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Conducting polypyrrole silicotungstate deposited on macroporous melamine sponge for electromagnetic interference shielding

Jaroslav Stejskal^{1,*}, Marek Jurča¹, Jarmila Vilčáková¹, Miroslava Trchová², Zdeňka Kolská³, Jan Prokeš⁴

¹ *University Institute, Tomas Bata University in Zlin, 760 01 Zlin*

² *University of Chemistry and Technology, Prague, 166 28 Prague 6, Czech Republic*

³ *J.E. Purkyně University, Faculty of Science, 400 96 Ústí nad Labem, Czech Republic*

⁴ *Charles University, Faculty of Mathematics and Physics, 180 00 Prague 8, Czech Republic*

**Corresponding author. E-mail: stejskal@utb.cz*

ABSTRACT: Macroporous melamine/formaldehyde sponge was coated in situ during the oxidation of pyrrole with iron(III) chloride hexahydrate in aqueous medium. The reaction mixture contained a heteropolyacid, silicotungstic acid, which protonated polypyrrole. Polypyrrole/silicotungstate deposits were prepared either in globular form or as nanotubes. The resulting hybrid composites thus combine an organic conducting polymer with inorganic component known, e.g., for its proton conductivity and electrocatalytic activity. The specific surface area of all materials was of the order of tens m^2g^{-1} . The molecular structure is discussed on the basis of FTIR and Raman spectra. The resistivity of the sponges was recorded as a function of compression to 10 MPa and it decreased from the order of 10 $\Omega\text{ cm}$ to 0.1 $\Omega\text{ cm}$. The sponges were tested in electromagnetic interference shielding and absorbed over 80% of 9 GHz radiation frequency. Hybrid composite sponges were subsequently carbonized at 650 °C in inert atmosphere when they converted to a sponge-like macroporous carbons enriched with nitrogen atoms. Their resistivity increased by two orders of magnitude after this process. The absorption of electromagnetic radiation, however, fell below 10%. Original and carbonized hybrid sponges may be of interest in the construction of macroporous electrodes.

KEYWORDS: heteropolyacid, melamine sponge, polypyrrole nanotubes, silicotungstic acid, electromagnetic interference shielding

INTRODUCTION

In the design of new materials, organic conducting polymers, e.g. polyaniline and polypyrrole, play an important role due to their electrical, electrochemical, and electrocatalytic properties [1–3]. Additional features outside their conductivity allow for the applications not associated with electrical parameters [4], such as in optical pH sensors [5], solar-driven steam generation [6], flame-retardation compositions [7] or in environmental issues, such as adsorbents for dye-pollution treatment of water [8, 9].

Heteropolyacids are mixed inorganic oxyacids of metals (typically tungsten and molybdenum) and non-metals (silicon, phosphorus). They are strong acids soluble in water that are able to produce salts with conducting polymers, i.e. to reprotonate non-conducting bases to conducting salts [10, 11]. Silicotungstic acid (SiW), also known as tungstosilicic acid, a member of polyoxometalate (heteropolymetalate) group, is a heteropolyacid of the general formula $H_4SiW_{12}O_{40} \cdot n H_2O$ having a characteristic Keggin structure. It is widely used as a catalyst of organic reactions [12] and displays properties valued in electrocatalysis of hydrogen evolution reaction as a mediator in production of hydrogen through water electrolysis at low current densities [13].

In order to prepare new functional materials, conducting polymers have often been combined with heteropolyacids. Concerning polyaniline, silicotungstic acid significantly delayed the oxidation of aniline and affected properties of resulting polymer [14] or altered polyaniline morphology [15]. Polyaniline silicotungstate was used in the catalysis of ethanol [16] or isopropanol conversions [17]. Polyaniline phosphomolybdate afforded corrosion protection of steel [18], was used for sensing of alcohol vapour [19], electrocatalysis of oxygen reduction reaction [20, 21], improved the capacitance of supercapacitors [22] and catalysed the synthesis of 2,5-diformylfuran from fructose [23] or the epoxidation of alkenes [24]. A corresponding phosphotungstate was similarly exploited for hydrogen peroxide generation [25], in a hydrazine [26] and humidity sensors [27] or for the production of conducting polyester fabrics.

The literature on hybrids based on polypyrrole is less numerous. Polypyrrole phosphomolybdate was used in sensors [28, 29] and in electrochemical supercapacitor [30, 31]. Polypyrrole protonated with phosphotungstic acid was used for detection of sodium cations [32], in supercapacitor electrodes [33], protected steel electrodes from corrosion [34], displayed linear actuation [35], and improved the adhesion of conducting coatings on polyester fabrics [36–38]. The promising direction is envisaged in electrocatalysis of hydrogen evolution reaction [39].

The combination of the conducting polymers with heteropolyacids is based on the ionic bonding because the conducting polymers are polycations that produce salts with anions of heteropolyacids [10, 11]. They are obtained as powders. The applications, however, often require materials with defined macroscopic structure and mechanical properties. The in-situ deposition of conducting polymers protonated with heteropolyacid, here polypyrrole silicotungstate, at macroporous melamine sponge carrier is demonstrated. The fact that the coating thickness of conducting polymers is enhanced in the presence of water-soluble tungsten compounds, including heteropolyacids, is exploited [38, 40]. Application in electromagnetic interference shielding in GHz frequency region is reported.

