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Melamine Sponges Decorated with Polypyrrole Nanotubes as Macroporous Conducting Pressure Sensors

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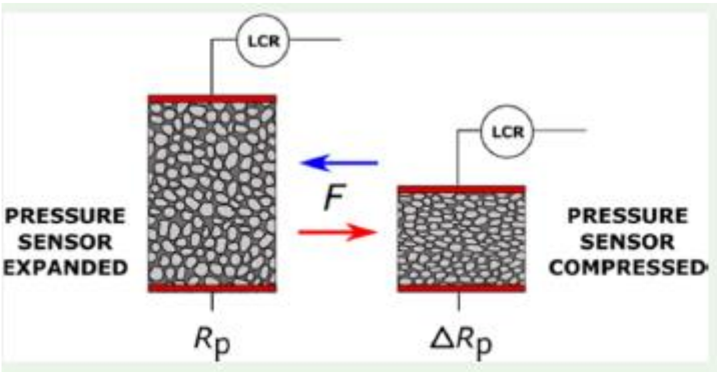

ABSTRACT

The macropores of melamine sponges were coated in situ during the polymerization of pyrrole with either polypyrrole globules or nanotubes and tested as pressure-sensing materials. The dependence of the conductivity of this compressible material on pressure was determined by the four-point van der Pauw method. The conductivity increased from the order of 10^{-2} S cm^{-1} to units of S cm^{-1} at 10 MPa, and it was higher for nanotubes. The pressure dependence of sponge resistance was also recorded in another experimental setup in the design of a simple low-pressure sensor. The information on electrical properties obtained by both methods is discussed. In addition, the use of the melamine sponge decorated with polypyrrole in fields that do not directly exploit conductivity, such as electromagnetic radiation shielding and/or adsorption of organic dye, is also demonstrated. The study proves the superior performance of polypyrrole nanotubes in all applications.

KEYWORDS: Melamine sponge, polypyrrole nanotubes, conductivity, resistance, pressure-sensitive material

1. INTRODUCTION

Polypyrrole ranks among the most studied conducting polymers. Polypyrrole nanotubes are superior to the globular morphology in terms of enhanced conductivity by at least 1 order of magnitude,[1] stability against deprotonation in aqueous media,[2] and improved specific surface area, a feature important for water-pollutant adsorbents[3] as well as in supercapacitor electrodes.[4] Polypyrrole nanotubes are produced easily by including a suitable dye,[1-5] typically methyl orange[6-9] or safranin,[10] in the synthesis route of pyrrole oxidation, which provides a template for polypyrrole deposition.[11] The preparation and application of polypyrrole nanotubes have recently been reviewed.[1] The recent examples of applications include the shielding of electromagnetic radiation,[12-15] magnetorheology,[16] adsorbents in oil-water separation,[17] elastic aerogels for stress sensing,[18] electrochemical sensing,[19] electrodes for supercapacitors[20-22] and batteries,[9,23-26] electrocatalysts,[27] conducting adhesives,[8] thermoelectric materi- als,[28-30] or conducting membranes.[31]

Polypyrrole is prepared by the oxidation of pyrrole with iron(III) chloride or ammonium peroxydisulfate, the former oxidant being preferred[1] (**Figure 1**). It is obtained as an intractable powder that is difficult to apply. For that reason, suitable substrates that provide mechanical support and other user-defined properties are sought for the deposition of polypyrrole. For example, polypyrrole nanotubes have been deposited on textiles[24,32,33] or various inorganic oxides.[9,12,16]

Coating of macroporous melamine sponges with globular polypyrrole,[34] followed by decoration with magnetite nano-particles,[35] has recently been reported.

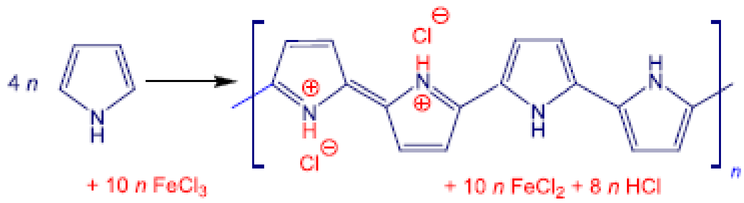

Figure 1. Oxidation of pyrrole with iron(III) chloride to polypyrrole.[16]

A comparison of a globular polypyrrole coating on a macroporous melamine sponge (**Figure 2**) with deposited polypyrrole nanotubes is provided in the present communication. The design of pressure-sensitive materials is the most prospective application. Alternative uses that do not exploit conductivity, such as electromagnetic radiation shielding or organic dye adsorption, are also offered.

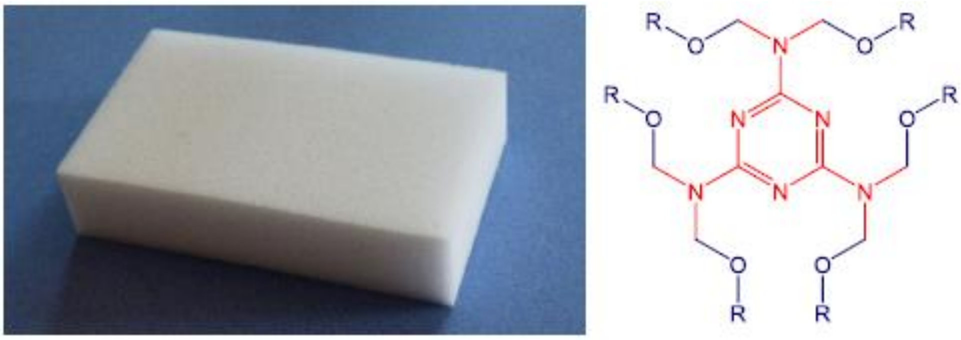

Figure 2. Melamine/formaldehyde sponge and its chemical structure.

