Chapter 49
Nanostructured Diamond Electrodes for Energy Conversion Applications

S. Pehlivanova, Ch. Petkov, C. Popov, P. Petkov, V. Boev, and T. Petkova

Abstract The subject of our work is the investigation of boron doped nanocrystalline diamond (NCD) layers functionalized with photosensitive molecules of manganese phthalocyanine. The functionalized NCD sample was used as a working electrode in a three electrode cell and electrochemically studied. The two methods applied were stationary volt-ampere (VA) measurements and cyclic voltammetry (CV) in dark and under illumination. The VA and CV measurements showed that the electrode has a wide potential range and a high photosensitivity. The results obtained are promising for future application of functionalized diamond electrodes in light conversion systems.

Keywords Diamond electrode • Photoelectrochemistry

49.1 Introduction

Diamond thin films have been proven to be excellent materials for electrochemical applications since the performance of diamond electrodes can be much superior to that of alternative materials, such as glassy carbon and graphite. Boron doped

---

S. Pehlivanova (✉)
Department of Physics, University of Chemical Technology and Metallurgy,
8 Kl. Ohridski blvd., 1756 Sofia, Bulgaria

Institute of Electrochemistry and Energy Systems, BAS, Acad. G. Bonchev bl.10,
1113 Sofia, Bulgaria
e-mail: silviya.pehlivanova@gmail.com

Ch. Petkov • C. Popov
Institute of Nanostructure Technologies and Analytics, University of Kassel,
Heinrich-Plett-Str. 40, 34132 Kassel, Germany

P. Petkov
Department of Physics, University of Chemical Technology and Metallurgy,
8 Kl. Ohridski blvd., 1756 Sofia, Bulgaria

V. Boev • T. Petkova
Institute of Electrochemistry and Energy Systems, BAS, Acad. G. Bonchev bl.10,
1113 Sofia, Bulgaria

P. Petkov et al. (eds.), *Nanoscience Advances in CBRN Agents Detection, Information and Energy Security*, NATO Science for Peace and Security Series A: Chemistry and Biology, DOI 10.1007/978-94-017-9697-2_49

diamond (BDD) electrodes possess many outstanding properties, including a wide electrochemical potential window in aqueous solutions (ca. 3 V), low and stable background currents, electrochemical stability, and corrosion resistance in aggressive media [1, 2].

For electrochemical applications, the diamond thin films must possess a significant conductivity, and the majority of work in this area has been carried out using very heavily doped boron diamond layers, which display almost metal-like properties.

The increasing energy demand and the environmental pollutions have led to a need for clean renewable energy. The photosynthesis is a well-known process for many years, and scientists are trying to mimic it, because of its possible application for energy harvesting. For electrocatalysis in reactive environments, such as those taking place in solar energy conversion processes, it is important to attach electrochemically active molecules to the surface of inert electrodes. Electrochemical polymerization of metal phthalocyanine (MePc) complexes onto electrodes is one of the most effective means of developing active surfaces for electrocatalytic purposes.

The metal phthalocyanines have attracted significant attention due to their diverse electronic, optical and structural properties, which make them very good candidates for photosensitizers, photoconducting agents and photovoltaic cells. Due to their extraordinary thermal stability, MePcs can capture or harvest more sun light than many conjugated polymers [2].

In the present work we studied NCD electrodes functionalized with manganese phthalocyanine (MnPc). The structure and the optical properties of the MnPc solution in dichloromethane were analyzed and the functionalized electrodes were electrochemically tested. We demonstrate differences in the electrochemical properties due to electrode illumination; the results indicate that the NCD films may be a preferred choice for a number of photoelectrochemical applications.

49.2 Experimental Details

49.2.1 Synthesis of Nanocrystalline Diamond (NCD) Films

Nanocrystalline diamond films were grown on silicon substrates using the chemical vapor deposition (CVD) technique from a mixture of methane and hydrogen. Typical CVD diamond synthesis includes activation of a gas mixture, gas phase reactions and a subsequent transfer of the diamond forming gas species onto the substrate surface [3]. To obtain conducting material boron was introduced in the reactions chamber during the growth process. NCD surfaces are chemically inert and have a hydrogen termination after the deposition. The surface can be modified by plasma- or photo-chemical processes in order to achieve a desired surface termination. In this work the samples were subjected to oxygen plasma modification (2.45 GHz) in an oxygen asher (TePla 200-G) for 5 min at 200 W discharge power and 0.67 mbar working pressure [4].

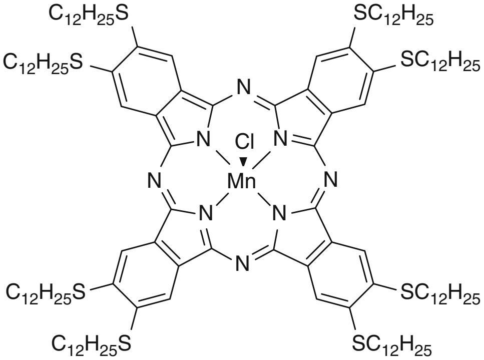

Fig. 49.1 Structure of the manganese (III) phthalocyaninato complex

49.2.2 Characterization of Manganese (III) Phthalocyanines

The manganese (III) phthalocyaninato complex ($C_{128}H_{208}ClMnN_8S_8$), MnPc, synthesized in the group of Prof. Siemeling, Institute of Chemistry, University of Kassel, Germany has a molecular structure with a square-planar configuration with a central metal atom of manganese, as shown in Fig. 49.1

The MnPc powder was dissolved in CH_2Cl_2 to a concentration of 1 μM. The structure of the MnPc in the solution was characterized by FT-IR spectrometry (VARIAN 660-IR). The spectra were recorded in the spectral region of 500–5,000 cm^{-1}.

The optical behavior of the MnPc solution was studied by UV-VIS spectroscopy using a Cary 100 instrument in the double beam mode. The samples were scanned in the region of 200–900 nm with a scan rate of 600 nm/min; CH_2Cl_2 was used as a reference solution.

The NCD films were kept in the MnPc solution for 12 h for attachment of the photosensitive molecules, afterwards electrodes were prepared from the functionalized NCD films.

49.2.3 Electrochemical Tests of the Diamond Electrode

The BDD layers deposited on silicon substrates were assembled as electrodes by covering the substrate backs and attaching a Pt wire.

The electrochemical tests were carried out in a three-electrode cell with a buffered electrolyte (a water-based salt solution containing sodium phosphate, sodium chloride and, in some cases, potassium chloride and potassium phosphate with pH 7.4). The working active surface area of the electrode was ~0.5 cm^2. Platinum served as a counter electrode, a reversible hydrogen electrode (RHE) was chosen as a reference.

The electrochemical behavior of the BDD electrodes were studied in dark and under illumination with a light-emitting diode (LED) with a wavelength of ~720 nm:

1. By measuring the change of the electrochemical potential with the time in dark and after short illumination (volt-ampere characteristics) and
2. By cyclic voltammetry at different experimental conditions.

The electrochemical variations due to light illumination were recorded with an experimental set-up consisting of a light chopper and a computerized UT 60 A measuring system.

The cyclic voltammetry experiments were carried out in a Faraday cell with a rate of 100 mV/s at room temperature.

49.3 Results and Discussion

The IR spectrum of manganese phthalocyanine (Fig. 49.2) displays a high number of bands which originate from the relatively large and complex molecule. Most of the peaks of phthalocyanine are located in the middle IR region since peaks associated with the central metal atom are not visible in this spectral range. The IR spectra, however, should reflect the changes in the configuration of phthalocyanine macrocycles due to the introduction of a template metal.

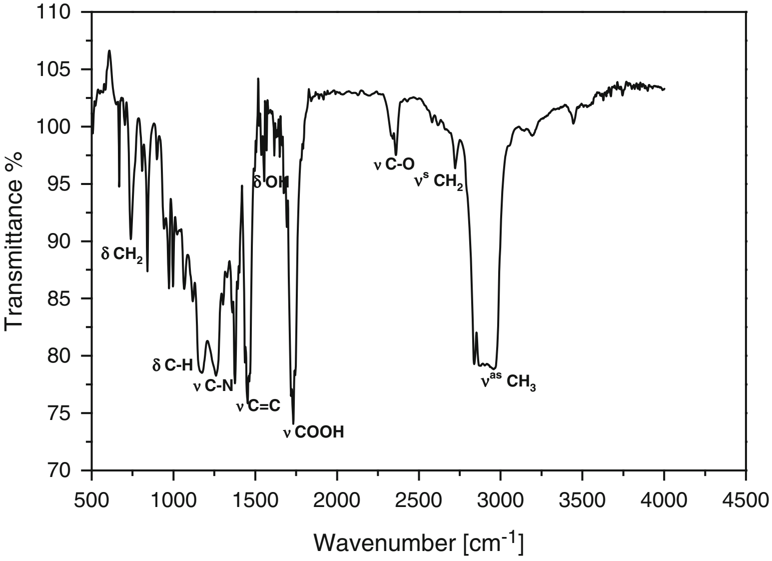

Fig. 49.2 IR spectrum of ($C_{128}H_{208}ClMnN_8S_8$) in the region of 500–4,000 cm^{-1}

The sharp band at about 1,700 cm^{-1} is due to stretching deformations of the aromatic rings consisting of carbon-carbon bonds. Deformation vibrations associated with carbon-hydrogen interactions stemming from the Pc rings and out-of-plane bending of the carbon-hydrogen bonds in the ring system are detected at 740 and 1,170 cm^{-1}. The broad bands of valence vibrations related to the same bonds are situated in the region 2,700–2,950 cm^{-1}. The valence vibrations observed at 1,450 and 1,360 cm^{-1} are due to C = C and C-N bonds typical for Pc rings. Some carbon-oxygen bonds around 2,500 cm^{-1} are also observed as well as complex C-O-OH vibrations at 1,750 cm^{-1} [5].

Figure 49.3 shows the absorption spectra of MnPc dissolved in CH_2Cl_2 in the spectral region of 300–900 nm. The UV–VIS spectra of MePcs strongly depend on the central metal atom; the absorption spectra can be shifted to the IR or UV region by changing the central metal atom in the phtalocyanine molecule. The MnPc complex shows strong absorption regions in the UV region at about 346 nm (B band) and in the visible region at 719 nm (Q band), respectively (Fig. 49.3). In the region from 450 to 600 nm the solution transmits the light to a large extent. The intense absorption peak at 719 nm and the shoulder with a lower intensity at 684 nm are very typical for phthalocyanines containing S and O, or S, O and N cyclic substituents [6].

The electrochemical studies under illumination were performed with a LED emitting at a wavelength of about 720 nm close to the absorption maximum of the MnPc under study. The surface properties of the BDD electrodes are important for the electrochemical reactions occuring at the interface between the electrolyte and the electrode surface. The functionalized BDD electrodes measured in dark

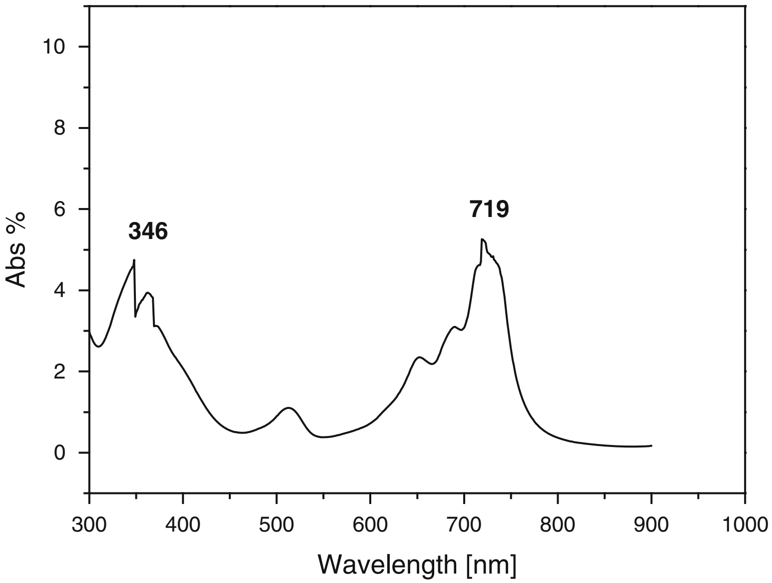

Fig. 49.3 UV-VIS spectrum of MnPc dissolved in CH_2Cl_2

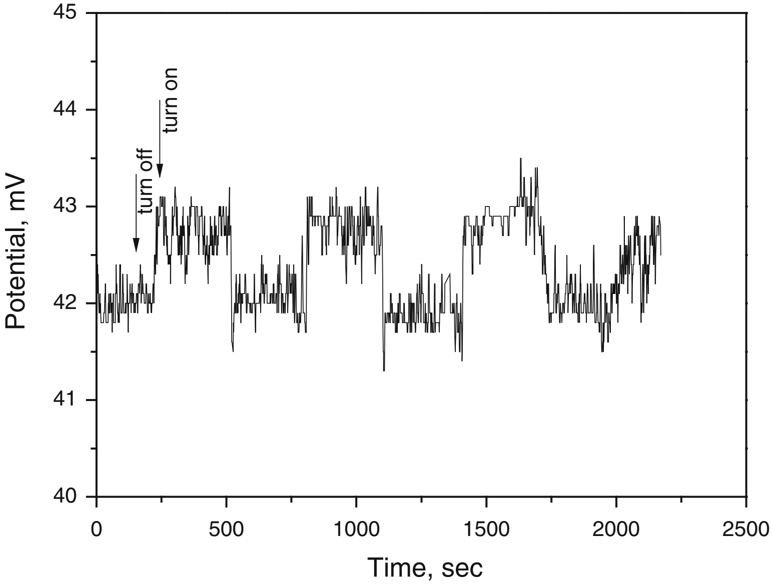

Fig. 49.4 Photo measurements of the BDD electrode functionalized with MnPc

and under illumination show a potential difference of several mV due to the photocurrent generated at the interface (Fig. 49.4). These measurements prove that the phthalocyanine molecules were successfully attached on the diamond electrode surface.

The diamond electrode was electrochemically studied also with cyclic voltammetry in the region between hydrogen and oxygen evolution with a scan rate of 100 mV/s in dark (1), under illumination (2) and after illumination (3) (Fig. 49.5). The four main peaks observed in curve 1 are labeled as I, II, III, IV. These peaks are due both to oxidation and reduction processes. The peak I is observed at about −50 mV and it is most probably related to the reduction from Mn^{3+} to Mn^{2+} of the central atom of the MnPc complex. The next peak is associated with a further reduction of the atom to Mn^{1+} (peak II). The phthalocyanine reduction is observed at about −650 mV associated with valence transition from Pc^{2-} to Pc^{3-} (peak III). The reverse reaction of the phthalocyanine oxidation is clearly seen at about −500 mV where most probably the phthalocyanine part of the complex changes the valence from Pc^{3-} to Pc^{2-} (peak IV).

The illumination with a LED modifies the curve (curve 2) increasing the intensity of the peaks. The light removes an electron from the phthalocyanine (the photosensitive part of the complex) and catalyzes the process. As a result an increase of the current is registered. After the illumination the current decreases (a relaxation of the system is observed).

The peak positions are slightly shifted in negative direction after the illumination. This may be attributed to modification and reconstruction of the phthalocyanine structure after the illumination [7].

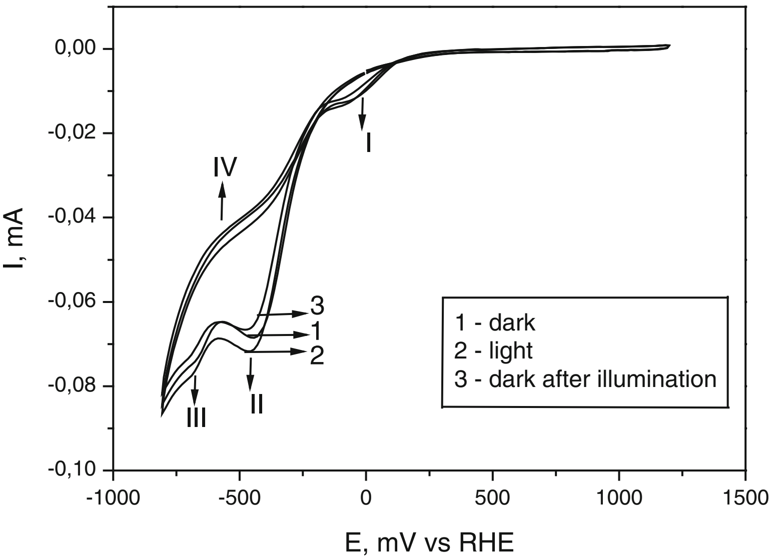

Fig. 49.5 Cyclic voltammograms of BDD electrodes functionalized with MnPc

49.4 Conclusions

Thin boron doped NCD films were deposited on silicon substrates using the CVD technique, and photosensitive MnPc molecules were successfully immobilized on the diamond surface.

The IR spectra of the MnPc showed stretching deformations of the aromatic rings consisting of carbon-carbon bonds, deformation vibrations associated with carbon-hydrogen interactions stemming from the Pc rings and vibrations due to C = C and C-N bonds typical for the Pc rings.

The complex exhibits a strong absorption at 719 nm in the UV-VIS spectra.

The electrochemical measurements revealed that the light catalyzes the process of oxidation and reduction. The process is associated with electron transfers between the central manganese atom and the phthalocyanine complex resulting in an increase of the current.

The experiments suggest that the NCD films functionalized with MnPc are suitable as catalyst for electrochemical reactions.

References

1. Salazar-Banda G, Einaga Y, Martinez-Huitle C (2012) Int J Electrochemistry 2012:1
2. Yuen AP, Jovanovic SM, Hor A, Klenkler RA, Devenyi GA, Loutfy RO, Preston JS (2012) Sol Energy 86:1683
3. Srikanth VVSS, Kumar PS, Kumar VB (2012) Int J Electrochemistry 2012:1

4. Petkov C, Glebe U, Petkov E, Pasquarelli A, Pietzka C, Veres M, Himics L, Merz R, Kulisch W, Siemeling U, Reithmaier JP, Popov C (2013) Phys Status Solidi A 210:2048
5. Singh S, Tripathi SK, Saini GSS (2008) Mater Chem Phys 112:793
6. Şaşmaz S, Kahveci B, Kantar GK, Hacıalioğlu E (2014) El-Cezerî J Sci Eng 1:1
7. Obiraia J, Rodriguesb NP, Bediouib F, Nyokong T (2003) J Porphyrins Phthalocyanines 7:508