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Research Article

PROPERTIES OF NANOCOMPOSITE BASED ON SULFUR AND MODIFIED KETJENBLACK EC-600JD CARBON

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ABSTRACT

This article reports on how sulfur - carbon nanocomposite was prepared by melt infiltration method with Ketjenblack EC-600JD carbon functionalized by H_2O_2. The mixture of sulfur and carbon was converted to the nanocomposite by sintering in nitrogen atmosphere at 160°C for 6 hours and 180°C for 2 hours. The nanocomposite's weight ratio of carbon to sulfur was confirmed by energy-dispersive X-ray spectroscopy. Structural properties and morphology of this nanocomposite was characterized by powder X-ray diffraction, scanning electron microscopy, and transmission electron microscopy analytical methods. The obtained nanocomposite contained 69 wt% sulfur and 31 wt% Ketjenblack EC600JD carbon which was modified by 30 wt% H_2O_2.

Keywords: Sulfur-carbon nanocomposite, Ketjenblack EC-600JD, hydrogen peroxide, melt infiltration method.

1. Introduction

Sulfur is the tenth most abundant element in the universe and exists as a component of various minerals such as galena (PbS), gypsum (CaSO4·2(H2O), pyrite (FeS2), sphalerite (ZnS or FeS), cinnabar (HgS), stibnite (Sb2S3), epsomite (MgSO4·7(H2O)), celestite (SrSO4), and barite (BaSO4) (Wen et al., 2014). Thus, sulfur is low-cost and environmentally friendly. Moreover, elemental sulfur possesses a high theoretical capacity of 1675 mAh g^{-1}, making it a promising cathode material for secondary batteries such as lithium-sulfur and sodium-sulfur batteries, which are notable for their high specific energy. However, sulfur also possesses certain drawbacks, including low conductivity and the dissolution of intermediate products, polysulfide phases, formed by electrochemical reaction between sulfur and anode material (Petzold et al., 2016; Suzuki et al., 2017). Therefore, it is necessary to increase the conductivity of cathode material and reduce

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dissolution of polysulfide by preparing composite of sulfur with conductive materials such as carbon nanotube, porous carbon, graphene, and conductive polymer. Among these materials, porous carbon has received the most interest due to its high conductivity and porous structure, providing shelters for sulfur and decreasing the movement of intermediate products into electrolyte (Bugga et al., 2017).

There have been numerous studies concerning the preparation of nanocomposite of sulfur and carbon. Research proposal challenges were the increase of the linkage of sulfur to conductive material and infiltration of sulfur particles into porous carbon. Elemental sulfur could be embedded into carbon by melt infiltration, vapor phase infiltration, solution infiltration, and mechanical intrusion. Sulfur element melts at 119.6^{o}C and achieves the minimum of viscosity at around 154^{o}C (Evers & Nazar, 2012). Switching from solid to liquid state, sulfur's specific volume increases, and it easily diffuses into the space of porous carbon. This technique does not require advanced equipment and can be carried out in an inert atmosphere to avoid oxidation of sulfur. For microporous conductive host material, melted sulfur encountered issues in transferring to microporous space (Suzuki et al., 2017). Therefore, sulfur is heated to initiate vapor phase infiltration. In case of fabrication of the composite at room temperature, sulfur is dissolved into suitable solvents, making it a solution-based infiltration. Subsequently, the organic solvents are separated from the sulfur-carbon composite. Furthermore, sulfur and carbon could be mixed by mechanical forces. However, it is difficult to transfer sulfur into porous carbon by mechanical intrusion as sulfur only interacts with the external surface of carbon. For melt infiltration, vapor phase infiltration, solution-based infiltration, and mechanical intrusion, sulfur and carbon could be distributed and dispersed evenly and uniformly. However, improving chemical bonds between sulfur and carbon requires more effective methods. Surface of carbon or sulfur should be modified by chemical methods, such as grafting polar functional groups on the surface or synthesis of sulfur-containing compounds with better solubility (Su & Manthiram, 2012; Elazari et al., 2011).