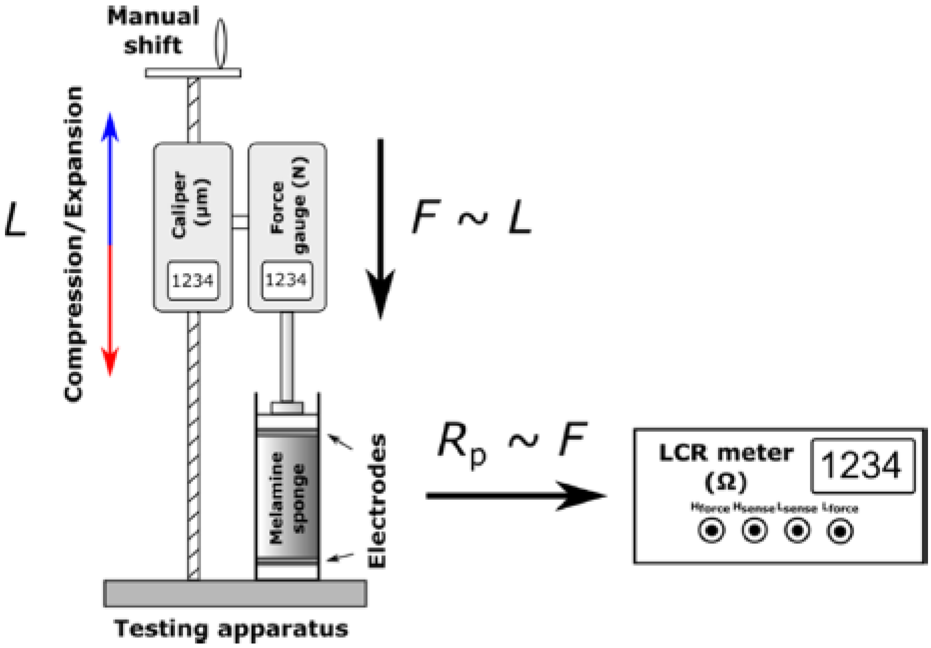

Figure 3. Schematic diagram of the testing apparatus for the resistance response to the sponge compression.

2.EXPERIMENTAL SECTION

2.1.Preparation

A commercial macroporous open-cell mela-mine/formaldehyde sponge (Basotect type, BASF, Germany) was coated with polypyrrole nanotubes in an aqueous reaction mixture containing 0.05 M pyrrole, 0.125 M iron(III) chloride hexahydrate, and 0.002 M methyl orange.[36] Pyrrole (3.35 g) and methyl orange (655 mg) were dissolved in water, and an aqueous solution of iron(III) chloride hexahydrate (33.8 g) was also made separately. The volume of both solutions was adjusted to 0.5 L. They were precooled to 4 °C, mixed, and poured over four melamine sponges with the size of 105 X 62 X 25 mm^3 (**Figure 2**). The sponges were gently squeezed to ensure the penetration of the reaction mixture into the sponge macropores. The oxidative polymerization of pyrrole was left to proceed for 1 h. The sponges were then removed and transferred repeatedly to 0.1 M hydrochloric acid until no colored byproducts were released. The sponge was immersed several times in ethanol to remove water and then left to dry at room temperature in open air. The polypyrrole powder generated outside the sponges was collected and treated in the same manner. Coating with globular polypyrrole was carried out in a similar manner in the absence of methyl orange.[35]

2.2. Characterization

The content of polypyrrole was calculated from the increase of mass after deposition of polypyrrole as 37.4 wt % for nanotubes and 40.2 wt % for globules. The morphology was observed with a scanning ultra-high-resolution electron microscope (MAIA3, Tescan, Brno, Czech Republic).

Cylinders measuring 10 mm in diameter were cut with a circular cork-cutter knife from the sponge and trimmed to ca. 8 mm length. Their conductivity was determined by the van der Pauw method in a laboratory-made cylindrical glass cell with an inner diameter of 10 mm between an insulating support and a glass piston carrying four platinum/rhodium electrodes on the perimeter of its base. The pressure exerted on the sponge was controlled with a load cell (L6E3, Zemic Europe BV, The Netherlands). The thickness of the sponge during the compression was recorded with a displacement meter (Digimatic Indicator 543-122FB, Mitutoyo Corp., Japan).

The apparatus for measurement of resistance response to the sponge compression used a force gauge (Sauter FH 50, KERN & SOHN GmbH, Germany; maximum force, 50 N; resolution, 0.01 N) attached to a testing stand (Sauter TVL, KERN & SOHN GmbH, Germany) with an in-built deflection gauge (10 μm resolution) and an LCR meter (GW Instek LCR-6002, GW Instek) (**Figure 3**). The testing proceeded on the cylinder (19.5 mm in diameter, 30-50 mm in length L) cut out from the sponge. The cylinder was inserted into the acrylic tube and sealed by phosphor bronze round electrodes on both sides. The tube directed the movement of the electrodes during the compression and expansion of the sponge. The electrical resistance of the cylinder was measured by a four-wire connection (AC measurement, voltage 1 V, frequency 1 kHz, C_p-R_p mode). The pressure P inside the cylinder was calculated using the formula $p= F/A$, where F is the force measured by the force gauge and A is a cross-sectional area of the sponge cylinder.

