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Superoxide-assisted electrochemical deposition of semiconductor polyhydroxyphenylporphyrin films

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Materials and Methods

Hydroxyphenyl porphyrins 5,10,15,20-tetrakis(3-hydroxyphenyl)porphyrin (**1**), 5,10,15,20-tetrakis(4-hydroxyphenyl)porphyrin (**2**), Zn-5,10,15,20-tetrakis(3-hydroxyphenyl)porphyrin (**3**), and Zn-5,10,15,20-tetrakis(4-hydroxyphenyl)porphyrin (**4**) were obtained according to the known two-step procedure.[S1,2] Their characteristics were in a good agreement with those reported previously.[S3,4] The film deposition was carried out from 10^{-3} M porphyrin solutions in dimethylsulfoxide (DMSO > 99.5%, Aldrich) containing 0.02 M tetrabutylammonium perchlorate (TBAP > 98.0%, Aldrich) as the supporting electrolyte. The experiments were performed in a three-electrode electrochemical cell using a SP-150 potentiostat (Bio-Logic Science Instruments, France) equipped with a QCM922A electrochemical quartz microbalance (SEIKO EG & G, Japan). One side of the Pt quartz microbalance electrode (0.196 cm^2), a Pt disc electrode (0.049 cm^2) or a glassy carbon disc electrode (0.126 cm^2, Siggradur, Germany) was used as the working electrode for the polyporphyrin film preparation. The semiconductor properties of the polyporphyrin film were determined by the Mott-Schottky method[S5,6] in a degassed 0.5 M KCl + 0.001 M $K_3Fe(CN)_6$ aqueous solution using a Solartron SI 1260 frequency response analyzer equipped with a Solartron SI 1287 electrochemical interface. The spectral properties of the solutions and films were estimated using a Cary 50 spectrometer (Varian, USA) and a Vertex 80v spectrometer (Bruker).

Data processing

The Mott-Schottky approach assumes an applicability of the one-dimensional Poisson equation to the distribution of the potential at the interphase boundary and the Boltzmann distribution for the charge carrier concentration. That assumption leads to a linear dependence of the inverse square of the capacitance of the interface (C^{-2}) on the working electrode potential, according to expressions 1 and 2.[S7]

$$\frac{1}{C^2} = \frac{2}{\varepsilon\varepsilon_0 e A^2 N_e}\left(E - E_{fb} - \frac{kT}{e}\right)$$ for *n*-type semiconductors, (1)

$$\frac{1}{C^2} = -\frac{2}{\varepsilon\varepsilon_0 e A^2 N_h}\left(E - E_{fb} - \frac{kT}{e}\right)$$ for *p*-type semiconductors, (2)

where ε is the film permittivity, ε_0 is the free space permittivity (8.85×10^{-12} F m^{-1}), e is the elementary charge (1.60×10^{-19}), A is the working electrode area, N_e and N_h are the electron and hole concentrations, respectively, E is the applied potential, E_{fb} is the flat zones potential, k is the Boltzmann constant (1.38×10^{-23} J K^{-1}), and T is the absolute temperature.

The information on the characteristics of the interface was obtained by electrochemical impedance spectroscopy (EIS). To determine the capacitance of the interfacial EIS, the data **[**Figure S1(*a*)**]** were simulated by the Randles-Erschler equivalent circuit,[S8] and the differential capacitance was then calculated by the Jovik method.[S9]

The obtained capacitance values were linearized in the Schottky coordinates. The experimental dependence was approximated by the function $C^{-2} = a+bE$. In the case of poly-**3** films, the correlation coefficient R^2 was equal 0.994 [Figure S1(*b*)]. The calculated parameters of the straight line were: $a = 1.384\times10^{11}$ Φ^{-2}, $b = -3.335\times10^{11}$ Φ^{-2} B^{-1}. The negative value of parameter b indicated the hole type of conductivity of the obtained material (*i.e.*, a *p*-type semiconductor). According to expression 2 for parameter b:

$$b = -\frac{2}{\varepsilon\varepsilon_0 e A^2 N_h}, \text{ so } N_h = -\frac{2}{\varepsilon\varepsilon_0 e A^2 b} \quad (3)$$