The composites containing conducting polymers can be carbonized to nitrogen-containing carbons [41]. This has recently been illustrated also for the polypyrrole-coated melamine sponges [42]. If the composites contain silicotungstate heteropolyacid, the carbons become enriched with tungsten atoms in addition to nitrogen ones [43]. The feasibility of such conversion is also demonstrated in the present study. The resulting macroporous carbons are suitable for the consideration especially in electrocatalytic applications.

EXPERIMENTAL

Preparation

Commercial macroporous melamine-formaldehyde sponges ($105 \times 62 \times 25$ mm³; Figure 1) available as "miraculous" or "magic" sponge cleaners of Basotec type (BASF, Germany) were coated with polypyrrole in aqueous reaction mixture containing 0.1 M pyrrole (6.7 g L⁻¹), 0.25 M iron(III) chloride hexahydrate (67.6 g L⁻¹), and 0.005 M silicotungstic acid (14.4 g L⁻¹). For the preparation of globular polypyrrole in 1 L of reaction mixture, pyrrole and heteropolyacid were dissolved in water to 500 mL of solution, similarly iron(III) chloride hexahydrate was dissolved separately to 500 mL of solution. Both solutions were pre-cooled to 4°C to slow down the subsequent polymerization, mixed, and poured over the melamine sponges. The sponges were gently squeezed to assure their penetration with reaction mixture. The oxidative polymerization of pyrrole was left to proceed for 1 h, the sponges were then removed, transferred repeatedly to 0.1 M hydrochloric acid until no solids or coloured by-products were released. The sponge was then immersed several times in ethanol to remove water, and left to dry at room temperature. The polypyrrole powder generated outside the sponges was collected and processed in the same manner. The deposition of polypyrrole nanotubes included in addition the presence of 0.15 wt% methyl orange sodium salt (1.5 g L⁻¹) dissolved together with pyrrole. All chemicals were purchased from the Sigma Aldrich.

A part of the sponges was carbonized in a cylindrical furnace GSL-1600X MTI Corp., USA) under nitrogen atmosphere. Temperature cycle consisted of heating ramp at a $3.3\text{ }^{\circ}\text{C min}^{-1}$ rate to $650\text{ }^{\circ}\text{C}$, at which sample remained for 15 min, followed by cooling to room temperature at a rate $3.3\text{ }^{\circ}\text{C min}^{-1}$.



Figure 1. Melamine sponge (a) before (left) and (b) after the deposition of polypyrrole in the presence of silicotungstic acid (right).

Characterization

Morphology was observed with an ultra-high-resolution scanning electron microscope MAIA3 (Tescan, Czech Republic). FTIR spectra were recorded with a Nicolet 6700 spectrometer (Thermo-Nicolet, USA) using a reflective ATR extension GladiATR (PIKE Technologies, USA) with a diamond crystal in the $4000\text{--}400\text{ cm}^{-1}$ wavenumber range. The spectra were corrected for carbon dioxide and humidity in the optical path.

Raman spectra were collected using a Thermo Scientific DXR Raman microscope equipped with 780 nm line. The spot size of the lasers was focused by $50\times$ objective. The scattered light was analyzed by a spectrograph with holographic grating 1200 lines per mm, and a pinhole width of $50\text{ }\mu\text{m}$. The acquisition time was 10 s with 10 repetitions.

Nitrogen adsorption was used to determine specific surface area and pore volume with a NOVA3200 apparatus (Quantachrome Instruments) using a NovaWin software. Sponges were degassed at 100°C for 24 h. Brunauer-Emmett-Teller (BET) approach has been applied for the determination of specific surface area and Barrett-Joyner-Halenda (BJH) model for the volume of pores.

The resistivity of sponges was determined by four-point van der Pauw method during the compression in a cylindrical glass cell with inner diameter 10 mm between an insulating

base and a glass piston carrying four platinum/rhodium electrodes on the perimeter. The set-up included a current source Keithley 220, a multimeter Keithley 2010, and a scanner Keithley 705 along with a matrix card Keithley 7052. The applied pressure was controlled with L6E3 load cell (Zemic Europe BV, The Netherlands). The sample thickness was monitored with a ABS Digimatic Indicator Mitutoyo, model ID-S112X.

Electromagnetic radiation shielding of sponges was evaluated with a PNA-L Network Analyzer Agilent N5230A (Agilent Technologies, CA, USA) by waveguide method in the X-band frequency range 8–12 GHz. The sample with the thickness of 10 mm was cut to perfectly fit the holder of 10×23 mm² size.

RESULTS AND DISCUSSION

Preparation

The content of polypyrrole with incorporated silicotungstic acid, 73.4 and 74.4 wt%, was determined from the increase of mass after the deposition of globular form and nanotubes, respectively. The apparent density of neat sponge calculated from the mass and geometry, 0.008 g cm⁻³, increased to 0.022 g cm⁻³ and 0.032 g cm⁻³ after the deposition of globular and nanotubular polypyrroles, respectively. The content of inorganic part 45.9 and 47.8 wt%, corresponding roughly the incorporated silicotungstic acid, respectively, was determined as an ash. In the contrast to globular polypyrrole, which accompanied the sponges as a free powder, the adherence of nanotubes to the melamine skeleton is considerably better. The yield after the carbonization at 650 °C of sponges in inert nitrogen atmosphere was 41.2 and 44.6 wt% for globular and nanotubular coatings, respectively.

Morphology

The original skeleton of macroporous melamine [44] becomes coated with polypyrrole (Figure 2). Polypyrrole is deposited as a film on the individual threads, which is well visible at the higher magnifications. Polypyrrole globules adhere directly to this film, but are also present as clusters of free polypyrrole aggregates. These are only loosely attached to the melamine skeleton, and may be liberated during the sponge handling or compression. This manifest itself as in the contamination of the surrounding areas with a black polypyrrole powder, which may be undesired in practical applications.