3. RESULTS AND DISCUSSION

3.1. Polypyrrole Coating

The melamine sponge has an open-cell structure with pore sizes of the order of tens of micrometers (**Figure S1**).

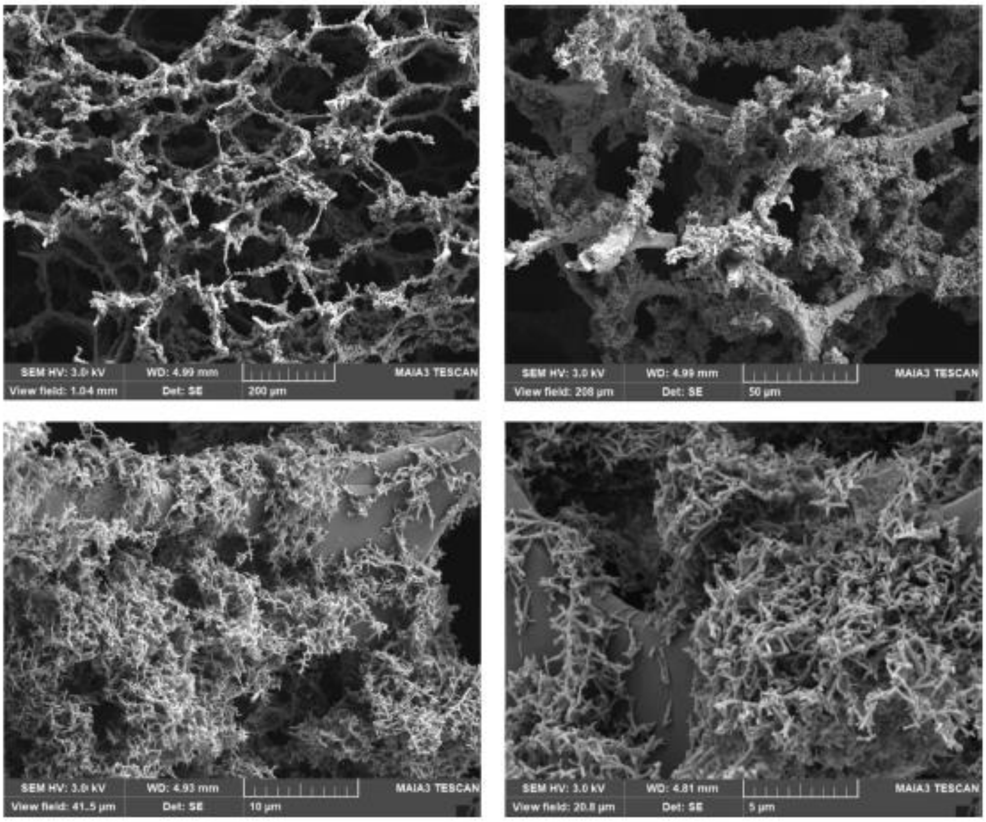

Figure 4. Melamine sponge with deposited polypyrrole nanotubes shown with gradually increasing magnification (scale bars 200, 50, 10, and 5 µm). For the globular coating, see refs [34, 35].

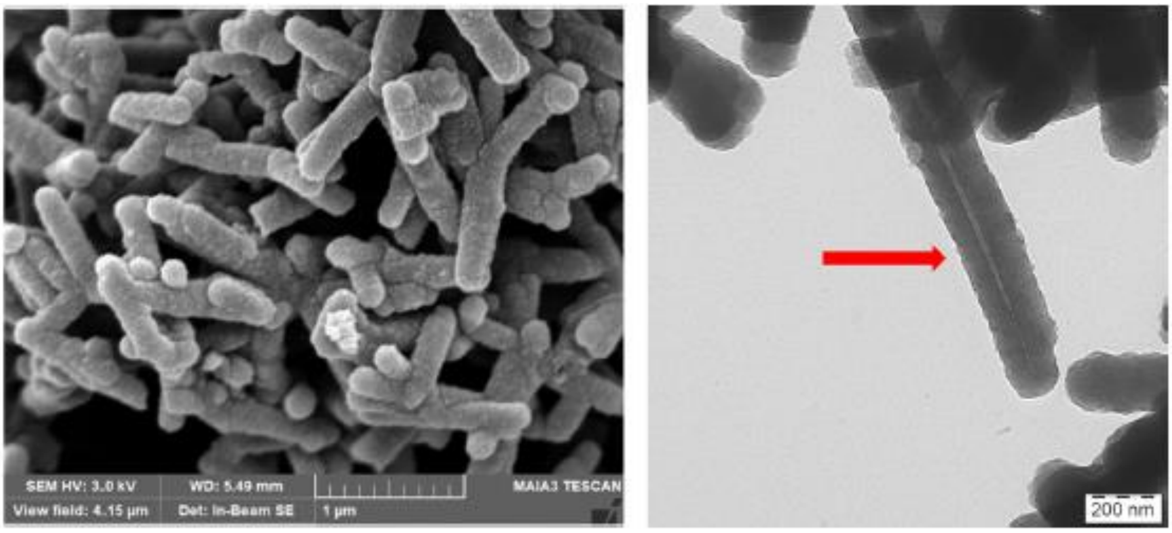

Figure 5. Polypyrrole nanotubes obtained as powders along with coated sponges observed with scanning (left) and transmission (right) electron microscopy. The cavity is marked with an arrow.

