}_2\text{O}_5$ heterostructure photocatalyst has been designed and prepared by electrospinning method and high temperature chemical vapor deposition. The heterostructure photocatalyst was obtained with unique nanowire morphology. $\text{MgFe}_2\text{O}_4/\text{rGO}/\text{V}_2\text{O}_5$ heterostructure photocatalyst was applied in the photodegradation of degrading tetracycline (TC) under visible light. The optimal photodegrading rate of $\text{MgFe}_2\text{O}_4/\text{rGO}/\text{V}_2\text{O}_5$ heterostructure photocatalyst was achieved through loading rGO and V_2O_5 on the surface of MgFe_2O_4 nanowires.

II. EXPERIMENTAL

Materials

Polyvinylpyrrolidone (PVP, K-90, Mw=1300000) (J&K Chemical) were used as polymer precursor. Magnesium nitrate hexahydrate (99% purity, $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, SCR),

iron(III) nitrate nonahydrate (99.9% purity, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) and vanadyl acetylacetonate (99.9% purity, $\text{VO}(\text{acac})_2$) were used without further purification. Deionized water and ethanol were used as solvents.

Preparation of MgFe_2O_4 nanowires

First, the precursor solution for electrospinning was prepared: 2.6 g PVP, 0.1 mol $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 0.2 mol $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ were mixed together and dissolved in 25 mL ethanol aqueous solution ($\text{H}_2\text{O}:\text{C}_2\text{H}_6\text{O} = 3:1$), and then the solution stirred for 10 hours to ensure all chemical reagents be dissolved completely. The obtained precursor sol was transferred into a 20 mL syringe with needle (tubular metal needles 0.5 mm), and then the syringe was played in the electrospinning installation. Under 25 KV, The precursor solution was quickly spun from syringe, and then white nanowires formed on a metal foil. The obtained precursor nanowires were calcined at 500 °C for 1 hour.

Preparation of $\text{MgFe}_2\text{O}_4/\text{rGO}$

The 5 mg GO was dispersed into 20 mL water, and 0.1 g MgFe_2O_4 was put into the above solution. Then the solution was irradiated under UV light (50 W) for 6 hours in order to reduce the GO to rGO. The samples in the solution was collected by centrifugation and washed by ethanol three times.

Preparation of $\text{MgFe}_2\text{O}_4/\text{rGO}/\text{V}_2\text{O}_5$

Photodegradation of TC was carried out at room temperature under visible light. The $\text{MgFe}_2\text{O}_4/\text{rGO}/\text{V}_2\text{O}_5$ was 10 mg and concentration of TC solution was 10 mg/L. After darkness for 30 min, the reaction became chemical adsorption equilibrium. Then, the photochemical reactor was irradiated with a 150 W Xenon lamp for 2 hours. The TC solution was extracted for absorption spectra measurement with 20 min interval.

The photocatalytic degradation ratio (DR) was calculated through the following formula:

$$\text{DR} = (1 - C)/C_0 \times 100\%$$

C_0 was the initial absorbency of TC, and C was the absorbency after sampling analysis. The absorbency was measured by Liquid UV-vis spectrophotometer with the maximum absorption wavelength at 357 nm.

Characterization

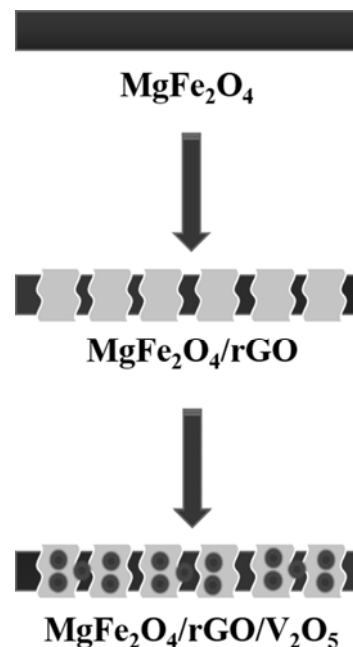
XRD was conducted using a D8 ADVANCE X-ray diffractometer. The morphology of $\text{MgFe}_2\text{O}_4/\text{rGO}/\text{V}_2\text{O}_5$ were measured by Scanning electron microscope (SEM). SEM was performed using a JSM6480 (Japan) field-emission scanning electron microanalyzer with an accelerating voltage of 25 kV, and ESEM was performed using a XL-30 ESEM (Philips).

