Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

Electrosynthesis and photoelectrochemical properties of polyaniline/SiC nanohybrid electrodes

CrossMark

Attila Kormányos[a,b], Róbert Ondok[a,b], Csaba Janáky[a,b,*]

[a] MTA-SZTE "Lendület" Photoelectrochemistry Research Group, Rerrich Square 1, Szeged, H-6720, Hungary
[b] Department of Physical Chemistry and Materials Science, University of Szeged, Rerrich Square 1, Szeged, H-6720, Hungary

ABSTRACT

The growing amount of carbon dioxide (CO_2) emission in parallel with the increasing greenhouse effect put the utilization of carbon dioxide in the focus of scientific interest in the past decade. Photoelectrochemical (PEC) conversion of CO_2 to useful products is one of the promising possibilities towards reaching this goal. In this paper, we report on the PEC behavior of polyaniline (PANI)/SiC photoelectrodes with various PANI/SiC ratios, obtained by electrochemical polymerization. Electrochemical polymerization allowed for the precise control over the composition and morphology; and ensured that PANI was only deposited on the surface of the SiC nanoparticles. The nanocomposite samples were characterized by scanning and transmission electron microscopy and Raman spectroscopy. Linear sweep photovoltammetry measurements showed improved PEC properties of the nanocomposites compared to their pristine counterparts (i.e., SiC and PANI). The enhancement was rooted in the (i) higher electrochemically available surface area, (ii) decreased bandgap (2.9 eV vs. 3.1 eV), and the (iii) mediating effect of PANI in both H_2 evolution and CO_2 reduction. Long-term CO_2 photoelectrolysis measurements coupled with analytical techniques (^{1}H NMR and GC-BID) confirmed the formation of hydrogen, carbon monoxide, methanol, and ethanol proving the capability of the nanocomposite material to reduce CO_2 to useful products. We think that lessons learned from this study may contribute to the rational design of nanocomposite photoelectrodes with enhanced performance for solar fuel generation.

1. Introduction

One promising way to fight against climate change is to reduce the amount of CO_2, released from anthropogenic sources. Photoelectrochemical (PEC) conversion of CO_2 to useful products is one of such options. This way sunlight can be utilized, and the collected energy can be stored in the form of chemical bonds [1,2]. To drive this process efficiently, a given photoelectrode material has to simultaneously fulfill a series of criteria. These include sufficiently narrow bandgap to harness a broad portion of the solar spectrum, appropriate band edge positions, high chemical-, electrochemical-, and photostability, low toxicity and cost-effective preparation, etc. [3–5]. Not surprisingly, no single material has emerged yet, which alone bears with all these features. As an alternative approach to single compounds, hybrid photoelectrode materials can be

developed, in which each component has a precisely defined function, thus achieving superior properties [6].

Silicon carbide is a wide-bandgap (E_{BG} = 2.4–3.1 eV) semiconductor (SC), which exhibits either n-, or p-type behavior depending on the polymorph (note that over a hundred different polytypes are known for SiC) [7–9]. Many of them have excellent mechanical properties and chemical stability, high thermal conductivity, biocompatibility, diverse surface chemistry, and affordable production cost [10–13]. These features enable their broad-range application, such as in the SC industry (mainly substrate for high-temperature and high-power electronics) [14], in optoelectronic devices [10], in biosensors [15,16], and even in quantum information processing [17]. Furthermore, the conduction band edge position of SiC allows its application for the photo-driven reduction of water and CO_2. PEC H_2 evolution was shown, using single crystal p-type 4H-SiC [18], and bulk/epitaxially-grown p-type 4H-, and 6H-SiC [19]. PEC CO_2 reduction was first demonstrated in 1979 [20]. The main products were hydrogen and methanol, along with some formaldehyde. Contrastingly, when we tried to employ the cubic polytype (3C-SiC, which

behaves as a p-type SC) for the PEC reduction of CO_2, only marginal photocurrents were detected (Fig. 1). Moreover, the photoresponse of SiC was very slow (note that the applied sweep rate was only 0.5 mV s^{-1} during measurements in Fig. 1) indicating that both H$^+$-, and CO_2-reduction processes are *kinetically hindered* on the surface of the SiC nanoparticles. This statement is also supported by the experiments performed in O_2 atmosphere: the photocurrents increased, mostly because O_2 acted as an e$^-$-scavenger and rapidly reacted with the photogenerated electrons. According to these observations, if the surface of the nanoparticles is modified with a co-catalyst which acts as a mediator of the targeted reactions, the sluggish surface kinetics can be improved and the promising properties of SiC can be harnessed.

Conducting polymers (CPs) are attractive candidates to act as co-catalysts, because CP-based nanocomposites can be prepared via mild synthetic routes and the monomer structure can be tailored to fit the requirements of the given application (e.g., tunable bandgap, higher CO_2-adsorption capacity) [21,22]. In this vein, CP/SiC nanocomposites were already synthesized using various CPs, such as polyaniline (PANI) [23–27], polypyrrole (PPy) [28–31], and poly(3-thiophene-acetic-acid) [32]. There are two common attributes in these studies: (i) the nanohybrids were synthesized by chemical polymerization, except our precedent study, where PANI was photodeposited on the surface of the SiC nanocrystals [24], and (ii) the PEC properties of these nanocomposite materials have not been explored yet. Importantly, chemical polymerization methods always lack the precise control over the structure and morphology of the hybrid, although the well-defined structure and morphology are prerequisite to obtain synergistic activity [6]. Thus photocatalytic [24], electrochemical-[33], and photoelectrochemical [34] deposition of CPs on the SC surface offer much better alternatives. Additionally, CPs themselves (without any co-catalyst or other SC) can act as photo-electrodes [35,36]. To the best of our knowledge, CP/SiC nanohybrids have not been studied as photoelectrodes, therefore the exploration of their PEC properties, along with the possible synergistic behavior toward the PEC reduction of CO_2, is a very interesting research topic, providing insights into nanocomposite design. This exercise is especially interesting for p-type SCs because most precedent works were focused on composites containing n-type SCs (e.g., TiO_2, ZnO, WO_3).

In this study, we report on the PEC behavior of PANI/SiC nanocomposite photoelectrodes, synthesized with various PANI/SiC ratios. Enhanced PEC behavior was experienced for all nanocomposite electrodes, and the underpinning physical-chemical and morphological factors were explored. The product distribution also altered, CO was found in higher concentration (along with higher FE values), while the amount of H_2 remained the same compared to the experiments with bare PANI. Methanol and ethanol were detected in the liquid phase samples, for both PANI and PANI/SiC photoelectrodes. Our findings may help to design better co-catalyst alternatives to further improve the PEC performance of such nanocomposite assemblies.

2. Experimental

2.1. Materials

Silicon carbide (3C-SiC, U.S. Research Nanomaterials Inc., d$_{average} \approx$ 50 nm), sulfuric acid (H_2SO_4, Sigma-Aldrich), sodium sulfate (Na_2SO_4, VWR), sodium hydrogen carbonate ($NaHCO_3$, VWR), and isopropanol (IPA, VWR) were of analytical grade and used without further purification. Nitrogen (N_2, 99.995%), carbon dioxide (CO_2, 99.995%), helium (He, 99.9999%), and argon (Ar, 99.999%) gases were purchased from Messer. Aniline (Sigma-Aldrich) was vacuum-distilled prior to each use. All solutions were prepared using deionized water (Millipore Direct Q3-UV, 18.2 MΩ cm).

2.2. Preparation of the SiC thin films

The SiC nanoparticles were dispersed in IPA (c = 10 mg ml^{-1}) by ultrasonication for 30 min prior to spray-coating. The as-prepared dispersion was spray-coated on a preheated (T = 140 °C) glassy carbon (GC) electrode surface, employing an Alder AD320 type airbrush and a homemade spray-coater robot, operated with 1 bar compressed air pressure. The mass of the spray-coated SiC was 0.4 mg cm^{-2} for each sample (studies were carried out between 0.1–1.0 mg cm^{-2} and 0.4 mg cm^{-2} was found to be optimal). No additional heat treatment procedure was applied after this step.

2.3. Physical characterization

Transmission electron microscopic (TEM) images were taken by using a FEI Tecnai G^2 20 X-Twin type instrument, operating at an acceleration voltage of 200 kV. A Hitachi S-4700 field emission scanning electron microscope was used for the scanning electron microscopy (SEM) measurements, operating at an accelerating voltage of 10 kV. Raman spectra were collected by using a DXR Raman Microscope using a λ = 532 nm green laser, operating at 5 mW laser power.

2.4. Electrochemical and photoelectrochemical measurements

All electrochemical measurements were performed on a Metrohm Autolab PGSTAT302 type potentiostat/galvanostat. The electropolymerization of aniline on the GC and SiC-coated GC electrode substrates was carried out in a classical three-electrode cell setup, using a Ag/AgCl/3 M NaCl as a reference-, and Pt sheet as a counterelectrode, respectively. Aniline was electropolymerized potentiodynamically from a solution, containing 0.2 M aniline monomer and 0.5 M H_2SO_4. The polymerization was performed by scanning the potential between −0.2 V to 0.9 V at 100 mV s^{-1} scan rate. In some cases, the polymerization charge density was so low, that the contribution of charging the double layer to the overall charge seriously affected the amount of the deposited polymer under coulometric conditions. To avoid this issue, the GC and SiC-coated GC electrodes were pretreated at E = 0.6 V for 120 s. After polymerization, the electroactivity of the PANI and PANI/SiC layers was monitored by cyclic voltammetry (CV). These measurements were carried out in a sealed, one-compartment custom-designed, three-electrode quartz cell. The PANI and PANI/SiC layers on the GC
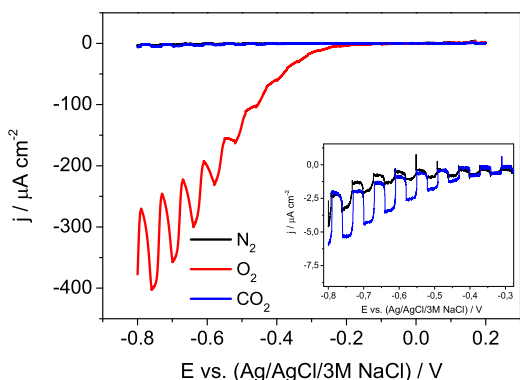
Fig. 1. Photovoltammograms recorded for SiC-modified GC electrodes (m$_{SiC}$ = 0.4 mg cm^{-2}); in N_2-saturated 0.1 M Na_2SO_4, O_2-saturated 0.1 M Na_2SO_4 and CO_2-saturated 0.1 M $NaHCO_3$ solutions (all pH ≈ 7.0). The sweep rate was kept at 0.5 mV s^{-1}, while the light-chopping frequency was 0.017 Hz. A 300W Hg-Xe lamp was used as a UV-vis light source.