It has been coated with polypyrrole by a routine in situ oxidation of pyrrole with iron(III) chloride (**Figure 1**) in the presence of methyl orange, which converts the globular morphology of the conducting polymer to nanotubes[1] (**Figure 4**). Polypyrrole nanotubes have better adherence to the sponge compared to the globular form, and they have a higher conductivity. Polypyrrole nanotubes produced in the reaction mixture outside the sponges have also been collected and characterized independently (**Figure 5**).

The polypyrrole-coated sponges are easily compressed. The double-logarithmic dependence of the thickness on applied pressure was linear for both sponges coated with globular and nanotubular polypyrrole (**Figure S2**), the slope being -0.45, i.e., the thickness is proportional to almost the reciprocal square root of the applied pressure. The fact that the slopes do not differ means that the method of coating does not have any influence on the mechanical properties, which are determined by the melamine skeleton.

3.2. Conductivity

Electrical properties are of prime interest when dealing with sponges coated with conducting polymers. Conductivity is an important intensive characteristic of the material, which usually does not depend on the sample size and shape. For the sponges, however, it is not a constant but it depends on the compression (**Figure 6**). Polypyrrole coats the individual threads of the melamine sponge (**Figure 4**), and the conducting polymer network is connective. During the compression, the number of conducting pathways remains constant, but their number per unit volume increases.

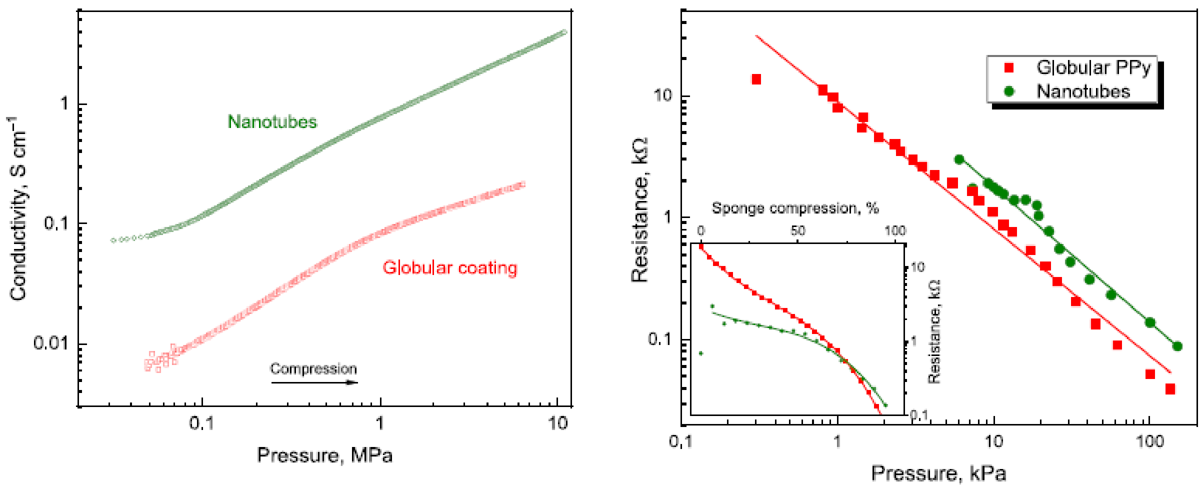

Figure 6. Dependence of the conductivity of sponges decorated with polypyrrole globules or nanotubes on applied pressure.

Moreover, new nodes are created at points where pathways touch each other under pressure. In an isotropic and homogeneous resistor-like mesh, such nodes would have only negligible influence. Nevertheless, a sponge under pressure is neither isotropic nor homogeneous. For these reasons, the conductivity of the sponge with the nanotubular coating increased from ca. 0.05 to 4 S cm^{-1} (**Figure 6**), i.e., 80X after compression to 10% of its original size. The doublelogarithmic dependence curves of conductivity on pressure are slightly sigmoidal **(Figure 6)**, the conductivity of the sponge with nanotubes being about 1 order of magnitude higher compared with the globular coating. The dependences for nanotubular and globular coatings are parallel because the response to pressure is determined by the mechanical properties of the melamine sponge. The mutual shift of the dependences corresponds to a well-known fact that deposited polypyrrole nanotubes have higher conductivity than globular polypyrrole.[1,5,7] In the present study, the conductivity of the separate polypyrrole nanotubes compressed into a pellet was indeed 16.3 S cm^{-1} and that of the globular form was 0.23 S cm^{-1}.

3.3. Resistance

For practical applications, e.g., in pressure sensors, the change of an extensive electrical quantity of the object on applying pressure is determined more frequently. A capacitor-like sample together with a low-frequency LCR meter was used in a simple demonstration setup. Here, the electrical resistance R_p of the presumed parallel resistor— capacitor model of the sponge was selected as a pressure indicator because the sponges behave almost like pure resistors at frequencies below 1 kHz (the phase angle falls below 2°).

For the system under study (cf. the **Experimental Section**), the resistance R_p was reduced as the pressure was applied (**Figure 7**). Alternatively, it can be plotted in dependence on the degree of compression (**Figure 7**, inset). Here, zero compression is defined as the first conducting contact established, and 100% compression is defined as an apparatus limit of the 50 N applied force.

The comparison of characteristic curves of both polypyrrole-coated sponges as low-pressure sensors brought several interesting observations. The measuring range of both sensors differs. Whereas the sponge coated with the globular form of polypyrrole works predictably in a wide pressure range from 0.3 up to 100 kPa, the high initial stiffness of the sponge coated with the nanotubular form of polypyrrole leads to the shift of the lower pressure limit to about 1 order of magnitude. Hence, the resulting range of the pressure sensor based on the sponge coated with polypyrrole nanotubes is from 3 up to 100 kPa.