In this research, nanocomposite based on sulfur and Ketjenblack EC-600JD carbon was fabricated by melt infiltration after modifying carbon surface by oxidizing carbon with hydrogen peroxide. Properties of this nanocomposite were evaluated by various analytical techniques such as scanning electron microscopy (SEM), energy-dispersive x-ray spectroscopy (EDS) and powder X-ray diffraction (XRD). The presence of polar functional groups on carbon surface was confirmed by Fourier Transform Infrared Spectroscopy (FTIR) and Raman spectroscopy (Fu & Manthiram, 2012; Wang et al., 2011).

2. Materials and methods

2.1. Modification of Ketjenblack EC-600JD carbon

After weighing by analytical balance, Ketjenblack carbon was put into 4M HCl solution. The mixture was stirred, heated to 80^{o}C, and kept at this temperature for 2 hours in order to wash away all impurities. The carbon was filtered from the mixture, then

washed several times by dilute NaOH solution and distilled water to reach to a pH value of 7. The carbon was then vacuum-dried to remove all moisture and then kept in a desiccator.

The experiment was then carried out in a 250 ml flask connected to a suitable condenser which was used in order to maintain volume of the solution. The flask was placed in the microwave oven operating at the frequency 2.45 GHz. One gram of treated Ketjenblack carbon with 100 ml of 30 % w/w H_2O_2 were put into the flask and heated by microwave energy for 60 minutes to reach the temperature of 70^{o}C. Then, the carbon, which was removed from the mixture by filtration, was rinsed by distilled water to reach a neutral pH and vacuum dried.

2.2. Preparation of sulfur-carbon nanocomposite

At first, the modified Ketjenblack carbon and sulfur were mixed and ground together to achieve a uniform mixture. Then, the mixture was heated to 160^{o}C for 6 hours in a sealed vacuum oven to let sulfur diffuse into the porous space of carbon. Next, the mixture was maintained in the oven at 180^{o}C for 2 hours to increase the diffusion of sulfur. After that, the oven was cooled down to room temperature and the nanocomposite was received. The sulfur content of the nanocomposite was determined by the modern SEM equipped with EDS.

2.3. Characterization

Modified KB was examined by FTIR spectra recorded by Brucker Tensor 27 and Raman spectroscopy measured by Horiba Jobin Yvon Labram HR300 system.

Sulfur-carbon nanocomposite structure was examined by a Rigaku/max 2500Pc X-ray Diffractometer. Morphology and element components were characterized by SEM and EDS with Hitachi SEM S4800-NHE equipment, in which SEM was used to observe surface morphology and particle size of the composite and EDS was used to evaluate the uniform distribution of carbon and sulfur. Moreover, EDS mapping was used to analyzed the elemental distribution in the composite. Microstructure of the composite was evaluated through TEM with JEOL JEM 1400 microscope.

3. Results and discussion

3.1. Properties of ketjenblack carbon oxidized by hydroperoxide

The modified Ketjenblack carbon's properties were examined by FTIR. The FITR spectra of pristine Ketjenblack carbon (CB00 sample) and modified Ketjenblack (CB60 sample) are presented in the Figure 1. In the FTIR spectroscopy, the peak at 3422.75 cm^{-1} shows the O-H stretching mode of hydroxyl functional groups. The band at 1570.98 cm^{-1} is assigned to the C=O stretching vibration of carboxyl groups. An intense band at 1160.10 cm^{-1} reflects the C-O stretching and O-H bending modes of polar functional groups. The FTIR spectrum of CB60 sample presents the functional groups which are attached on carbon surface. In contrast, there is no peak in the FTIR spectrum of CB00. The existence of 3422.75 cm^{-1}, 1570.98 cm^{-1}, and 1160.10 cm^{-1} peaks proves that after oxidation by H_2O_2, there are various hydroxyl and carboxyl groups appearing in Ketjenblack carbon samples.