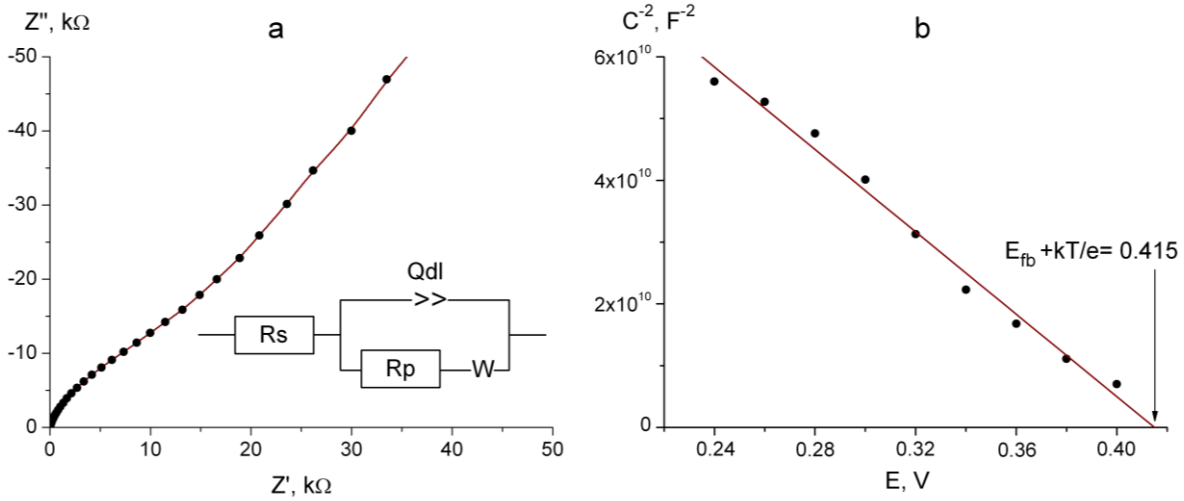

Figure S1 (*a*) Typical Nyquist diagram for the interface of poly-**3** film/solution (points) and simulation result (line). (*b*) Interphase boundary capacitance of poly-**3** film/solution in Schottky coordinates.

Charge carrier concentration was calculated according to expression 3. For calculation, the film permittivity was assumed lying in the range of 5–20,[S10] the true area of the interface film/solution was evaluated for typical film morphology.[S11]

The intersection point of the obtained dependence [see Figure 1(*b*)] with the abscissa axis allowed us to determine the potential of the flat bands E_{fb} of the obtained semiconductor, by the relation:

$$-\frac{a}{b} = E_{fb} + \frac{kT}{e}$$

To determine the optical band gap, the spectral dependence of films absorptions near long wave absorption edge of were represented in the Tauc coordinates.[S12–14] The band gap values could be estimated by extrapolating of plots using straight line to the energy (hν) axis at $(D/\lambda)^2=0$ (Figure S2).

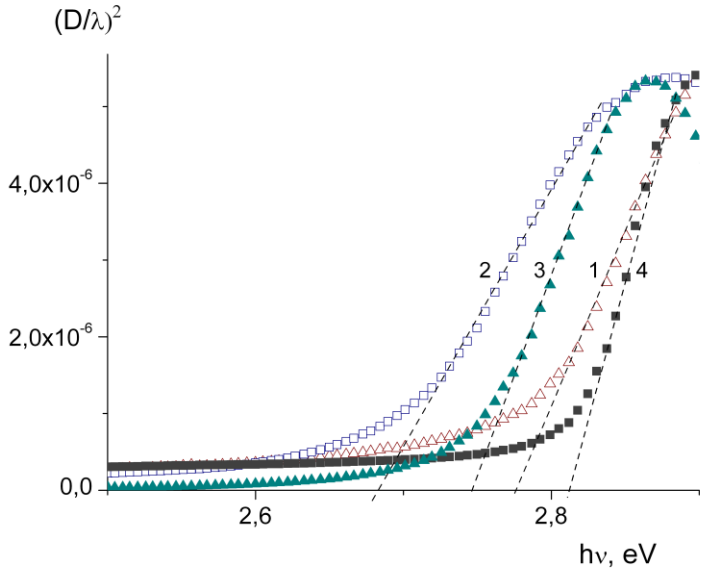

Figure S2 Spectral dependences of films absorptions near long wave absorption edge in the Tauc coordinates**.** 1,2,3, 4: poly-**1**, poly-**2,** poly-**3,** and poly-**4** film, respectively.

References

S1 S. Semeikin, O. I. Koifman and B. D. Berezin, *Chem. Heterocycl. Compd.*, 1982, **10**, 1046 (*Khim. Geterotsikl. Soedin*., 1982, 1354).

S2 A. B. Ormond and H. S. Freeman, *Dyes Pigm.*, 2013, **96**, 440.

S3 V. D. Rumyantseva, A. S. Gorshkova and A. F. Mironov, *Makrogeterotsikly*/*Macroheterocycles*, 2013, **6**, 59.

S4 M. Rojkiewicz, P. Kuś, P. Kozub and M. Kempa, *Dyes Pigm.*, 2013, **99,** 627.

S5 K. Gelderman, L. Lee and S. W. Donne, *J. Chem. Educ*., 2007, **84**, 685.

S6 L. Shi, L. Yang, H. Zhang, K. Chang, G. Zhao, T. Kako and J. Ye, *Appl. Catal. B*, 2018, **224**, 60.

S7 J. Bisquert, *Nanostructured Energy Devices: Equilibrium Concepts and Kinetics*, CRC Press, Boca Raton, FL, 2015.

S8 M. Sluyters-Rehbach, *Pure Appl. Chem.*, 1994, **66**, 1831.

S9 V. D. Jovic and B. M. Jovic, *J. Electroanal. Chem.*, 2003, **541**, 1.

S10 J. P. F. Mota, J. A. E. da Costa, V. G. P. Ribeiro, S. G. Sampaio, N. M. A. Lima, F. L. F. da Silva, C. S. Clemente, G. Mele, D. Lomonaco and S. E. Mazzetto, *J. Braz. Chem. Soc.*, 2017, **28**, 1063.

S11 S. M. Kuzmin, S. A. Chulovskaya, M. V. Tesakova, A. S. Semeikin and V. I. Parfenyuk, *J. Porphyrins Phthalocyanines*, 2017, **21**, 555.

S12 J. Tauc, R. Grigorovici and A. Vancu, *Phys. Status Solidi B*, 1966, **15**, 627.

S13 E. A. Davis and N. F. Mott, *Philos. Mag. A*, 1970, **22**, 903.

S14 O. Stenzel, *The Physics of Thin Film Optical Spectra: An Introduction*, Springer, 2005.