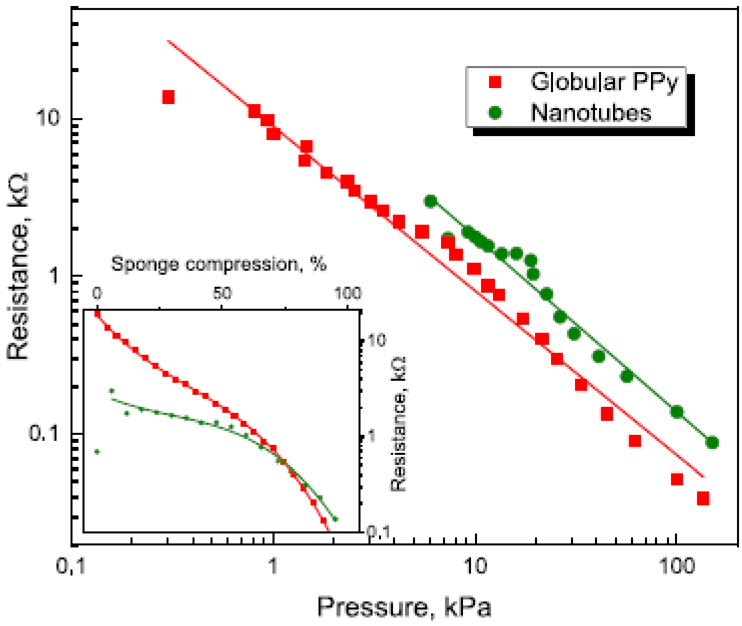

Figure 7. Resistance of the cylindrical sponges as low-pressure sensors under applied pressure. Inset: The resistance of the polypyrrole-coated sponges in dependence on compression.

A low initial sensitivity to compression (from 0 up to 40%) could also be observed in the case of the sponge coated with polypyrrole nanotubes (**Figure 7**, inset). According to our opinion, this behavior is due to a lower content of precipitated polypyrrole nanotubes in the sponge cells compared to the globular counterpart. The mechanism of compression of the sponge coated with nanotubular polypyrrole is given by a gradual collapse of the cells at the beginning (0—40% of compression), which does not lead to resistance decrease. In the later stage of compression (40—100% of compression), the cell walls are close to make contact and any addition of pressure leads to an increase in the contact area and thus to an increase of the density of the conducting pathways indicated as a decrease in sensor resistance.

The absolute value of the resistance R_p of both sensors is irrelevant here, as it depends on the initial choice of sensor dimensions. However, the recalculation of the impedance of sponges to the conductivity according to the formula $\sigma(P) = 1/ R(P) X d(P)/\pi r^2$, where R is the resistance as a function of pressure p, d is the sample thickness depending also on pressure, and r its radius, leads to similar trends and differences for both sponges as observed in **Figure 6**. The above-described seemingly straightforward recalculation can be misleading because the current measured is perpendicular to the force in the former arrangement but is parallel with the force in the latter one.

3.4. Discussion of Electrical Characterization

The difference between the measurements of conductivity and resistance outlined above can be briefly summarized as follows: The conductivity was determined in the present study by the van der Pauw method (**Figure 5**). The DC voltage is applied on the tip electrodes placed on the perimeter of the cylindrical sample base, and the passing current (parallel with the bases) is recorded (**Figure S3**). The potential polarization effects have been avoided by the switching of electrodes. Nevertheless, a simple linear dependence of the resistivity on the sample thickness, which holds for thin samples, had to be replaced by a more complex dependence[37] when the thickness is greater than the radius of the base.

In the determination of the resistance, flat electrodes cover the bases of the cylindrical sample. The dependence of current I passing (perpendicularly to the bases) under applied voltage U yields the resistance $R = U/I$. The polarization of electrodes is prevented using an alternating current of 1 kHz frequency that is often used in electroanalytical chemistry. This is, in fact, rather the absolute value of the complex impedance, which would be identical to the resistance only if the phase angle would approach zero, but this condition is approximately satisfied.

4. ADDITIONAL APPLICATIONS

In addition to the applications as pressure-sensitive conducting materials, other uses can be proposed. The conductivity need not always be the prime parameter,[38] but still the superior performance of the polypyrrole nanotubes can be demonstrated.

4.1. Electromagnetic Radiation Shielding

Melamine sponges coated with globular polypyrrole combined with magnetite have recently been tested in the shielding of electromagnetic radiation in GHz frequencies.[35] The melamine sponge is practically transparent to the radiation and both the absorption and reflection contributions are low (**Figure 8**).

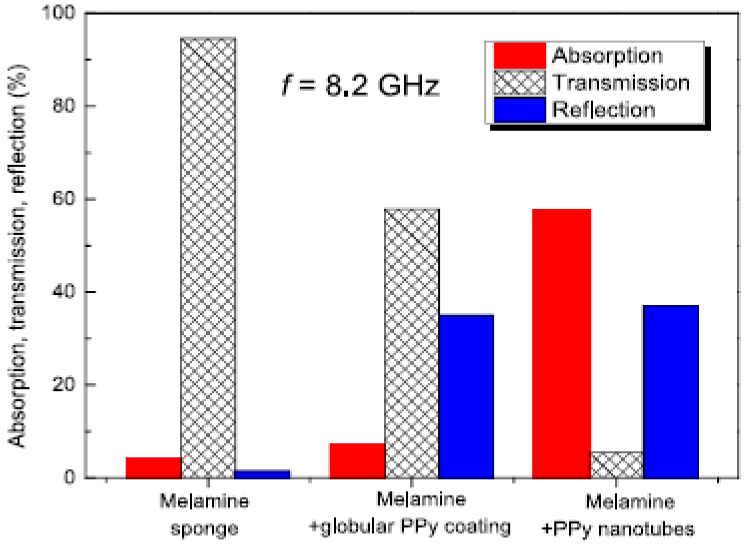

Figure 8. Absorption, transmission, and reflection fractions of 8.2 GHz electromagnetic radiation for the sponge coated with globular polypyrrole or with polypyrrole nanotubes. Sponge thickness was 20 mm.