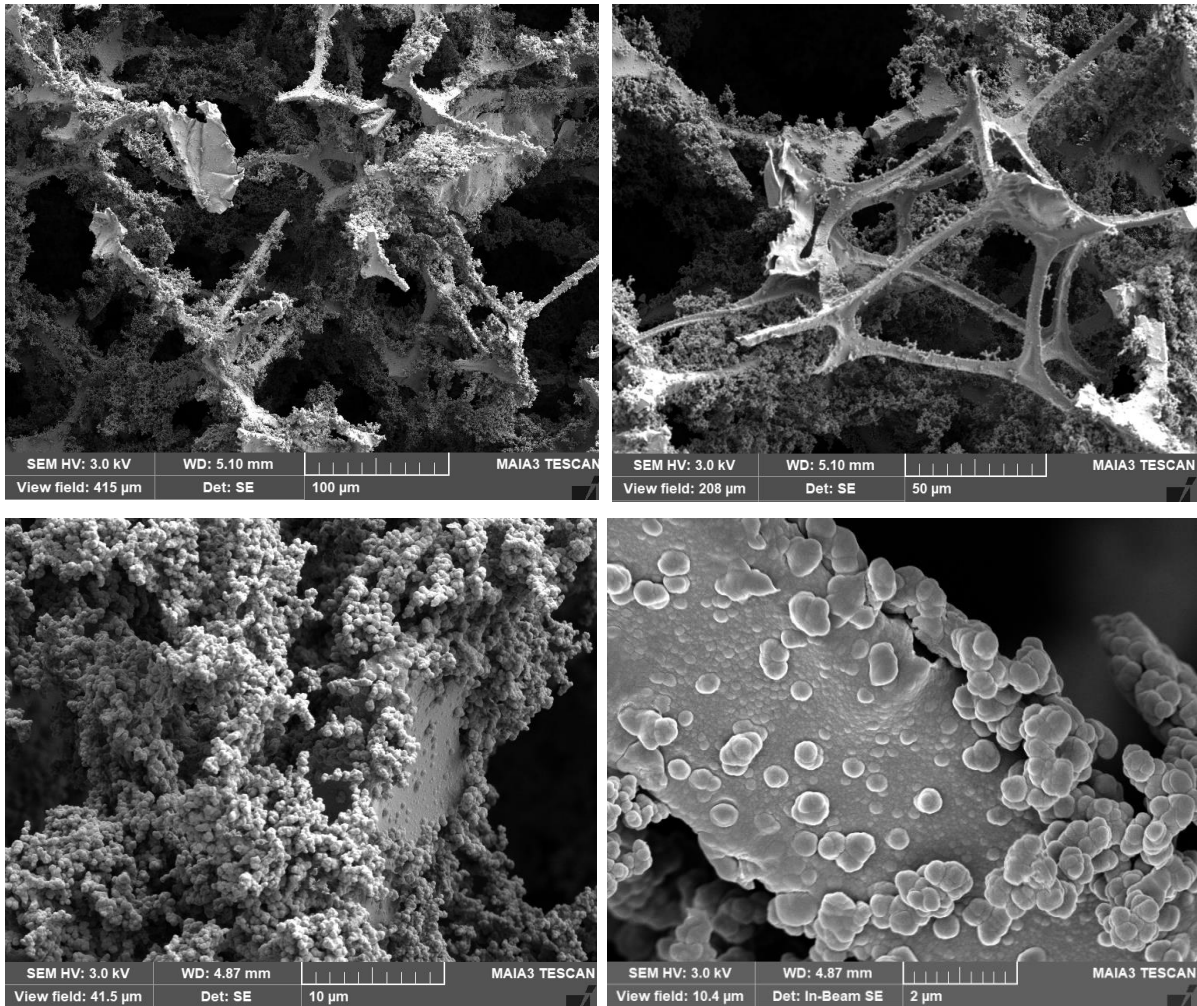


Figure 2. Scanning electron micrographs of melamine sponge coated with globular polypyrrole in the presence of silicotungstic heteropolyacid taken at gradually increasing magnification (scale bars 100, 50, 10 and 2 μm). For the micrographs of original uncoated melamine sponge see Ref. [44].

The situation is considerably improved if polypyrrole is produced as nanotubes instead of globules (Figure 3). Such nanostructure is obtained when the polymerization of pyrrole is carried out in the presence of methyl orange [45]. The nanotubes better adhere to the melamine scaffold due to their mutual entanglement. The nanotubular structure has been well established in the literature by transmission electron microscopy [45]. Polypyrrole nanotubes are also more conducting, their conductivity being at least one order of magnitude higher compared with the globular form. The macroporosity of the hybrid composite sponges is preserved as documented by the apparent density of the order $10^{-2} \text{ g cm}^{-3}$.

