



Photoactivity of S-doped nanoporous activated carbons: A new perspective for harvesting solar energy on carbon-based semiconductors

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ABSTRACT

Photoactivity of S-doped nanoporous carbons was tested using photocurrent generation, cyclic voltammetry and photodegradation of methylene blue (MB) under artificial solar irradiation. The results were compared to those obtained on unmodified carbons and on commercial TiO₂. A significant generation of photocurrent at visible and NIR radiation from 400 to 1200 nm was found. An exposure to ambient light has a strong effect on an open circuit potential indicating the strong activity of S-doped carbons in oxidation reactions. The activity in the process of MB degradation was about 2.2 and 1.9 higher than that obtained on a commercial TiO₂. The extent of photoactivity depends both on the composition of the activated carbon and on the sulfur content. The results suggest that incorporation of sulfur decreases the energy band gap in activated carbon.

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1. Introduction

The sun energy harvesting and its technological usage are one of the challenges of contemporary science and engineering [1,2]. Solar energy is produced by photovoltaic devices using semiconductor-based materials such as silicon, carbon, titanium dioxide or zinc oxides. Semiconductors and quantum dots of specific band gap energy are widely explored in order to increase the quantum efficiency of energy conversion [1]. Even though an activated carbon addition to titanium oxide has been studied previously with the intention to enhance the charge separation and decrease the particle size of the semiconductor [3–6], recent developments in graphene science directed the attention of scientist to graphene-semiconductor composites as photocatalysts for solar energy conversion and visible light water splitting reactions [7–10]. Recently Yeh et al. reported the semiconductor properties of graphene oxide (GO) and their application to hydrogen production from water splitting process [11]. The photoactivity of GO was linked to its high dispersion in water and the presence of oxygen groups. Some unspecified groups, not reduced during irradiation process were suggested as responsible for a sustained gap width. That initial band gap was evaluated to be between 2.4 and 4.3 eV. The catalytic properties of activated carbons toward

formation of oxygen superions taking an important part in oxidation reactions were investigated by Strelko et al. [12] and Matzer and Boehm [13]. Theoretical calculations indicated that incorporation of certain nitrogen or phosphorus groups decreases the energy gap from 4.8 to 2.88 eV and thus increases the catalytic reactivity of carbons. One of the important applications of this catalytic activity, which can only gain from engagement of photoactivity, is degradation of organic contaminants on activated carbons. Up to now TiO₂ is the best photocatalyst, however it is only photoactive under UV irradiation, which clearly limits its usage in water photodetoxification under real solar conditions [14]. Previous studies have shown that an introduction of oxygen groups to carbon surfaces not only plays a photo-assisting role and enhances TiO₂ photoactivity in the degradations of various organic contaminants [15–19] but also enhances hydrogen photoproduction by water splitting [20] under artificial solar conditions. Recently, the direct photoactivity of activated carbons in UV range was reported by Velasco et al. [21]. Also, Wang et al. [22] and Zhang et al. [23] have showed that graphitic carbon nitrides structures are photoactive under visible light for the hydrogen evolution. Selective oxidation of benzene to phenol was investigated on this kind of materials by Chen et al. [24]. Although a possible decrease in the energy gap caused by introduction of sulfur heteroatoms to a carbon matrix has been hypothesized by Strelko et al. [12], to the best of our knowledge, the present work is the first report on the direct semiconductor photoactivity in visible light of sulfur-doped activated carbons. Very high activity of these kind of carbons for oxidation reactions of ammonia [25] or arsine [26] was reported previously and the activation of oxygen to superoxy ions as active species

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