After coating with globular polypyrrole, the reflection substantially increased but was about the same also for the deposited polypyrrole nanotubes. The dramatic difference, however, is observed in the radiation absorption, when the nanotubes clearly outperform the globular morphology and only about 5% of radiation power passes through the sponge. We conclude that the reflection is controlled by the chemical structure of polypyrrole, while the radiation absorption by its morphology, which is responsible for the level of conductivity.

4.2. Dye Adsorption

Conducting polymers have often been used in the literature for the adsorption of organic dyes that are regarded as water pollutants.[3, 39] The adsorption is explained by the similarity in the molecular structure of conducting polymers and dyes. They both contain aromatic rings available for π−π nteractions and share a conjugated system of alternating single and double bonds. It has recently been reported that the adsorption capacity of Reactive Black 5 on polypyrrole significantly depended on the polymer morphology, nanotubes being more efficient than globules.[33] In the present study, these two polymer morphologies deposited on melamine sponges are compared. The macroporous sponge modified at the surface with polypyrrole may represent a suitable material for practical applications in environmental issues.

Dye adsorption efficiency of polypyrrole-coated melamine sponges has been tested with an anionic azo dye, Reactive Black 5 (**Figure 9**). The sponges were immersed in the aqueous dye solution, and the optical adsorption at a local maximum of 598 nm was monitored as a function of time.

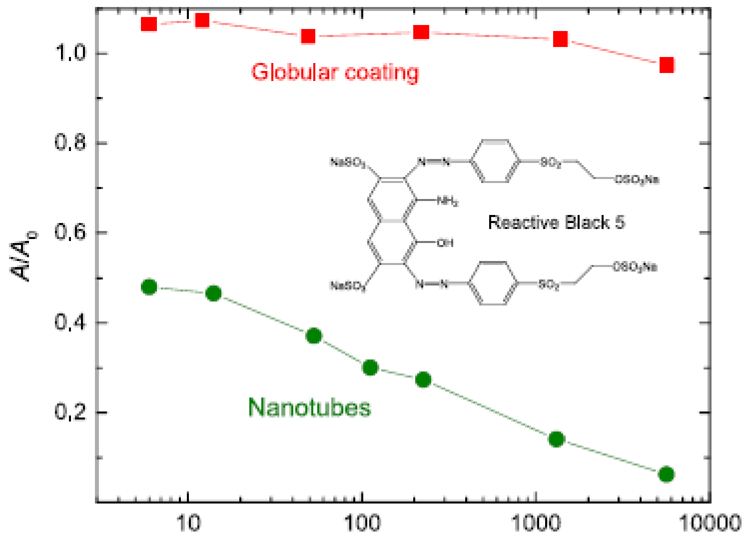

Figure 9. Time dependence of relative optical absorbance A/A_0 at 598 nm wavelength in the solution of Reactive Black 5 (5 mg per 50 mL) after addition of the melamine sponge (100 mg) coated with globular polypyrrole (squares) or polypyrrole nanotubes (circles).

For the globular coating, the adsorption was almost constant, indicating that the dye adsorption was poor. The optical absorbance even exceeded unity because some free polypyrrole nanoparticles were expelled from the sponge to the medium and provided a gray background that lifted the baseline and thus the whole spectrum.

The polypyrrole nanotubes deposited on the sponge adsorbed about one-half of the dye within a few minutes, obviously at the surface of nanotubes. The adsorption then involved diffusion of the dye, which was slow, but led virtually to the complete dye removal within 10^4 min allocated for the experiment. Polypyrrole morphology thus has great importance and has to be considered in all applications of this conducting polymer.

5. CONCLUSIONS

Conducting polypyrrole globules and nanotubes were deposited on macroporous melamine sponges. The study clearly demonstrates the superior performance of nanotubes in applications based on conductivity, viz., pressure-sensitive materials. The methodology of conductivity determination and resistance measurement of the compressible composites is discussed. Additional applications that are not based directly on conductivity are demonstrated. The composite materials are active in the shielding of electromagnetic radiation or in the adsorption of organic dyes in water-pollution treatment. In these cases, the decoration of sponges with nanotubes provided again the best results.

REFERENCES

(1) Stejskal, J.; Trchová, M. Conducting Polypyrrole Nanotubes: a Review. Chem. Pap. 2018, 72, 1563—1595.

(2) Stejskal, J.; Trchová, M.; Bober, P.; Morávková, Z.; Kopecký, D.; Vmata, M.; Prokeš, J.; Varga, M.; Watzlová, E. Polypyrrole Salts and Bases: Superior Conductivity of Nanotubes and their Stability towards the Loss of Conductivity by Deprotonation. RSC Adv. 2016, 6, 88382—88391.

(3) Stejskal, J. Interaction of Conducting Polymers, Polyaniline and Polypyrrole, with Organic Dyes: Polymer Morphology Control, Dye Adsorption and Photocatalytic Decomposition. Chem. Pap. 2020, 74, 1 — 54.

(4) Naskar, P.; Maiti, A.; Chakraborty, P.; Kundu, D.; Biswas, B.; Banerjee, A. Chemical Supercapacitors: a Review Focusing on Metallic Compounds and Conducting Polymers. J. Mater. Chem. A 2021, 9, 1970—2017.

(5) Stejskal, J.; Prokeš, J. Conductivity and Morphology of Polyaniline and Polypyrrole Prepared in the Presence of Organic Dyes. Synth. Met. 2020, 264, No. 116373.

(6) Yang, X. M.; Zhu, Z. X.; Dai, T. Y.; Lu, Y. Facile Fabrication of Functional Polypyrrole Nanotubes via a Reactive Self-Degraded Template. Macromol. Rapid Commun. 2005, 26, 1736—1740.

(7) Sapurina, I.; Li, Y.; Alekseeva, E.; Bober, P.; Trchová, M.; Morávková, Z.; Stejskal, J. Polypyrrole Nanotubes: The Tuning of Morphology and Conductivity. Polymer 2017, 113, 247—258.

(8) Cao, G.; Wang, L. L.; Tian, Y. Q. Highly Dispersed Polypyrrole Nanotubes for Improving the Conductivity of Electrically Conductive Adhesives. J. Mater. Sci.: Mater. Electron. 2020, 31, 9675—9684.

(9) Wen, G. G.; Sui, Y. L.; Zhang, X. P.; Li, J. P.; Zhang, Z. W.; Zhong, S. K.; Tang, S. B.; Wu, L. Mn3O4 Anchored Polypyrrole Nanotubes as an Efficient Sulfur Host for High Performance Lithium-Sulfur Batteries. J. Colloid Interface Sci. 2021, 589, 208—216.

(10) Minisy, I. M.; Bober, P. Frozen-State Polymerizationas a Tool in Conductivity Enhancement of Polypyrrole. Macromol. Rapid Commun. 2020, 41 , No. 2000364.

(11) Stejskal, J. Strategies towards the Control of One-Dimensional Polypyrrole Nanomorphology and Conductivity. Polym. Int. 2018, 67, 1461 — 1469.

(12) Zhang, C. M.; Chen, Y. J.; Li, H.; Tian, R.; Liu, H. Z. Facile Fabrication of Three-Dimensional Lightweight RGO/PPy Nanotube/ Fe3O4 Aerogel with Excellent Electromagnetic Wave Absorption Properties. ACS Omega 2018, 3, 5735—5743.

(13) Gai, L. X.; Zhao, Y. M.; Song, G. L.; An, Q. D.; Xiao, Z. Y.; Zhai, S. R.; Li, Z. Construction of Core-Shell PPy@MoS2 with Nanotube-Like Heterostructures for Electromagnetic Wave Absorption: Assembly and Enhanced Mechanism. Composites, Part A 2020, 136, No. 105965.

(14) Moucka, R.; Sedlacík, M.; Prokes, J.; Kasparyan, H.; Valtera, S.; Kopecky, D. Electromagnetic Interference Shielding of Polypyrrole Nanostructures. Synth. Met. 2020, 269, No. 116573.

(15) Moučka, R.; Sedlačík, M.; Kasparyan, H.; Prokeš, J.; Trchová, M.; Hassouna, F.; Kopecký, D. One-Dimensional Nanostructures of Polypyrrole for Shielding of Electromagnetic Interference in the Microwave Region. Int. J. Mol. Sci. 2020, 21, No. 8814.

(16) Stejskal, J.; Sapurina, I.; Vilčáková, J.; Plachý, T.; Sedlačík, M.; Bubulinca, C.; Gořalík, M.; Trchová, M.; Kolská, Z.; Prokeš, J. Conducting and Magnetic Composites Polypyrrole

Nanotubes/ Magnetite Nanoparticles: Application in Magnetorheology. ACS Appl Nano Mater. 2021, 4, 2247—2256.

(17) Jha, P.; Koiry, S. P.; Sridevi, C.; Putta, V.; Gupta, D.; Chauhan, A. K. A Strategy towards the Synthesis of Superhydrophobic/ Superoleophilic Non-Fluorinated Polypyrrole Nanotubes for Oil— Water Separation. RSC Adv. 2020, 10, 33747—33752.

(18) Ying, S.; Zheng, W. Q.; Li, B. R.; She, X.; Huang, H. B.; Li, L.; Huang, Z. L.; Huang, Y. N.; Liu, Z. T.; Yu, X. H. Facile Fabrication of Elastic Conducting Polypyrrole Nanotube Aerogels. Synth. Met. 2016, 218, 50—55.

(19) Zhang, X. J.; Sheng, Q. L.; Zheng, J. B. Synthesis of Palladium Nanocubes Decorated Polypyrrole Nanotubes and its Application for Electrochemical Sensing. J. Iran. Chem. Soc. 2019, 16, 1061 — 1069.

(20) Wolfart, F.; Dubal, D. P.; Vidotti, M.; Gomoz-Romero, P. Hybrid-Core—Shell Nanostructured Electrodes Made of Polypyrrole Nanotubes Coated with Ni(OH)2 Nanoflakes for High Energy-Density Supercapacitors. RSC Adv. 2016, 6, 15062—15070.

(21) Dong, J. J.; Lin, Y.; Zong, H. W.; Yang, H. B. Hierarchical LiFe5O8@PPy Core-Shell Nanocomposites as Electrode Materials for Supercapacitors. Appl. Surf. Sci. 2019, 470, 1043—1052.