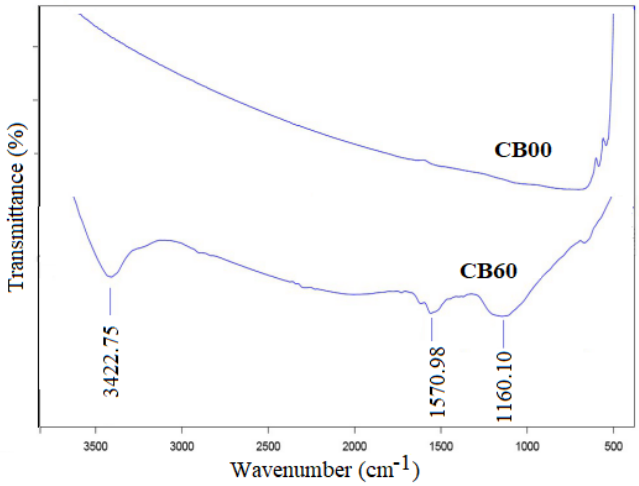

Fig. 1. *FTIR spectra of modified Ketjenblack carbon*

The Raman spectra of Ketjenblack carbon are shown in Figure 2. The intensity ratio of D-band and G-band of Raman spectra determines the impurity and defect concentration of the carbon. G-band indicates the graphite structure and D-band presents the formation of defects in the structures. Therefore, the high I_D/I_G ratio confirms that carbon sample possesses a high number of defects, proving its strongly oxidized surface. The I_D/I_G ratios of pristine Ketjenblack carbon (CB00) and modified Ketjenblack carbon (CB60) are 1.108 and 1.226, respectively (Fig. 2 and Table 1). These results reflect that the surface of CB60 is oxidized by H_2O_2. Therefore, CB60 was used for the next experiment of fabrication of nanocomposite.

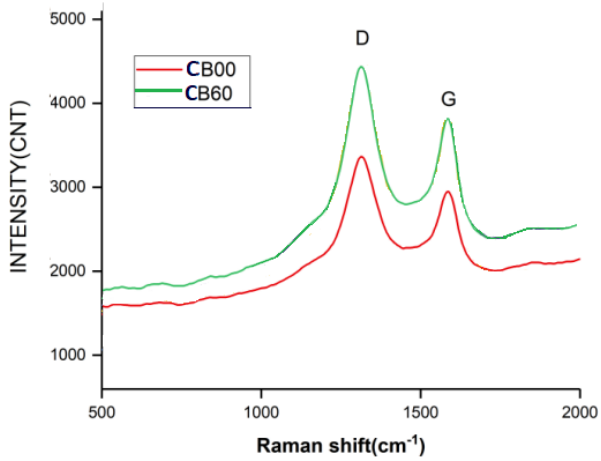

Fig. 2. *Raman spectra of modified Ketjenblack carbon*

Table 1. *Intensity ratios of D-band and G-band of Raman spectra of modified Ketjenblack carbon*

Sample	I_D	I_G	I_D/I_G
CB00	3246.99	2932.98	1.108
CB60	4693.76	3829.28	1.226

3.2. Structure of the sulfur-carbon nanocomposite

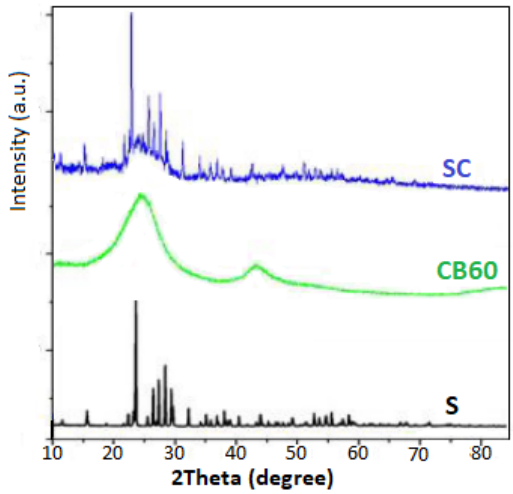

Fig. 3. *XRD patterns of sulfur (S), modified carbon (CB60), sulfur-carbon nanocomposite (SC)*

The XRD patterns of sulfur, modified carbon, and sulfur-carbon nanocomposite are illustrated in Fig. 3. Sulfur presents typical orthorhombic crystal structure with strong diffraction peaks at 2θ=23–29°, while CB60 carbon shows amorphous structure with two broad diffraction peaks at 24° and 45°. The XRD pattern of SC exhibits a similarity compared with the patterns of CB60 and sulfur, containing the peaks at 2θ=23–29° and the broad peak appearing at 24° with weaker intensity. The existence of these peaks proves that the SC nanocomposite contains modified carbon and sulfur.

