SÍNTESE, CARACTERIZAÇÃO E AVALIAÇÃO DA DEGRADAÇÃO ORGÂNICA DE POLUENTES DE MATERIAIS HETEROESTRUTURADOS À BASE DE $CuWO_4$

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Resumo: O $CuWO_4$ foi sintetizado pelo método hidrotérmico com o objetivo de estudar a possível formação do sistema heteroestruturado $CuWO_4$/CuO. A análise do padrão de DRX dos materiais obtidos revela a formação de $CuWO_4$ como fase principal e Cu_2WO_4 como fase minoritária. Uma modificação no pH antes do processo hidrotérmico leva à formação de óxido de tungstênio não estequiométrico. Através da comparação com outra heteroestrutura $CuWO_4$/CuO obtida anteriormente, esperamos verificar as propriedades fotocatalíticas dos materiais obtidos neste trabalho.

Palavras-chave: $CuWO_4$, Hidrotérmica, Caracterização, Heteroestrutura, Fotocatálise.

SYNTHESIS, CHARACTERIZATION AND EVALUATION OF POLLUTANTS ORGANIC DEGRADATION OF HETEROSTRUCTURED MATERIALS BASED ON $CuWO_4$

Abstract: $CuWO_4$ was synthesized by hydrothermal method with the purpose to study the formation possible of $CuWO_4$/CuO heterostructured system. XRD pattern analysis of materials obtained reveals the formation of $CuWO_4$ like a principal phase and Cu_2WO_4 like minority phase. A modification on the pH before hydrothermal process leads to the formation of non-stoichiometric tungsten oxide. Through the comparison with another $CuWO_4$/CuO heterostructure previously obtained, we hope to check the photocatalytic properties of the obtained materials in this work.

Keywords: $CuWO_4$, Hydrothermal, Characterization, Heterostructure, Photocatalysis.

1. Introduction

Cooper tungstate ($CuWO_4$) is a ternary oxide semiconductor that crystallize in a triclinic structure at room temperature. $CuWO_4$ has two molecular formula units per unit cell (Z =2) at high and low-pressure (SOUZA et al., 2017). This oxide has considerable attention due to interesting technological properties such as ionic conductivity (MATHEW et al., 1992) and photoluminescence (SCHMITT et al., 2011). In particular, its electronic properties enable it to photocatalytic degradation of organic dyes (MONTINI et al., 2010) (CHEN et al., 2015) (DUTTA et al., 2015) and visible and solar-assisted water splitting (GAILLARD et al., 2013), among other environmental applications of semiconductors. With respect to the preparation, different synthesis methods have been used to obtain $CuWO_4$ such as co-precipitation (GARCÍA et al., 2012) (CHEN et al., 2014), sol-gel (DAMIÁN et al., 2003), hydrothermal (MA et al., 2014) and sonochemistry (SOUZA et al., 2017) (DUTTA et al., 2015) method.

Heterostructure is a material with distinct crystalline phase in one particle and sharing at least one surface in a coherent manner. The charge migration between interconnected phases occurs and because the Fermi levels may be equals at the semiconductor's interface, the charge separation

in the phases will occur when the system is stimulated (ALVES de CASTRO et al., 2015). Coupling $CuWO_4$ with other semiconductors has shown better performance photocatalytic of oxide due to that this configuration results an effective way to reduce the charge recombination (CHEN et al., 2014) (CHEN et al., 2015). Type-I ($CuWO_4/WO_3{\cdot}0.33H_2O$, $CuWO_4/WO_3$) and type-II ($CuWO_4/Cu_2O$, $CuWO_4/Cu_2O/CuO$, $CuWO_4/CuO$) heterojunction were obtained as function of pH (KANNAN et al., 2017). These nanocomposites exhibited the enhanced visible light absorption and the band gap (1.7 eV) of $CuWO_4$ is smaller than the early reported value (2.1-2.3 eV). As to photocatalytic degradation, the $CuWO_4/Cu_2O/CuO$ and $CuWO_4/WO_3{\cdot}0.33H_2O$ were showed 1.66 fold times higher and nearly equal apparent rate constant respectively than that of $CuWO_4$. The surface modification of $CuWO_4$ with 1.8 wt% of CuO can increase the activity by approximately 9 times under UV light and by 5 times under visible light, for phenol degradation in aerated aqueous suspension (CHEN et al., 2014). In this work also was demonstrated through a (photo) electrochemical method, the processes of the electron transfer from CuO to $CuWO_4$ and the hole transfer from $CuWO_4$ to CuO, so that the efficiency of charge separation is improved, and organic degradation is accelerated.

