Photoelectrochemical degradation of microplastics using a boron-doped diamond modified with $BiVO_4$ photoanode electrode

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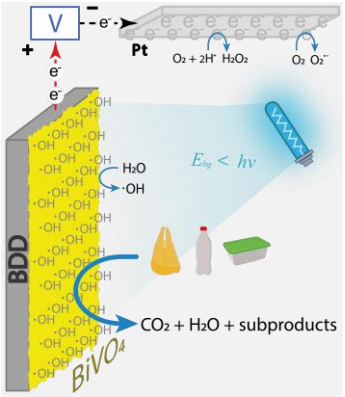

Microplastic in the environment has been cataloged as an emerging risk due to de fact they have been found both ecosystems and into living being, even humans. Thus, the remotion and elimination of microplastics (MPs) from wastewater and urban water systems has become a crucial issue. Herein, we present a novel system to degrade high density polyethylene (HDPE) microplastics in water by mean photoelectrocatalysis (PEC) using a photoanode composed of modified boron-doped diamond (BDD) with $BiVO_4$. The photoanode was made by annealing treatment using a precursor solution and hydrothermal treatment. It showed and high response under visible light and production of hydroxyl radicals which showed to be an optimal material to degrade organic material. In the microplastic degradation, the PEC system exhibited to be more efficient than electrocatalysis and photocatalysis.

Introduction

Over the past year, microplastics (MPs) have become omnipresent particles, mainly in groundwater, drinking water, and some animals including humans. Due to their particle size (particles less than 5 mm) and their chemical composition, MPs in the environment are dangerous because they can be vectors to viruses and bacteria, transport other organic or inorganic pollutants, and enter the food chain by smaller animals.

Considering their persistence in the environment, scientists have studied the remotion of microplastics in water by several physical methods such as adsorption, coagulation/flocculation, flotation, filtration, and magnetic separation [1]. These methods are aimed at separating the solids of the water but not degrade them.

New oxidation-advanced processes (OAPs) have gained popularity for the degradation of MPs. Technics like photocatalysis (PC) and electrocatalysis (electrooxidation, EO) have been shown to achieve up to 89% using a boron-doped diamond electrode by EO of polystyrene, or 65% using ZnO nanorods by PC degradation of polypropylene. In our previous study, we explore a photoelectrochemical (PEC) system in the degradation of MPs using TiO_2/BDD photoanode [2]. Now we studied the degradation of polyethylene (PE), which is one of the plastics most commonly found in marine environments and one of the most produced annually.

So, in this study, we present the degradation by PEC of high-density PE (HDPE) microplastics using $BiVO_4$/BDD photoanodes made by mean calcination and hydrothermal methods. The behavior of the photoanode was studied by electrochemical analysis (transient photocurrent, linear sweep voltammetry, cyclic voltammetry, and electrochemical impedance spectroscopy), and another analysis of morphology and structural compositions was also studied. Finally, a comparison of photocatalysis and electrocatalysis is given to compare the enhancement of the system.

Material and Methods

The photoanode was made by the seed-assisted hydrothermal method. Briefly, 0.33 M of $Bi(NO_3)_3{\cdot}5H_2O$ was dissolved in 23% HNO_3 solution then 0.33 M of NH_4VO_3 and 0.66 M of citric acid were added into the last solution and stirred until dissolving. The BDD electrode (Si-substrate) was dipped into the precursor solution and dried at room temperature, then the electrode was annealed at 450°C (3 °C/min) for 2 h. Finally, 1.8 mmol of $Bi(NO_3)_3{\cdot}5H_2O$ was added to 1 mL of HNO_3 (68%) with 2 mL of DI water. With constant stirring, 1.8 mmol of NH_4VO_3 was added to the last solution. After solubilizing, the solution and the electrode (15 mL, with the seed layer facing down) were transferred into the autoclave and heated at 180 °C for 18 h. Finally, the photoanode was annealed at the same condition as the seed layer [3].

The electrochemical measures were carried out in a potentiostat (PalmSens) using $BiVO_4$/BDD photoanode as a work, platinum as a counter electrode, Ag/AgCl (KCl sat.), and LED light (7 W). For the cyclic voltammetry, transient photocurrent and chopped light linear sweep voltammetry analysis a 0.1 M of Na_2SO_4 was used, and the electrochemical impedance spectroscopy was carried out in 4 mM Fe^{2+}/Fe^{3+} solubilized in 0.1 M of KCl.