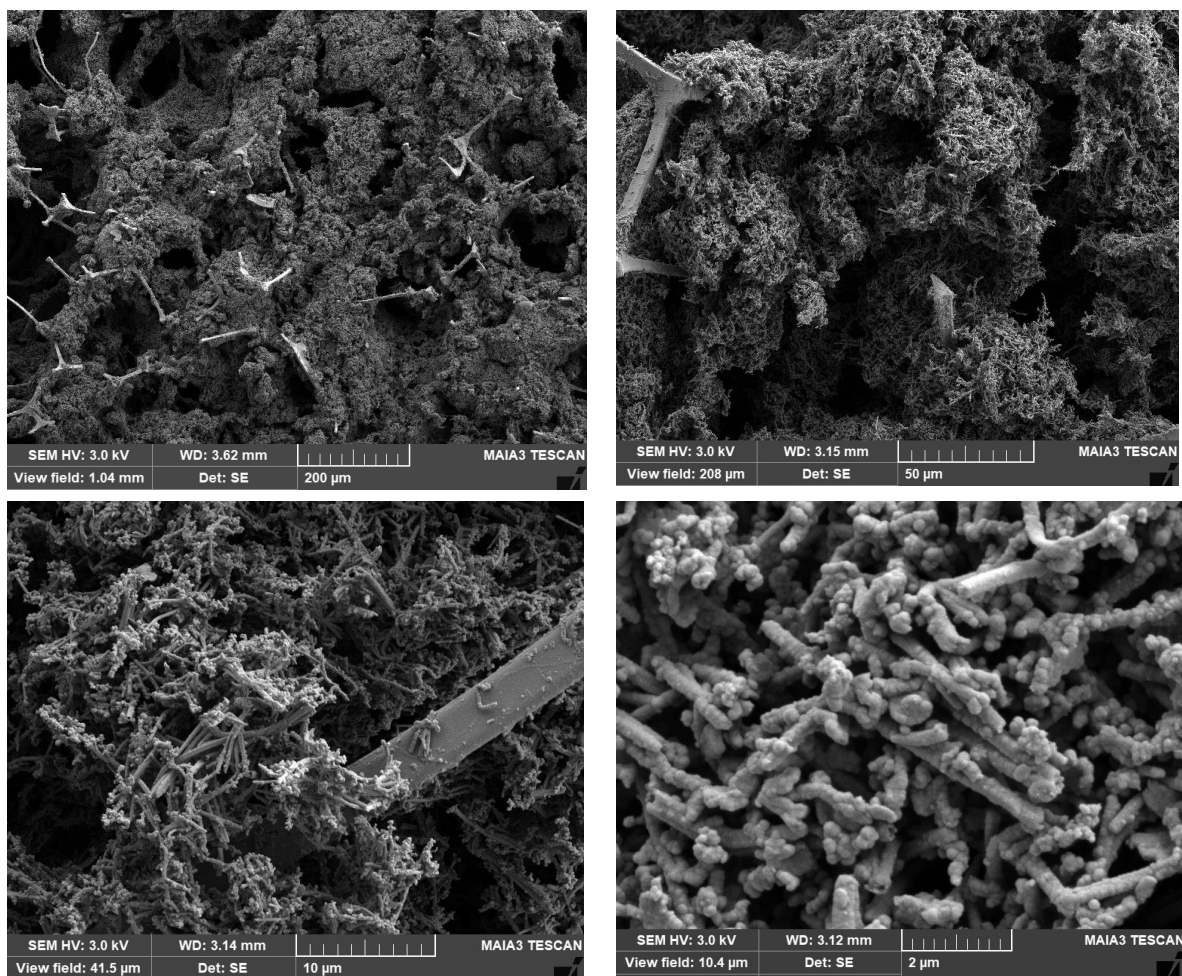


Figure 3. Scanning electron micrographs of melamine sponge coated with polypyrrole nanotubes in the presence of silicotungstic heteropolyacid taken at gradually increasing magnification (scale bars 200, 50, 10 and 2 μm).

During the polymerization of pyrrole, polypyrrole is generated also in the medium outside the sponges (Figure 4). It is collected as a powder with either globular morphology of nanotubes.

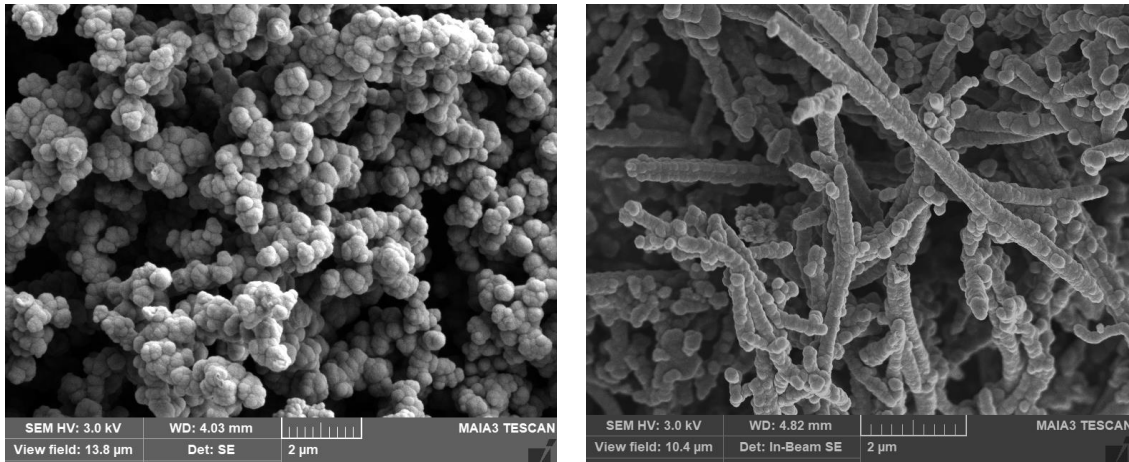


Figure 4. Micrographs of polypyrrole powder produced in the presence of silicotungstic heteropolyacid outside the coated sponges: globules (left) and nanotubes (right).