These previous works have reported that $CuWO_4$/CuO system improves the response photocatalytic both of $CuWO_4$ because the recombination of the photogenerated charge carriers can be reduced which is a process desirable to optimize the photocatalytic performance under light solar. Thus, in this work we report the hydrothermal synthesis of $CuWO_4$ with the purpose to study the formation possible of $CuWO_4$/CuO heterostructured system. The solids obtained will be characterized with XRD, DRS, SEM, EDS, IR and Raman spectroscopy. Their photocatalytic response for organic degradation in water will be measured under UV light.

2. Materials and Methods

$CuWO_4$-(1) was prepared by using a hydrothermal method modifying the process reported in Chen (2014). 2.416 g of cooper (II) nitrate 3-hydrate ($Cu(NO_3)_2{\cdot}3H_2O$) were dissolved in 200 mL of distilled water and the solution pH was adjusted to 5.0 with NaOH aqueous solution dropwise, followed by heating to 60°C. 3.2985 g of sodium tungstate dihydrate ($Na_2WO_4{\cdot}2H_2O$) were dissolved in 50 mL of distilled water and right away added to solution of cooper. Immediately after the solution was heated to 90°C during 1 h. After cooling until room temperature aqueous NaOH and aqueous HNO_3 was added drop by drop until pH was adjusted to 5.0. The precipitated was transferred into a stainless autoclave, and heated at 180°C for 24 h. After the reactor cooled down the particles were collected by centrifuge, washed with water, rinsed with ethanol and dried at 60°C for 18 h. Finally, the sample was sintered in air at 500°C for 2 h.

For obtaining $CuWO_4$/CuO heterostructures, an appropriate amount of a solution containing $CuWO_4$ and Cu complex will be prepared. In order to prepare Cu complex, a specific amount of cooper (II) Nitrate 3-hydrate will be dissolved in distilled water. PEG400 will be poured in the cooper aqueous solution and after that PEG400 is uniformly dispersed, NaOH pellets will be put into the above solution. After 30 min stirring, a solution containing $CuWO_4$ and an appropriate amount of Cu complex will be prepared in order to study three different molar ratios of $CuWO_4$/CuO, 0:1, 1:1, 2:1. Subsequently, the suspension obtained will be transferred to an autoclave, at 80°C for 12 h. After cooling to room temperature, the formed precipitates will be washed with water and dried in air at 60°C for 24 h.

The determination of the present phases was realized by X-ray Diffraction (XRD) through Shimadzu XRD 6000; CuKα radiation with $\lambda = 1{,}5488$ Å was used. The 2θ angle range was 10-80°, with a step of 1.0°/min. Additionally, it is hoped to characterize the samples obtained through Diffuse Reflectance Spectroscopy (DRS), Scanning Electronic Microcopy (SEM), Energy Dispersive Spectroscopy (EDS), Infrared (IR) and Raman spectroscopy. Experiments of pollutants organic degradation in water under visible light will be carried out.

3. Results and Discussion

XRD pattern of the $CuWO_4$-(1) bulk material is shown in Figure 1. This pattern show the characteristic peaks of $CuWO_4$ phase (JCPDF No. 01-070-1732) and other minority peak indexed too, associated to Cu_2WO_4 phase. It is hoped to obtain the $CuWO_4$ phase with the purpose to study the formation possible of $CuWO_4$/CuO heterostructured system.