3.3. Surface morphology and elemental distribution of the sulfur-carbon nanocomposite

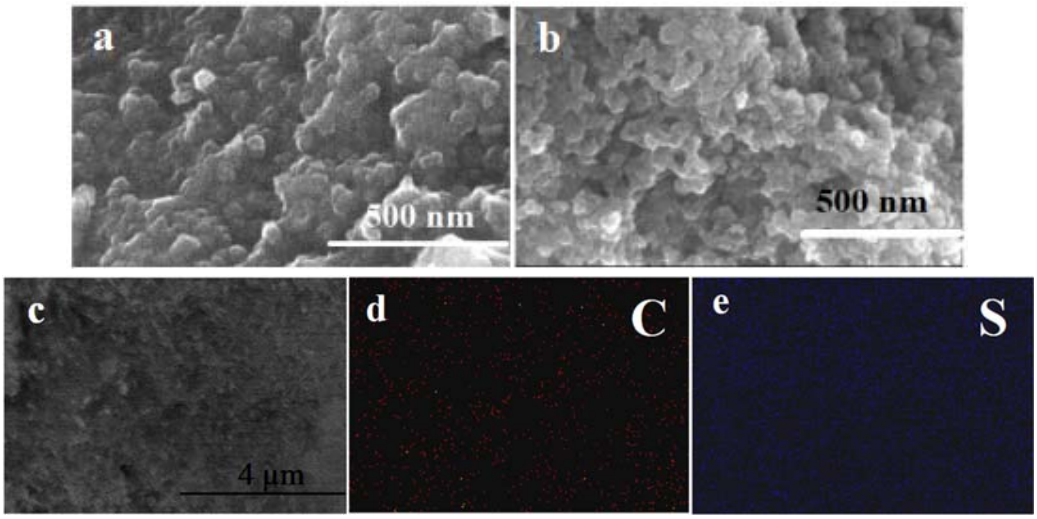

Fig. 4. *SEM images of SCB (a), SC (b) and EDS mapping of SC*

The morphologies and particle size of sulfur-carbon nanocomposite are described by SEM images (Fig. 4). The nanocomposites samples are labelled SC. SCB is named for the nanocomposite before being heated. SEM image (Fig. 4a) of SCB shows that the carbon and sulfur are distributed uniformly with a loose-particle aggregation and narrow particle size at about 50 to 100 nm. This image is different from that of SC (Fig. 4b) which are the nanocomposites being heated. Through melt infiltration, sulfur element diffuses and disperses in the porous structure of carbon, increasing the linkage of composite components and aggregation of carbon and sulfur particles. The elemental distribution of carbon and sulfur in the sulfur-carbon nanocomposite is illustrated in Fig. 4 (c, d, e). It can be seen that the carbon and sulfur elements are uniformly distributed and dispersed in the nanocomposite.

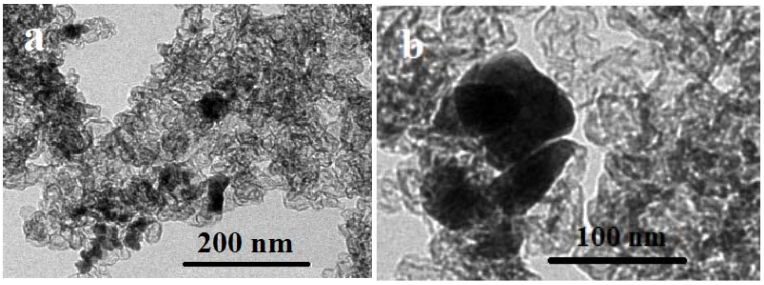

Fig. 5. *TEM images of SC*

The microstructure of the sulfur-carbon nanocomposite is revealed by TEM images which are shown in Fig. 5. It can be seen that the composite consists of carbon and sulfur, and sulfur element corresponds to the darker area in the image. It is apparent that sulfur particles are partially covered by the carbon layer which can be seen in Fig. 5b.