Surface properties

It has already been reported that the specific surface area increased after the deposition of globular polypyrrole and even more with polypyrrole nanotubes as expected on the basis of morphology observed by the electron microscopy [9, 46] (Table 1). When the deposition was carried out in the presence of silicotungstic acid (Figure 5), the area was again reduced and the similar trend applies also to the pores volume (Table 1). The subsequent carbonization had practically no effect on the specific surface area for globular coating and caused its reduction in the case of nanotubular coating (Table 1). In all materials, the specific surface areas were of the order of tens m^2g^{-1} .

Table 1. Specific surface area, S , and the pores volume, V , of melamine sponges coated with globular (G) or nanotubular (NT) polypyrrole in the presence of silicotungstic heteropolyacid (+SiW) before and after carbonization (/C).

Sample	$S, \text{m}^2\text{g}^{-1}$	$V, \text{cm}^3\text{g}^{-1}$
Original sponge ^a	39.2±0.6	0.067±0.007
PPy-G ^a	75.2±2.8	0.081±0.006
PPy-G+SiW	41.6±3.8	0.051±0.002
PPy-G+SiW/C	48.8±3.3	0.035±0.017
PPy-NT ^a	65.5±4.7	0.130±0.004
PPy-NT+SiW	60.6±3.3	0.073±0.005
PPy-NT+SiW/C	26.4±3.9	0.029±0.003

^a Taken from Ref. [9].

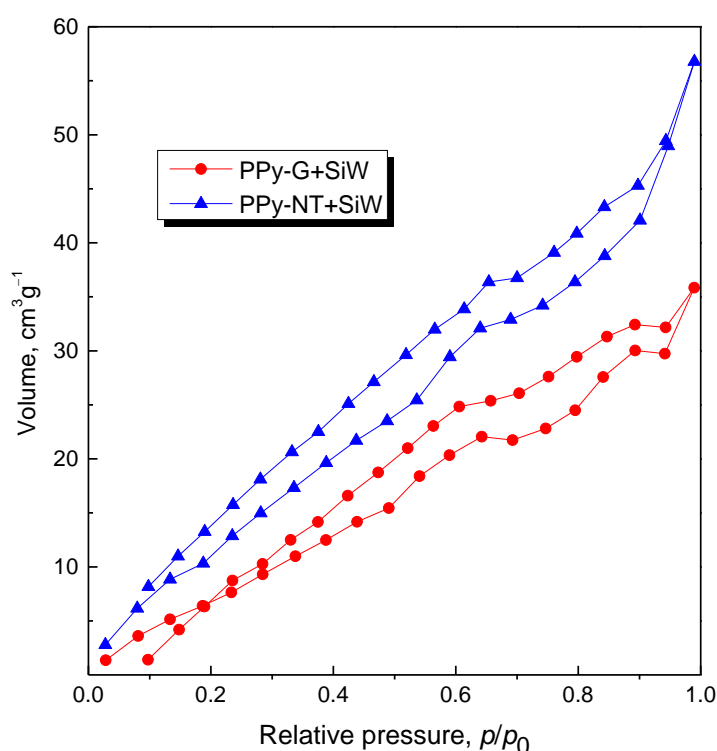


Figure 5. Adsorption/desorption isotherms of polypyrroles deposited along with silicotungstic acid at melamine sponges.

Spectroscopic characterization

In the ATR FTIR spectra of the both globular and nanotubular polypyrrole deposited in the presence of silicotungstic acid on melamine sponge (Figure 6a) we observed the main bands of polypyrrole situated at 1536, 1448, 1298, 1151, 1091, 1035, 968, and 853 cm^{-1} described in details in the literature [42, 44]. The peak typical for melamine sponge situated at 807 cm^{-1} is missing in the spectra. This indicates the complete coating of melamine threads with a conducting polymer. We observe the shoulders at 1017 and 905 cm^{-1} and a maximum at 769 cm^{-1} , which reflect the presence of silicotungstic acid in both samples.

After heating to 650 $^{\circ}\text{C}$ in inert atmosphere, the spectra of both globular and nanotubular polypyrroles deposited in the presence of silicotungstic acid on melamine sponge are transformed into the spectra of carbon-like materials with two broad bands with local maxima at 1585 cm^{-1} and 1209 cm^{-1} (Figure 6a). Some additional maxima may correspond to the intermediate products of polypyrrole or melamine carbonization, or to the modified silicotungstic acid.

Due to the strong resonance effect of the laser excitation 780 nm, we mainly observe in the Raman spectra of the both globular and nanotubular polypyrrole deposited in the presence

of silicotungstic acid on melamine sponge (Figure 6b) the bands of polypyrrole with maxima situated at 1593, 1492, 1374, 1237, 1088, 1055, 940, 687, 623, and 381 cm^{-1} , described in detail earlier [42, 44]. The peaks of silicotungstic acid have not been detected in the spectra.

After exposure to 650 $^{\circ}\text{C}$, the Raman spectra attain a shape typical of carbon-like materials with typical two broad bands with maxima at 1593 cm^{-1} and 1343 cm^{-1} . This proves that the polypyrrole coating was carbonized.