The cell used for the degradation of MPs for the PEC, EO, and PC was composed of $BiVO_4$/BDD photoanode as a work, platinum as a counter electrode, Ag/AgCl (KCl sat.) as a reference electrode to control the anodic potential, LED light (7 W), and DC power supply. To stabilize the MPs in

suspension, 0.0074% of Tween 20 was added to the 0.1 M Na_2SO_4 solution and 200 µL of Tween 20 was added every 2 h of degradation for 8 h (3 times in all).

Results and Discussion

PEC performance of the obtained $BiVO_4$ photoanode showed an increase in the photocurrent of ~13 times more than the bare BDD (**Figure 1a**), also it showed a light decrement over time possibly produced by its natural photocorrosion and the formation of oxygen bubbles on its surface. LSV studies with chopped light revealed the nature of n-type semiconductors since, in oxidative potentials, it has the highest photocurrent (**Figure 1b**). Finally, EIS studies showed the $BiVO_4$/BDD under visible light had the smallest semi-circular arc diameter which is related to the diminution in the charge transfer resistance (R_{ct}).

The XRD spectra show characteristic peaks at 18° and 28° corresponding to (110) and (121) planes of the monoclinic $BiVO_4$ crystalline phase, also no other peaks of Bi_2O_3 and V_2O_5 impurities appeared. SEM images depicted the homogenous distribution of $BiVO_4$ thin film on the BDD and elemental analysis revealed the approximate proportion of Bi, V, O in the semiconductor.

Regarding the degradation of MPs, a first exploratory analysis was developed by the degradation of N-dimethyl-p-nitrosoaniline (RNO) which is well-known as a hydroxyl radical scavenger. A scan of potentials was carried out in order to find the anodic potential with more production of radicals. As can be seen in **Figure 1c**, 2.70 V (*vs.* Ag/AgCl) presents a decrement in the kinetic constant which could be attributed to the preferent oxygen production in the system. Nevertheless, high potentials could agglomerate the MPs due to the bubbles and also produce the detachment of the $BiVO_4$ film. Hence, lower potentials were tested in PEC degradation.

Overall, figures obtained by COD show the degradation of MPs follows the same trend as other homogenous systems where the pollutant is degraded preferably as PEC > EO > PC.

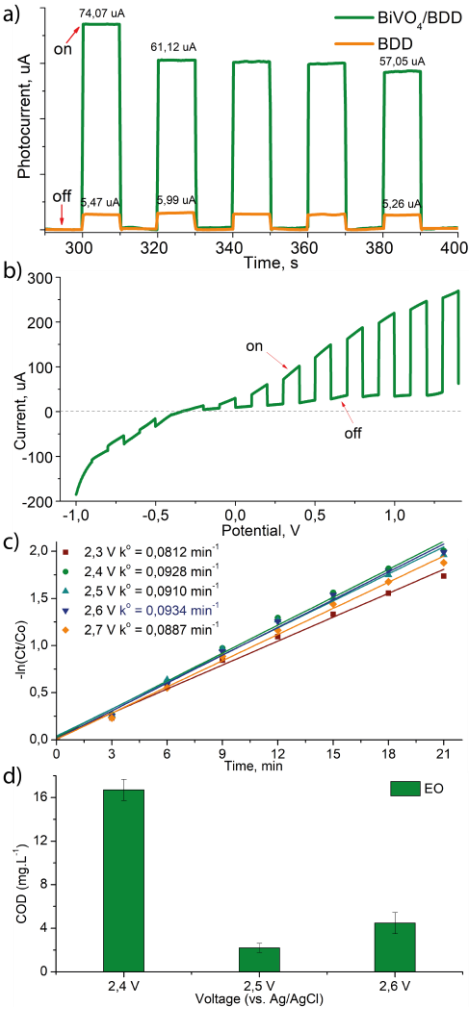

Figure 1. a) Photocurrent, b) Linear sweep voltammetry with chopped light, c) regression of degradation of RNO as a hydroxyl radical scavenger d) degradation of MPs.

Conclusions

In summary, the target photoanode exhibits strong photochemical performance, which is supported by EIS, LSV, and transient photocurrent. The most relevant results are depicted in photocurrent, which achieves up to 74.1 µA at 1.60 V (*vs.* Ag/AgCl). The RNO essays showed the production of hydroxyl radicals is higher in PEC than EC and PC, which had the same tendency in the degradation of microplastics, obtaining the highest COD figures in 2.4V. We can conclude that the applicability of this photoanode could be extensive in environmental treatments and fuel production.

Acknowledgments

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