III. RESULTS AND DISCUSSION

According to the described experiments and observations, a proposed formation process of $\text{MgFe}_2\text{O}_4/\text{rGO}/\text{V}_2\text{O}_5$ nanowires were shown in Scheme1.

Fig. 1 shows the XRD patterns of MgFe_2O_4 and $\text{MgFe}_2\text{O}_4/\text{rGO}/\text{V}_2\text{O}_5$, respectively. The peaks located at

30° , 35° , 43° , 53° , 57° and 63° can be attributed to the (2 2 0), (3 1 1), (4 0 0), (4 2 2), (5 1 1) and (4 4 0) lattice planes of pure MgFe_2O_4 (PDF#88-1935). A new peaks appeared at 32° corresponding to the (0 1 1) of V_2O_5 (PDF#89-0612), and the intensities of MgFe_2O_4 XRD patterns was reduced, resulting from the cover of V_2O_5 and rGO. The XRD results indicated that the V_2O_5 has been successfully introduced on the surface of MgFe_2O_4 .



Scheme 1. Proposed formation process of $\text{MgFe}_2\text{O}_4/\text{rGO}/\text{V}_2\text{O}_5$ nanowires

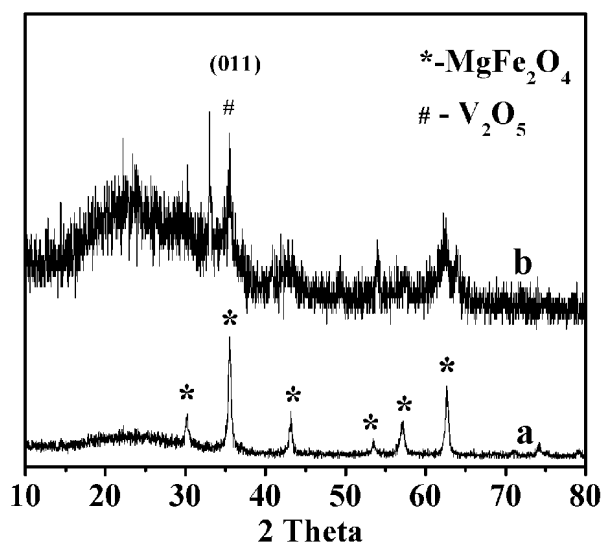


Figure 1. XRD patterns of MgFe_2O_4 (a) and $\text{MgFe}_2\text{O}_4/\text{rGO}/\text{V}_2\text{O}_5$ (b).

The morphology of MgFe_2O_4 and $\text{MgFe}_2\text{O}_4/\text{rGO}/\text{V}_2\text{O}_5$ are further characterized by SEM images. Figure 2a reveals that MgFe_2O_4 synthesized by electrospinning method exhibited uniform one-dimensional nanowires, which indicated that the one-dimensional morphology has been remained after calcination. According to Figure 2b,

the thin film has formed on the surface of MgFe_2O_4 nanowires, this gave a well proof that the rGO has been fabricated in $\text{MgFe}_2\text{O}_4/\text{rGO}/\text{V}_2\text{O}_5$. Moreover, several small particles has also appeared in the samples, due to the introduction of V_2O_5 . Therefore, SEM images further confirm the formation of heterostructure built from MgFe_2O_4 , rGO and V_2O_5 .

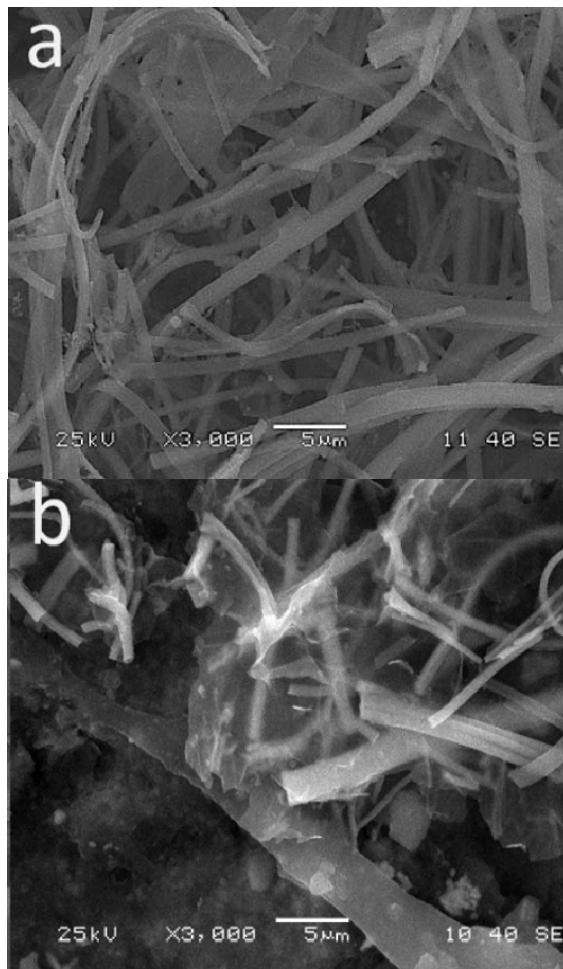


Figure 2. SEM images of MgFe_2O_4 (a) and $\text{MgFe}_2\text{O}_4/\text{rGO}/\text{V}_2\text{O}_5$ (b).

The morphology of MgFe_2O_4 and $\text{MgFe}_2\text{O}_4/\text{rGO}/\text{V}_2\text{O}_5$ are further characterized by SEM images. Figure 2a reveals that MgFe_2O_4 synthesized by electrospinning method exhibited uniform one-dimensional nanowires, which indicated that the one-dimensional morphology has been remained after calcination. According to Figure 2b, the thin film has formed on the surface of MgFe_2O_4 nanowires, this gave a well proof that the rGO has been fabricated in $\text{MgFe}_2\text{O}_4/\text{rGO}/\text{V}_2\text{O}_5$. Moreover, several small particles has also appeared in the samples, due to the introduction of V_2O_5 . Therefore, SEM images further confirm the formation of heterostructure built from MgFe_2O_4 , rGO and V_2O_5 .

The degradation of TC versus reaction time was carried out under visible light (Figure 3). The degradation ratios were calculated through the absorbancy of photodegraded TC solution, and the absorbancy gradually decreased with increasing the reacting time, which indicated that the TC has been significantly

decomposed by photocatalyst. The degradation ratios of TC by MgFe_2O_4 and $\text{MgFe}_2\text{O}_4/\text{rGO}/\text{V}_2\text{O}_5$ were 18% and 40%, respectively. The enhancement of degradation ratios indicated that the heterostructure efficiently increased. The conduction band of MgFe_2O_4 is more negative than that of V_2O_5 , so the photogenerated electrons can transfer from the conduction band of V_2O_5 to MgFe_2O_4 , which benefited the separation of photogenerated holes and electrons. Moreover, both MgFe_2O_4 and V_2O_5 are corresponding to narrows semiconductor, and the absorption spectra of heterostructure can also been improved. The rGO as conductive link between V_2O_5 to MgFe_2O_4 has further accelerated the transfer rates of photogenerated holes and electrons.

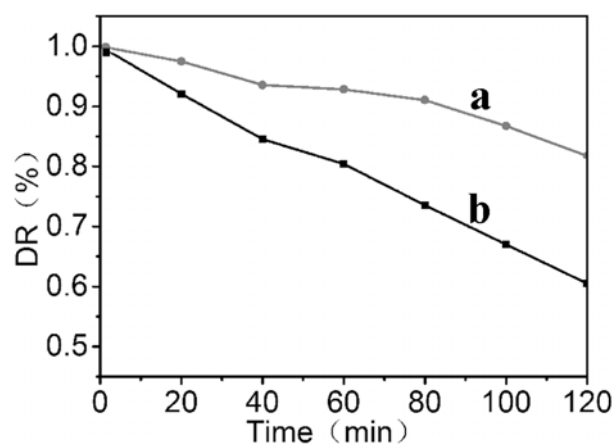


Figure 3. Photocatalytic degradation ratios of MgFe_2O_4 (a) and $\text{MgFe}_2\text{O}_4/\text{rGO}/\text{V}_2\text{O}_5$ (b).

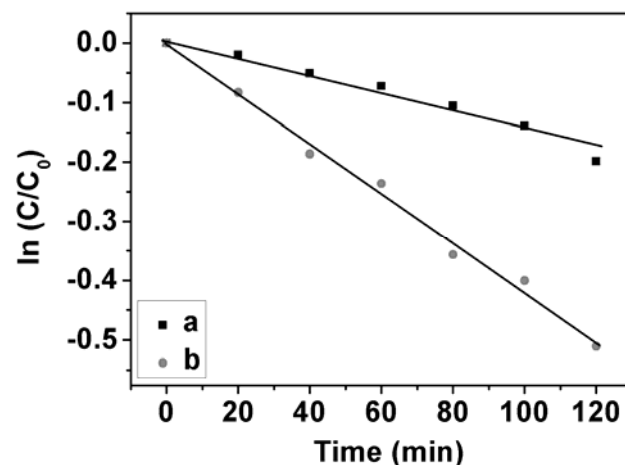


Figure 4. Photodegradation kinetics of MgFe_2O_4 (a) and $\text{MgFe}_2\text{O}_4/\text{rGO}/\text{V}_2\text{O}_5$ (b).

According to the photocatalytic degradation ratio, photodegradation kinetics of TC over MgFe_2O_4 and $\text{MgFe}_2\text{O}_4/\text{rGO}/\text{V}_2\text{O}_5$ has been also characterized as shown in Figure 4. The photodegradation of the TC aqueous solution fitted pseudo first-order reaction well, the formula can be expressed as: $\ln(C/C_0) = -kt$ (k is the apparent first-order reaction constant; C_0 and C are the initial and the reaction absorbency of TC aqueous solution, respectively). Based on the photocatalytic performance of samples, we can conclude that the rational design and fabrication of $\text{MgFe}_2\text{O}_4/\text{rGO}/\text{V}_2\text{O}_5$ heterostructure have been realized in this work.

IV. CONCLUSION

Uniform MgFe_2O_4 nanowires was prepared by electrospinning method at 25 kV. Then V_2O_5 and rGO were successfully introduced on the surface of MgFe_2O_4 nanowires to fabricate the heterostructure $\text{MgFe}_2\text{O}_4/\text{rGO}/\text{V}_2\text{O}_5$, where one-dimensional morphology has been remained during the process of high temperature chemical vapor deposition. The existence of MgFe_2O_4 , rGO and V_2O_5 were confirm by the SEM images and XRD patterns. Due to the synergistic effect of MgFe_2O_4 , rGO and V_2O_5 , the separation of photogenerated holes and electrons in the samples have been significantly enhanced. The photocatalytic degradation ratios further confirm the rational design of $\text{MgFe}_2\text{O}_4/\text{rGO}/\text{V}_2\text{O}_5$ heterostructure. The optimal photodegradating rate of $\text{MgFe}_2\text{O}_4/\text{rGO}/\text{V}_2\text{O}_5$ heterostructure photocatalyst has achieved 40% under visible light irradiation for 2 hours, which suggested that the rational design and fabrication of $\text{MgFe}_2\text{O}_4/\text{rGO}/\text{V}_2\text{O}_5$ heterostructure have been realized.

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