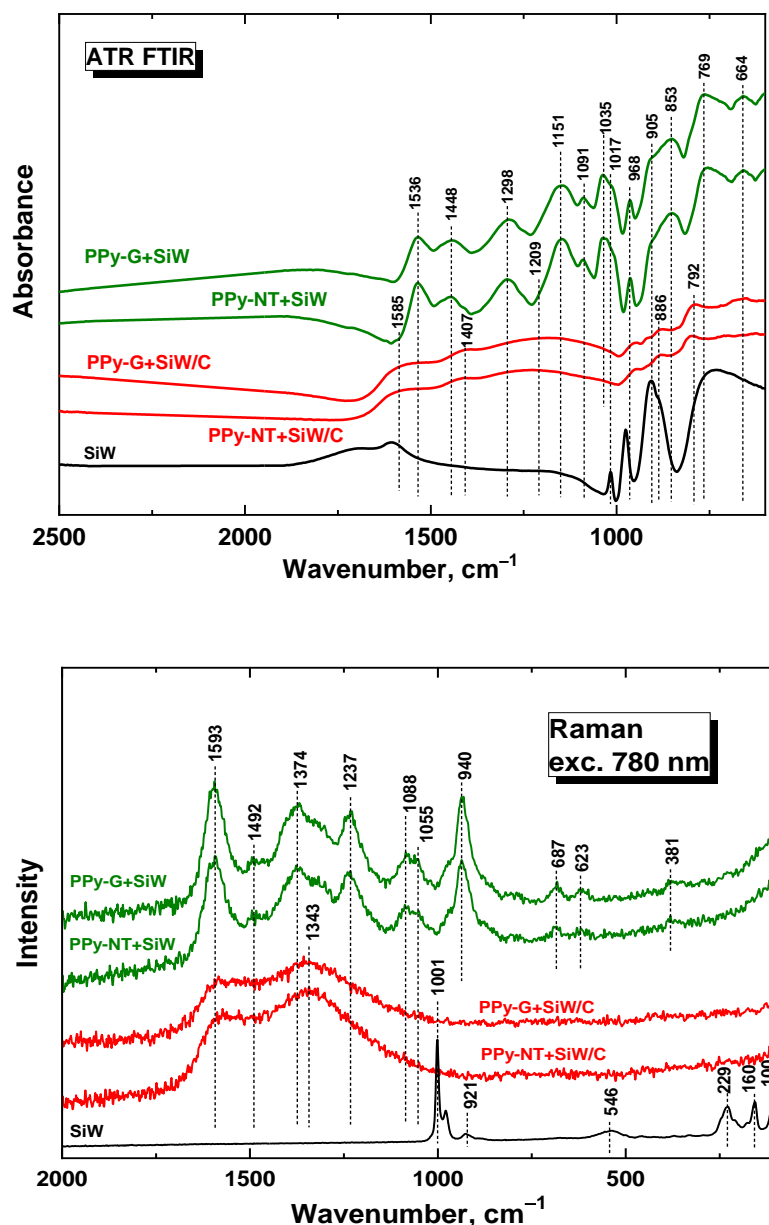


Figure 6. (a) FTIR and (b) Raman spectra of globular and nanotubular polypyrroles deposited on melamine sponge in the presence of silicotungstic heteropolyacid (green) and carbonized analogues (red). The spectrum of silicotungstic acid (SiW) is included.

Electrical properties

The resistivity of the sponges under applied pressure has been determined in the experimental setup designed especially for this purpose. It has to be stressed that the resistivity is reported, i.e. the parameter characterizing the material as whole, and not just a resistance, which depends on the sample size and geometry. The resistivity of the sponges coated with polypyrrole is comparable for both morphologies (Figure 7), globules and nanotubes, despite the fact that the resistivities of polypyrroles with silicotungstic acid produced outside the sponges determined on compressed pellets, 0.26 and 0.022 Ω cm for globules and nanotubes, respectively, differ by one order of magnitude. Indeed, as a rule, polypyrrole nanotubes have always lower resistivity than globules [45].

The resistivity of the polypyrrole-coated sponges decreased as the sponge was compressed and, consequently, volume fraction of conducting phase grew. The structure of polypyrrole-coated melamine sponges is bicontinuous. The connective melamine phase is responsible for the mechanical properties and integrity. Because the conducting polypyrrole phase has also the continuous character, there is no percolation threshold typical of conducting objects dispersed in a non-conducting matrix. The extrapolation of resistivity dependence to higher pressure approaches the value of neat polypyrroles compressed to pellets.

The similar dependences for the carbonized sponges follow the same pattern but they are shifted to the resistivity about three orders of magnitude higher (Figure 7). As demonstrated below, this has a detrimental effect on the electromagnetic interference shielding but may be still sufficient when applied in macroporous electrode materials.