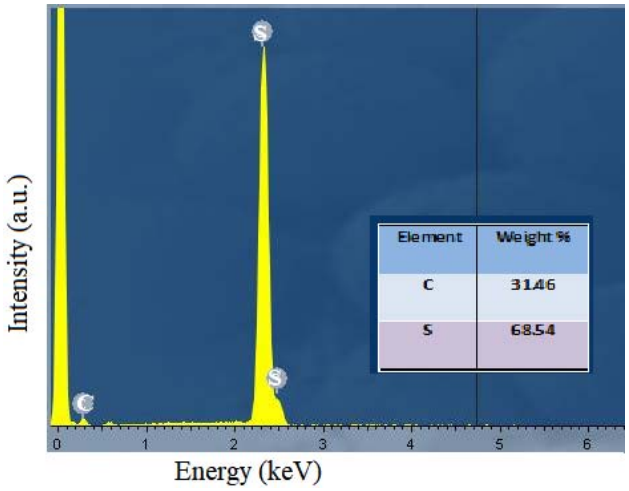

Fig.6. *EDS spectrum of the sulfur-carbon nanocomposite*

The content of the nanocomposite is presented by EDS spectrum (Fig. 6). It can be observed that the contents of carbon and sulfur are about 31 wt% and 69 wt%, respectively.

4. Conclusions

In this research, the sulfur-carbon nanocomposite based on sulfur and modified carbon was successfully fabricated with a composition of 69 wt% sulfur and 31 wt% modified Ketjenblack EC600JD carbon by melt infiltration method. The process of modifying carbon was conducted by oxidation of 30 wt% H_2O_2 for 1 hour. The FTIR and Raman spectrum of modified carbon revealed that it possessed polar functional groups grafting on the surface carbon. The properties of the carbon sulfur nanocomposite were examined by XRD, SEM, TEM, EDS. Through these methods, the structure, morphology, and composition of the nanocomposite were confirmed that the nanocomposite contained nano-sized sulfur and carbon particles and sulfur particle was partially enveloped by carbon.

❖ ***Conflict of Interest:*** *Authors have no conflict of interest to declare.*

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KHẢO SÁT TÍNH CHẤT CỦA NANOCOMPOSITE ĐƯỢC CHẾ TẠO TỪ LƯU HUỲNH VÀ CACBON KETJENBLACK EC-600JD BIẾN TÍNH

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TÓM TẮT

Trong bài báo này, tác giả đã chế tạo nanocomposite lưu huỳnh – cacbon bằng phương pháp nóng chảy từ cacbon Ketjenblack EC-600JD đã được chức hóa bằng hydrogen peroxide. Quá trình hỗn hợp lưu huỳnh và cacbon chuyển sang dạng nanocomposite được thực hiện bằng phương pháp gia nhiệt ở nhiệt độ 160^{o}C trong 6h và 180^{o}C trong 2h ở môi trường khí nitơ. Tỉ lệ khối lượng thành phần cacbon và lưu huỳnh trong nanocomposite được xác định bằng phổ tán xạ năng lượng tia X. Tính chất, cấu trúc và hình thái bề mặt của nanocomposite được phân tích bằng phương pháp nhiễu xạ tia X, kính hiển vi điện tử quét và kính hiển vi điện tử truyền qua. Kết quả nhận được nanocomposite chứa 69 % lưu huỳnh và 31 % Ketjenblack EC-600JD đã được biến tính bằng dung dịch H_2O_2 30 %.

Từ khóa: Nanocomposite lưu huỳnh – cacbon, Ketjenblack EC-600JD, hydrogen peroxide, phương pháp nóng chảy.