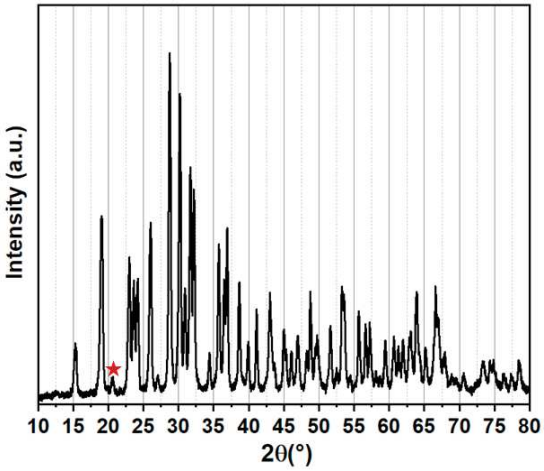

Figure 1. XRD of $CuWO_4$-(1) sample. Peak corresponding to other phase had been indicated.

Since the synthesis process we identified that if the solution was not heated to 90°C WO_3 phase will be formed. Similarly, to bring the pH at 6, after cooling until room temperature, promotes the formation of non-stoichiometric tungsten oxide.

We hope compare the properties of $CuWO_4$/CuO heterostructured system with the properties of $CuWO_4$/CuO heterostructure obtained through a simple sol-gel method, since ammonium paratungstate and annealing at 300°C. XRD pattern of this heterostructure allowed identify the CuO and $CuWO_4$ crystalline phases. IR analysis showed the vibrational bands of the CuO and $CuWO_4$ phases. In FE-SEM images, well-defined polyhedral ($CuWO_4$) coverage with agglomerates of nanoparticles (CuO) are distinguished, indicating the heterostructure was obtained (Figure 2). Two indirect gap values were obtained: 1.35 eV for CuO and 2.11 eV for $CuWO_4$. All these results show that $CuWO_4$/CuO heterostructure was obtained and their properties make it a promising candidate for testing of photocatalytic degradation, which was confirmed by a single Rhodamine-B degradation experiment.

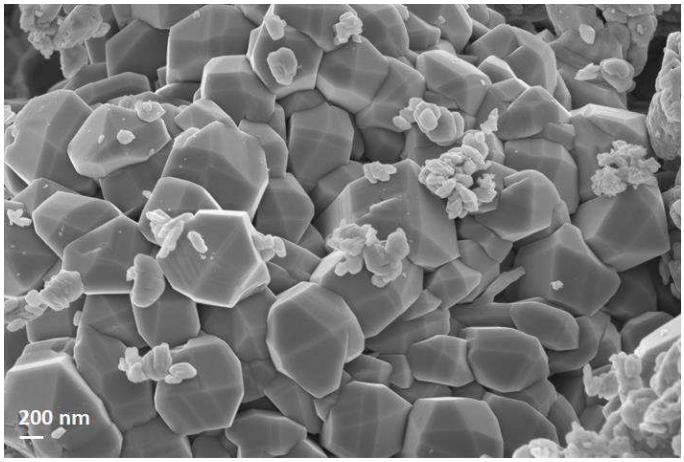

Figure 2. FE-SEM image CuO/$CuWO_4$ heterostructure.

4. Conclusions

XRD pattern of the CuWO4-(1) bulk material showed the characteristic peaks of $CuWO_4$ phase and one minority peak associated to Cu_2WO_4 phase. $CuWO_4$/CuO heterostructure was obtained through a simple sol-gel method like a sample comparison. This material is the base of this

study, because will allow us to compare the structural, morphological and optical properties of the $CuWO_4$/CuO heterostructured system with the properties of that heterostructure obtained previously.

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