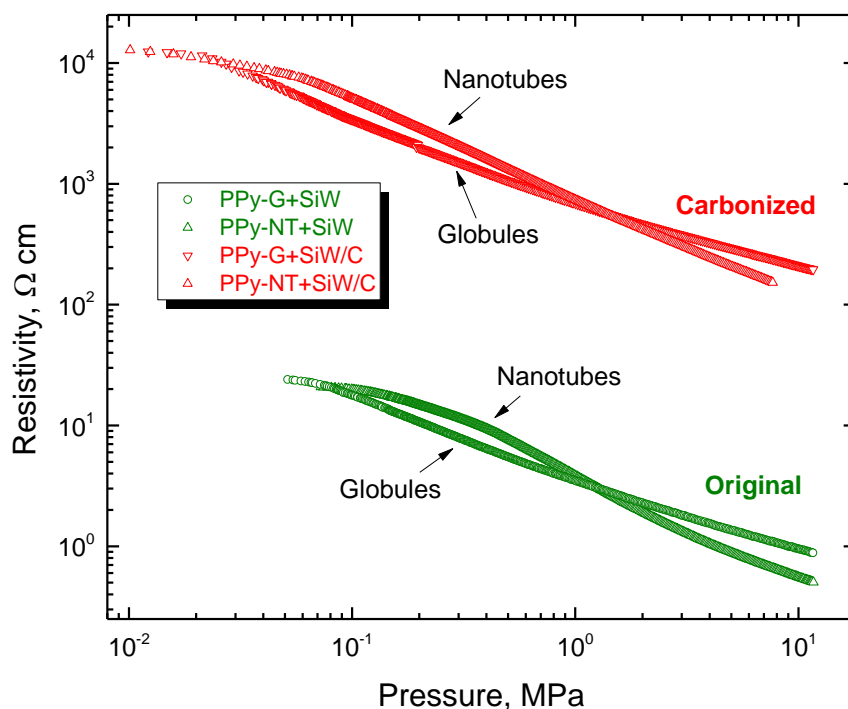


Figure 7. The pressure dependence of resistivity of globular polypyrrole or polypyrrole nanotubes deposited on melamine sponges (green) and their carbonized analogues (red).

Electromagnetic interference shielding

The deposition of conducting polymers, such as polyaniline and polypyrrole, has frequently been used to endow various support with the ability to reflect and/or absorb the electromagnetic radiation in GHz region [47–51]. They are responsible especially for the reflection contribution [47, 48] while the radiation absorption is small [44]. This was demonstrated also for the melamine sponges coated with polypyrrole, when the absorption component could be substantially increased by the introduction of ferromagnetic component, magnetite [44].

Any shielding of melamine sponge alone is marginal [44]. The coating with polypyrrole combined with silicotungstic acid provides a relatively small fraction of reflection, but the presence of heteropolyacid is responsible for the excellent radiation absorption, which still increases at higher frequencies (Figure 8). This presence of tungsten atoms organized in a Keggin structure is most probably responsible for this effect (Figure 9a). After the carbonization, which destroys the molecular structure of polypyrrole, the reflection contribution disappears (Figure 9b). The absorption is substantially reduced despite the residual presence of tungsten atoms but now in disorganized manner. Polypyrrole nanotubes provide the better reduction of transmittance than globules in the original samples due to their higher conductivity.

After carbonization, the level of transmission becomes high and about the same for both samples (Figure 9b), also but not only, as a result of increased resistivity (Figure 7).

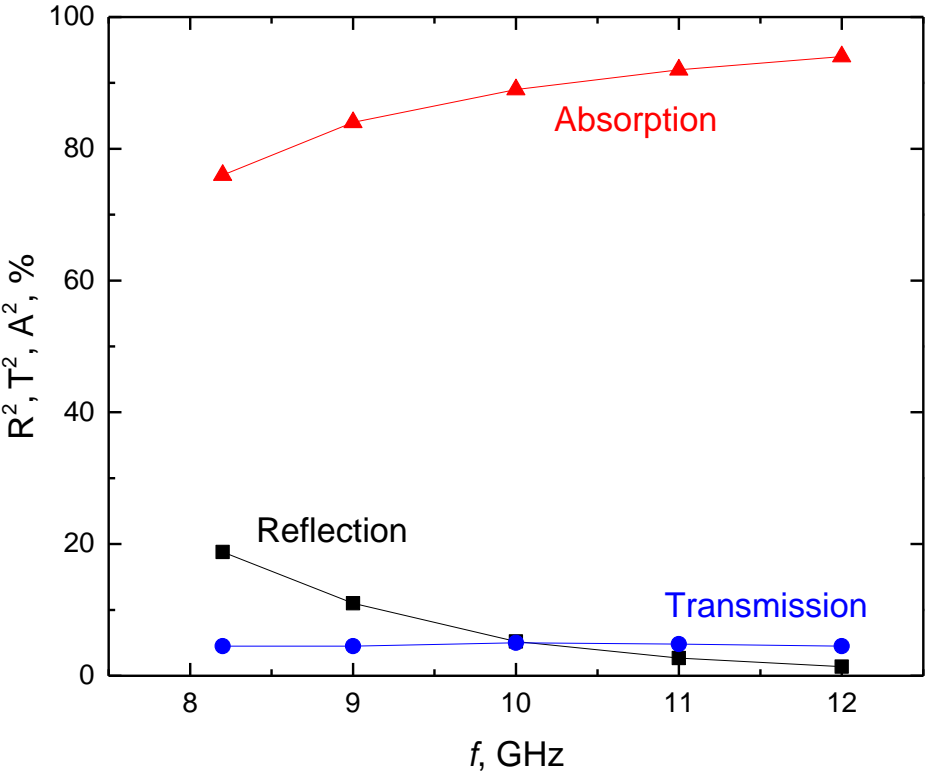


Figure 8. Frequency dependence of the reflection (squares), transmission (circles), and absorption contributions (triangles) for the sponge coated with polypyrrole nanotubes in the presence of silicotungstic acid.