(22) Zou, Y. H.; Wang, H. N.; Sun, H. X.; Lin, Z. X.; Wang, F.; Zhang, X.; Wang, L. J.; Meng, X.; Zhou, Z. Y. Construction of Polypyrrole Nanotubes Interconnected ZIFs-Templated Nickel-Cobalt Layered Double Hydroxide via Varying the Mass of ZIF-67 for Supercapacitors with Tunable Performance. Mater. Chem. Phys. 2020, 255, No. 123497.

(23) Chen, X. F.; Huang, Y.; Zhang, K. C.; Feng, X. S.; Wang, M. Y. Synthesis and High-Performance of Carbonaceous Polypyrrole Nanotubes Coated with SnS2 Nanosheets Anode Materials for Lithium Ion Batteries. Chem. Eng. J. 2017, 330, 470-479.

(24) Wei, W. L.; Du, P. C.; Liu, D.; Wang, Q.; Liu, P. Facile One-Pot Synthesis of Well-Defined Coaxial Sulfur/Polypyrrole Tubular Nanocomposites as Cathodes for Long-Cycling Lithium-Sulfur Batteries. Nanoscale 2018, 10, 13037-13044.

(25) Dubal, D.; Jagadale, A.; Chodankar, N. R.; Kim, D. H.; Gomez-Romero, P.; Holze, R. Polypyrrole Nanopipes as a Promising Cathode Material for Li-Ion Batteries and Li-Ion Capacitors: Two-In-One Approach. Energy Technol 2019, 7, 193-200.

(26) Wu, J.; Dai, Y.; Pan, Z. J.; Huo, D. X.; Wang, T.; Zhang, H. P.; Hu, J.; Yan, S. Co3O4 Hollow Microspheres on Polypyrrole Nanotubes Network Enabling Long-Term Cyclability Sulfur Cathode. Appl. Surf. Sci 2020, 510, No. 145529.

(27) Zhang, D.; Sun, P. P.; Zuo, Z.; Gong, T.; Huang, N.; Lv, X. W.; Sun, Y.; Sun, X. H. N, P-Co Doped Carbon Nanotubes Coupled with Co2P Nanoparticles as Bifunctional Oxygen Electrocatalyst. J. Electroanal. Chem. 2020, 871, No. 114327.

(28) Xin, S. C.; Yang, N.; Gao, F.; Zhao, J.; Li, L.; Teng, C. FreeStanding and Flexible Polypyrrole Nanotube/Reduced Ggraphene Oxide Hybrid Film with Promising Thermoelectric Performance. Mater. Chem. Phys. 2018, 212, 440-445.

(29) Wang, Y. H.; Yin, Q.; Du, K.; Mo, S. T.; Yin, Q. J. Thermoelectric Properties of Polypyrrole Nanotubes. Macromol Res. 2020, 28, 973-978.

(30) Wu, J. S.; Sun, Y. M.; Pei, W. B.; Huang, L.; Xu, W.; Zhang, Q. C. Polypyrrole Nanotube Film for Flexible Thermoelectric Application. Synth. Met. 2014, 196, 173-177.

(31) Zhao, C. E.; Wu, J. S.; Kjelleberg, S.; Loo, J. S. C.; Zhang, Q. C. Employing a Flexible and Low-Cost Polypyrrole Nanotube Membrane as an Anode to Enhance Current Generation in Microbial Fuel Cells. Small 2015, 11, 3440-3443.

(32) Bober, P.; Stejskal, J.; Šeděnková, I.; Trchová, M.; Martinková, L.; Marek, J. The Deposition of Globular Polypyrrole and Polypyrrole Nanotubes on Cotton Textile. Appl. Surf. Sci. 2015, 356, 737-741.

(33) Wang, L. C.; Zhang, C. G.; Jiao, X.; Yuan, Z. H. Polypyrrole-Based Hybrid Nanostructures Grown on Textile for Wearable Supercapacitors. Nano Res. 2019, 12, 1129-1137.

(34) Stejskal, J.; Trchová, M.; Kasparyan, H.; Kopecký, D.; Kolská, Z.; Prokeš, J.; Křivka, I.; Vajďák, J.; Humpolíček, P. Pressure-Sensitive Conducting and Antibacterial Materials Obtained by In-Situ Dispersion Coating of Macroporous Melamine Sponges with Polypyrrole ACS Omega 2021, 6. DOI: 10.1021/acsomega.1c02330.

(35) Stejskal, J.; Sapurina, I.; Vilčáková, J.; Jurča, M.; Trchová, M.; Kolská, Z.; Prokeš, J.; Křivka, I. One-Pot Preparation of Conducting Melamine/Polypyrrole/Magnetite Ferrosponge. ACS Appl. Polym. Mater. 2021, 3, 1107-1115.

(36) Stejskal, J.; Kohl, M.; Trchová, M.; Kolská, Z.; Pekárek, M.; Křivka, I.; Prokeš, J. Conversion of Conducting Polypyrrole Nanostructures to Nitrogen-Containing Carbons and its Impact on the Adsorption of Organic Dye. Mater. Adv. 2021, 2, 706-717.

(37) Kasl, C.; Hoch, M. J. R. Effects of Sample Thickness on the van der Pauw Technique for Resistivity Measurements. Rev. Sci. Instrum. 2005, 76, No. 033907.

(38) Stejskal, J. Conducting Polymers are not just Conducting: a Perspective for Emerging Technology. Polym. Int. 2020, 69, 662-664.

(39) Sapurina, I. Y.; Shishov, M. A.; Ivanova, V. T. Sorbents for Water Purification based on Conjugated Polymers. Russ. Chem. Rev. 2020, 89, 1115-1131.