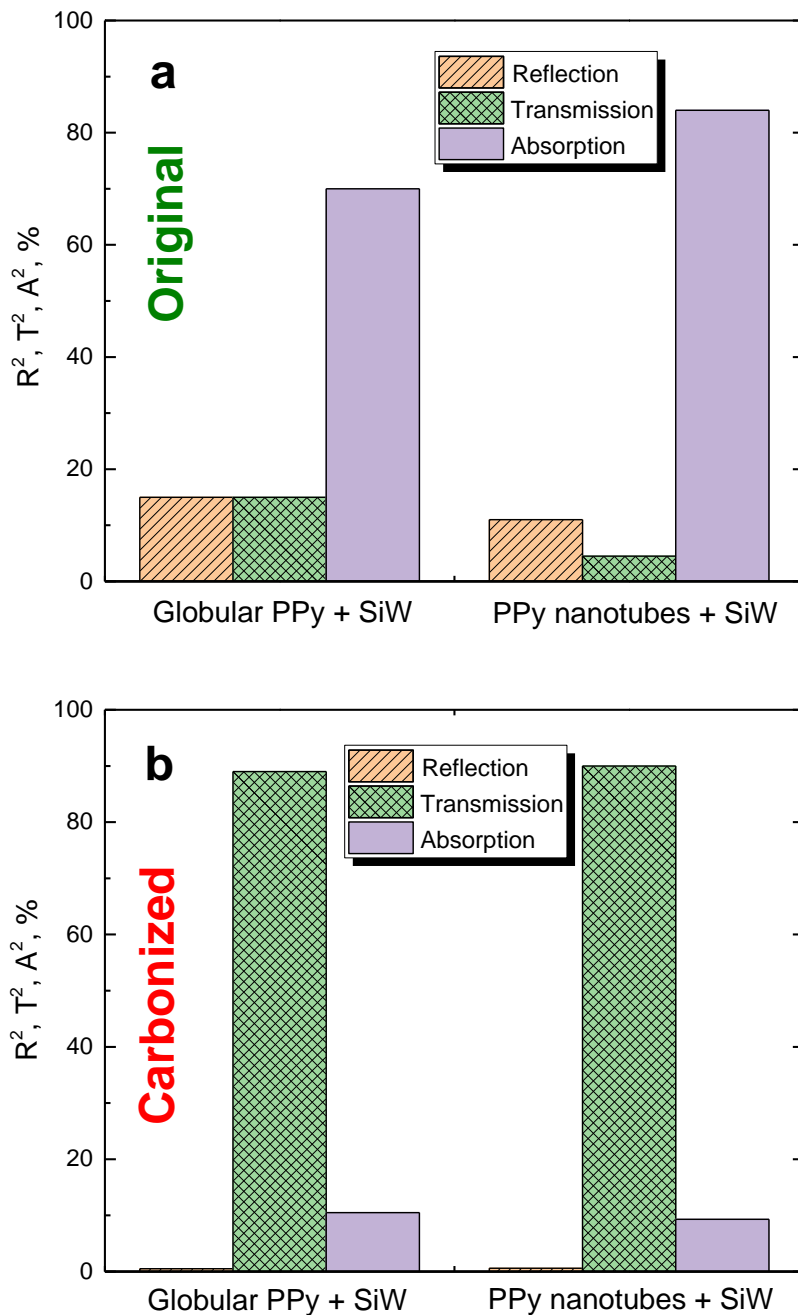


Figure 9. Reflection, transmission and absorption contributions at 9 GHz frequency for the sponges coated with globular polypyrrole or polypyrrole nanotubes in the presence of silicotungstic heteropolyacid. (a) Original sponges, and (b) the samples carbonized at 650°C. Sample thickness 10 mm.

CONCLUSIONS

The hybrid organic/inorganic lightweight macroporous materials with bicontinuous structure were prepared by the coating of threads in melamine sponges with polypyrrole in the presence

with silicotungstic acid. They are lightweight with apparent density 0.022 and 0.032 g cm⁻³, the content of polypyrrole silicotungstate was 73.4 and 74.4 wt% and the fraction of inorganic component was 45.9 and 47.8 wt%, i.e. their parameters are similar for the deposition of globular polypyrrole or polypyrrole nanotubes, respectively. The hybrid composites had resistivity of the order 10 Ω cm (i.e. the conductivity 10⁻² S cm⁻¹), which decreased by three orders of magnitude when the sponges were compressed at ≈10 MPa. The yield of macroporous nitrogen-containing carbon obtained after the carbonization of sponges was 41.2 and 44.6 wt% for both types of polypyrrole coatings. The absorption of electromagnetic radiation at 9 GHz frequency exceeded 80 % at 10 mm sample thickness for the original samples but was reduced below 10 % after the carbonization. The resistivity increased by about three orders of magnitude after carbonization and attained the order 10² Ω cm for compressed samples. Both the original hybrid materials and carbonized analogues are also likely to serve as novel macroporous electrode materials.

Notes

The authors declare no competing financial interest.

AUTHOR INFORMATION

Corresponding Author

Jaroslav Stejskal – *University Institute, Tomas Bata University in Zlin, 760 01 Zlin, Czech Republic; and University of Chemistry and Technology, Prague, 166 28 Prague 6, Czech Republic; orcid.org/0000-0001-9350-9647; Email: stejskal@utb.cz*

Authors

Marek Jurča – *University Institute, Tomas Bata University in Zlin, 760 01 Zlin, Czech Republic; orcid.org/0000-0001-5917-4468*

Jarmila Vilčáková – *University Institute, Tomas Bata University in Zlin, 760 01 Zlin, Czech Republic; and Faculty of Technology, Tomas Bata University in Zlin, 760 01 Zlin, Czech Republic; orcid.org/0000-0002-1216-2862*

Miroslava Trchová – *University of Chemistry and Technology, Prague, 166 28 Prague 6, Czech Republic; orcid.org/0000-0001-6105-7578*

Zdeňka Kolská – J.E. Purkyně University, Faculty of Science, 400 96 Ústí nad Labem, Czech Republic; orcid.org/0000-0003-0239-9046

Jan Prokeš – Charles University, Faculty of Mathematics and Physics, 180 00 Prague 8, Czech Republic; orcid.org/0000-0002-8635-7056

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GRAPHICAL ABSTRACT:

