

One-Pot Preparation of Conducting Melamine/Polypyrrole/Magnetite Ferrosponge

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ABSTRACT

Polypyrrole was deposited in situ on the macroporous open-cell melamine sponge by the oxidation of pyrrole with iron(III) chloride. The oxidant was used in excess, and the reaction mixture after the polymerization thus contained both iron(II) and iron(III) chlorides. These subsequently provided magnetite after treatment with ammonia solution. The conducting melamine/polypyrrole produced in the first step thus afforded melamine/polypyrrole/magnetite ferrosponge in the second. The composite sponge was characterized with respect to molecular structure by FTIR spectroscopy. The dependence of conductivity on the sponge compression is provided and magnetic properties have also been determined. The performance of sponge in electromagnetic radiation shielding in GHz region is demonstrated. While conducting polypyrrole afforded the radiation reflection, magnetite added the absorption component.

Keywords: Ferrosponge; Melamine sponge; Polypyrrole; Magnetite; Fe₃O₄; Electromagnetic radiation shielding

1. INTRODUCTION

Magnetic hydrogels and sponges that incorporate magnetic particles have become of interest especially in biomedical applications.¹ Such composite materials can be used as drug carriers with tunable release by external magnetic field. The system is composed of (1) carrier sponge that provides the macroporous mechanical support, and (2) a magnetic component, typically represented by iron oxides, that affords the attractive response to the external magnetic field. Such macroporous materials are referred to as ferrosponges¹ and they can contain various paramagnetic or superparamagnetic components and they are not limited to ferromagnetic ones as the ferrosponge name may suggest.

In the next step, however, another component, for example, a conducting polymer providing electrical, electrochemical, responsive or other value-added properties can be introduced. The present study is aimed at the preparation of *conducting ferrosponge* that uses open-pore macroporous melamine sponge as a template for the deposition of conducting polypyrrole followed by incorporation of magnetite nanoparticles.

The range of potential applications of composites that combine the conducting and magnetic component extends far beyond biomedicine and suitable materials forms are sought. Here, the

discussion is limited to a conducting polymer, polypyrrole, and inorganic magnetic component, magnetite. Polypyrrole/magnetite composite has often been used for the water-pollution treatment by the removal of organic dyes, where polypyrrole took over the role of an adsorbent and magnetite afforded its separation from the medium by magnetic field.² Both the adsorptions of anionic³⁻⁸ and cationic dyes^{7,9-11} have been reported. They have also been tested as photocatalysts for the dye decomposition¹²⁻¹⁴ or for the separation of heavy-metal ions¹⁵⁻¹⁷ or other pollutants.¹⁸ The composite was applied in photothermal therapy because of its absorption of near-infrared radiation,¹⁹ in microwave absorption,^{20,21} electromagnetic radiation shielding,²²⁻²⁴ magnetorheology²⁵ or in the design of new materials for supercapacitor electrodes.²⁶⁻²⁸ The list demonstrates that other than electrical properties of conducting polymers often come to the forefront.²⁹

The routine preparation of a composite has proceeded as a rule in two steps:¹⁹ (1) In the standard approach, magnetite was prepared at first. The coprecipitation method using the mixture of iron(II) and iron(III) chlorides in ammonia solution is the most common.^{7,21,24,30,31} Magnetite may be generated in particulate form or as a colloid stabilized by surfactants or water-soluble polymers that afford the control of particle size and colloidal stability of magnetite nanoparticles. (2) In the second step, the oxidation of pyrrole with iron(III) chloride,^{19,21} ammonium peroxydisulfate^{7,22} or by electropolymerization³² to polypyrrole took place in magnetite presence. The process resulted in a magnetite core–polypyrrole shell structures, often denoted as Fe₃O₄@PPy.^{15,20,32}

Both steps can be also reversed. (1) When pyrrole was oxidized to polypyrrole with excess iron(III) chloride, only a part of oxidant converted to iron(II) chloride.^{19,33} (2) As the system contained both the iron(II) and iron(III) ions, the magnetite was produced after the addition of ammonia in the second step. Polypyrrole decorated with magnetite particles is a result. Because polypyrrole produced in the first reaction need not be separated before the addition of ammonia, such synthesis is referred to as "one-pot".

Polypyrrole/magnetite composites have typically been prepared as intractable powders. For the individual applications, a material form is important, i.e. a carrier substrate that provides the mechanical support is required for the deposition of conducting and magnetic component. The preparation of a macroporous conducting ferrosponge is discussed in the present study and melamine sponge is offered as a suitable template. The synthetic strategy, when polypyrrole is

generated in situ on the sponge at first followed by the deposition of magnetite nanoparticles in same reaction mixture is demonstrated.

2. RESULTS AND DISCUSSION

2.1. Preparation

One of the most important conducting and electroactive polymers, polypyrrole is prepared by the oxidation of pyrrole, iron(III) chloride being an oxidant of a choice (Figure 1).

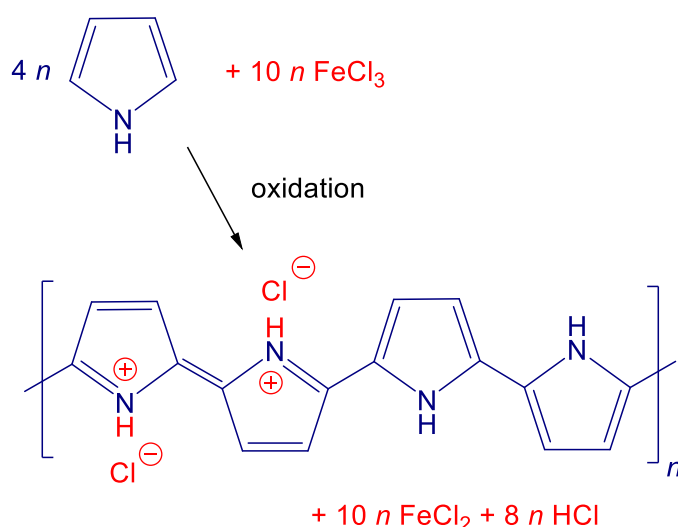
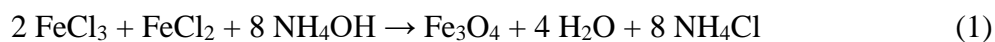


Figure 1. When oxidized with iron(III) chloride, pyrrole converts to polypyrrole. Iron(II) chloride is a by-product.

Magnetite, Fe_3O_4 , is prepared usually by the chemical co-precipitation method based on the treatment of the mixture of iron(III) and iron(II) chlorides with ammonium hydroxide as a precipitant^{19,30}:



The obvious strategy how to produce the conducting and magnetic polypyrrole/magnetite composite is to use stoichiometric *excess* of iron(III) chloride in the preparation of polypyrrole followed by the conversion of resulting mixture of iron oxides to magnetite by treatment with ammonia. This makes the composite preparation extremely simple.

It has to be stressed that conducting polypyrrole salt converts to a less conducting polypyrrole base by the treatment with ammonia³⁴ (Figure 2).

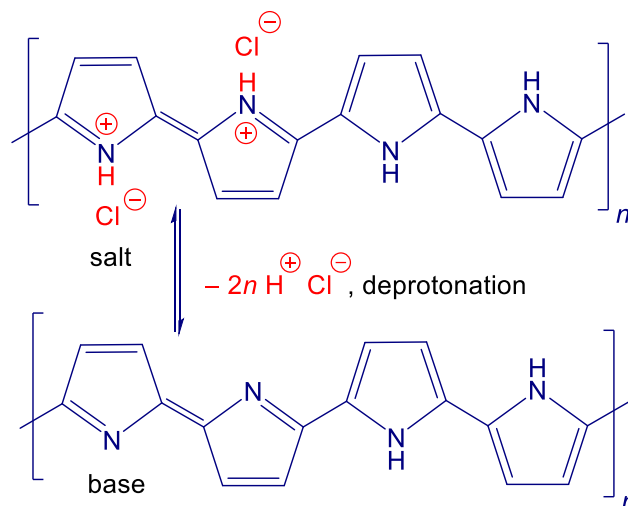


Figure 2. Polypyrrole hydrochloride converts to polypyrrole base under alkaline conditions.

When the composite preparation is carried out in the presence of a melamine sponge, the sponge becomes coated with polypyrrole at first (Figure 3) and with magnetite after the subsequent treatment with ammonia. The content of polypyrrole in the composite with melamine was 21.1 wt% as determined from the mass increase after polymer deposition. After the generation of magnetite inside polypyrrole-coated sponge, the content of inorganic part represented by iron oxides, 14.1 wt%, was determined as an ash. The content of polypyrrole in this ternary composite was thus reduced to 18.1 wt%.

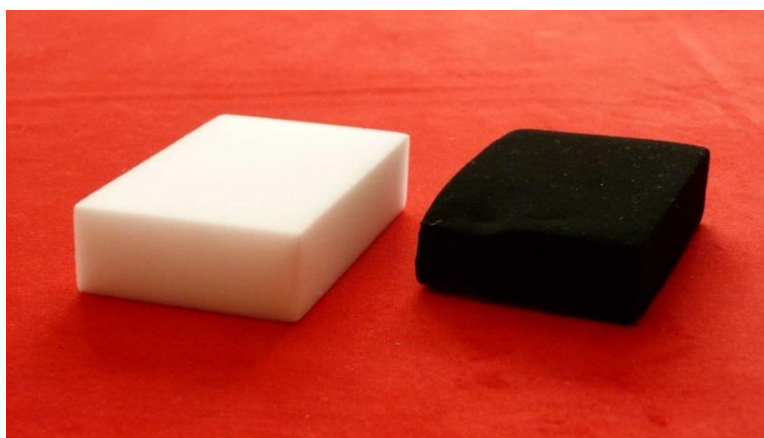


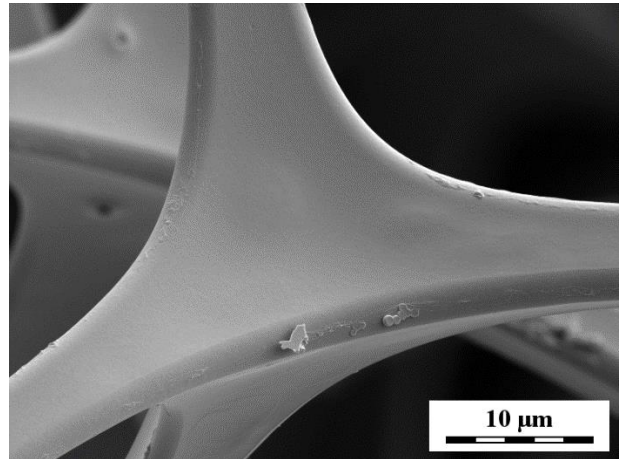
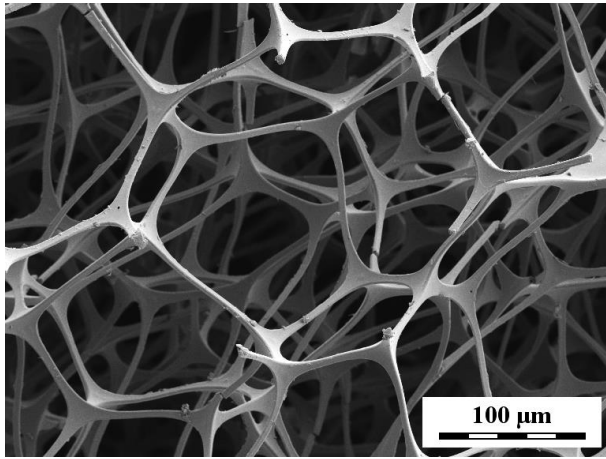
Figure 3. Original (left; 105×62×25 mm³) and polypyrrole-coated melamine sponge (right).

2.2. Morphology

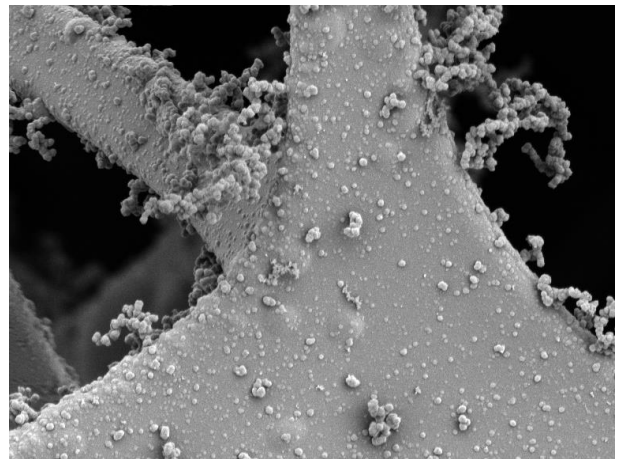
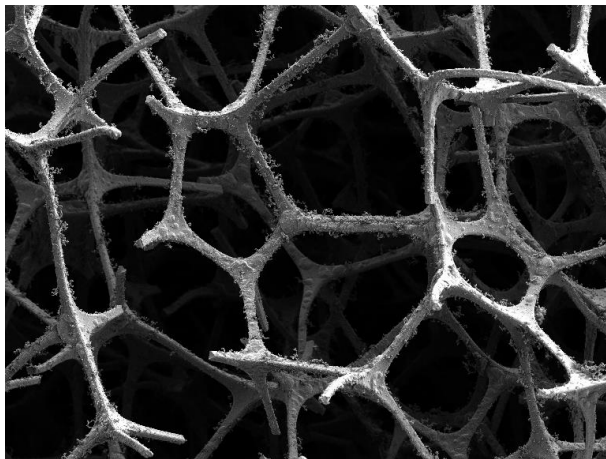
The coating of melamine sponge with a black polypyrrole (Figure 3) is well visible by the electron microscopy (Figure 4). Macroporous structure of the sponge is preserved and polypyrrole is deposited on melamine as a thin polymer film with some adhering polypyrrole nanoparticles. There are also some free polypyrrole nanoparticles in the pores that are not observed by microscopy but seen as a "smoke" emanating from sponge during its cutting to smaller pieces. In the next step, magnetite deposits as clusters of nanoparticles onto polypyrrole coating. The open-pore structure is maintained and the macropores are not blocked by magnetite.

Corresponding polymer or composite powders were produced also in the aqueous medium surrounding the immersed sponges and their morphology is provided in Supporting Information. It is reasonable to expect that their characteristics are about the same as those of components generated inside the sponge. Polypyrrole has a typical morphology of fused globules, which become coated with magnetite after subsequent treatment by ammonia (Figure S1). The magnetite prepared under the similar conditions in the absence of pyrrole had a needle-like morphology with the length *ca* 100–200 nm and cross-section *ca* 30–50 nm (Figure S2).

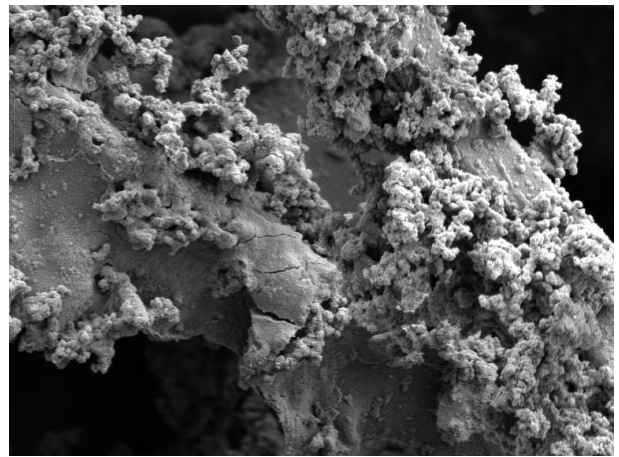
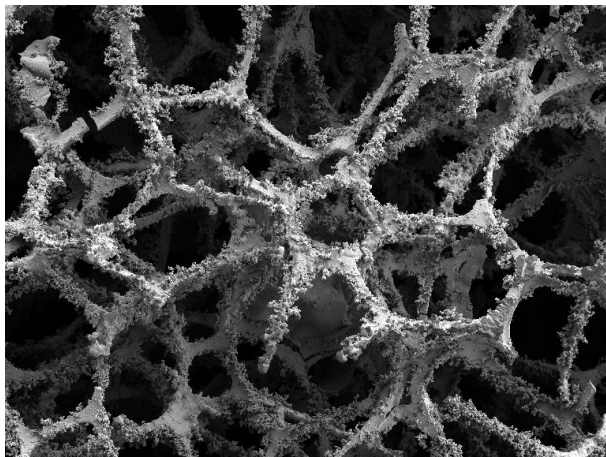
Iron has not been detected in polypyrrole alone by EDAX (Figure S3a), i.e., all iron chlorides were removed by washing after the synthesis. The presence of chlorine reflects the protonation of polypyrrole with hydrochloric acid (Figure 1). On the other hand, 51.5 wt% Fe is found in the composite with magnetite (Figure S3b). The result proved the presence of iron but it is distorted by the high content of carbon due to a carbon paste used in the sample fixation for microscopy. On the other hand, nearly all chlorine atoms disappeared as a result of deprotonation in ammonia solution (Figure 2). EDAX is basically a method of surface characterization, and the high content of iron atoms confirms the coating polypyrrole/melamine with magnetite. Integral content of magnetite, 14.1 wt%, was quantitatively determined as an ash.



Melamine sponge



Melamine/polypyrrole



Melamine/polypyrrole/magnetite

Figure 4. Melamine sponge: original, polypyrrole-coated, and after additional deposition of magnetite. Lower magnification (left) and higher one (right).

2.3. FTIR Spectra

Spectra of sponges. The ATR FTIR spectrum of the composite melamine/polypyrrole/magnetite sponge (M/PPy/Fe₃O₄) is close to the spectrum of standard polypyrrole (PPy std) (Figure 5), which exhibits the main bands with maxima at 1536 cm⁻¹ (C–C stretching vibrations in the pyrrole ring), 1448 cm⁻¹ (C–N stretching vibrations in the ring), 1287 cm⁻¹ (C–H or C–N in-plane deformation modes), 1160 cm⁻¹ (breathing vibrations of the pyrrole rings), at about 1030 cm⁻¹ (C–H and N–H in-plane deformation vibrations), 966 and 847 cm⁻¹ (C–H out-of-plane deformation vibrations of the ring).³⁵ The overlapping with the peaks observed in the spectrum of magnetite (Fe₃O₄) situated at 1420, 1018 and 847 cm⁻¹ is perceptible. A sharp peak at 807 cm⁻¹ belongs to the melamine sponge (M). The decreased absorption above 1600 cm⁻¹ signifies a partial deprotonation of polypyrrole in the melamine/polypyrrole/magnetite sponge in response to ammonia treatment (Figure 3) during the magnetite deposition (Stejskal et al. 2016). In the spectrum of the melamine/polypyrrole sponge (M/PPy), the main bands of polypyrrole situated at 1536 and 1160 cm⁻¹ in the spectrum of standard polypyrrole are slightly shifted to 1515 and 1138 cm⁻¹ and two new sharp peaks are detected at 1638 and 1606 cm⁻¹.

Spectra of powders. ATR FTIR spectrum of polypyrrole/magnetite (Fe₃O₄+(PPy)) powder produced along with melamine/polypyrrole/magnetite sponge (M/PPy/Fe₃O₄) contains the main bands of polypyrrole (Figure 5) in which the bands shifted to 1536 and 1434 cm⁻¹ in comparison to the bands of standard polypyrrole. The presence of magnetite manifests itself by the baseline which imitates the shape of the spectrum of neat magnetite (Fe₃O₄). The broad band with local maximum at 1620 cm⁻¹ may correspond to the band of magnetite or to the overoxidation of the polypyrrole powder, because iron(III) in magnetite may act as an oxidant. The last explanation is supported by the observation of this band also in the spectrum of polypyrrole powder produced during synthesis of the composite melamine/polypyrrole sponge (M/PPy) outside the sponges (PPy) which is expected to be overoxidized.

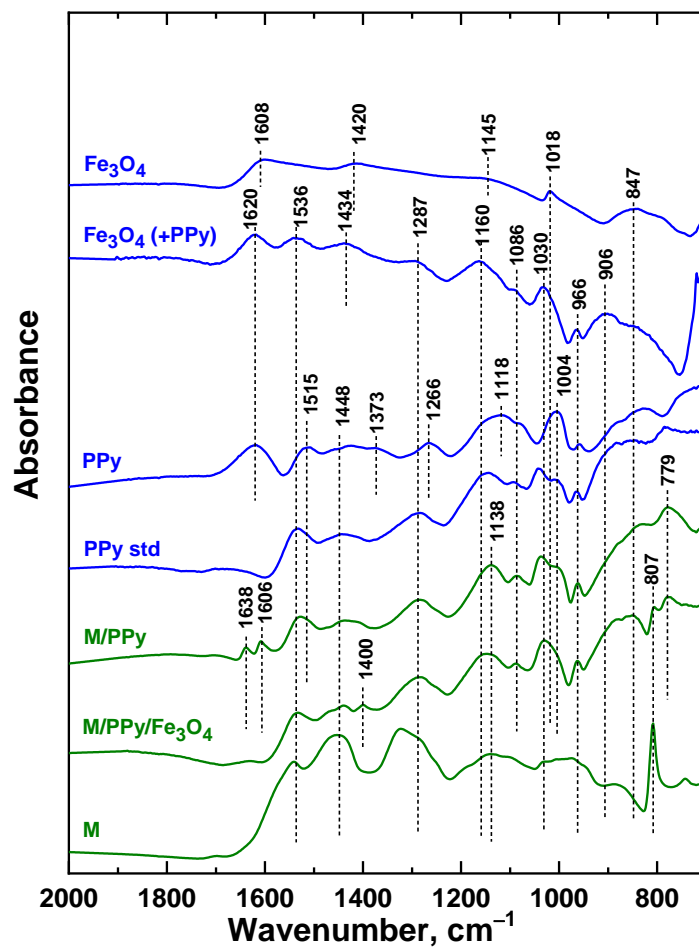


Figure 5. ATR FTIR spectra the neat melamine sponge (M) melamine/polypyrrole sponge (M/PPy) and melamine/polypyrrole/magnetite sponge (M/PPy/Fe₃O₄). The spectra of polypyrrole (PPy) and polypyrrole/magnetite (Fe₃O₄ (+PPy)) powders produced outside the sponges are included and compared with the spectrum of standard polypyrrole (PPy std) and magnetite (Fe₃O₄). Powdered samples are depicted in blue and sponges in green.

2.4. Surface Properties

The specific surface area and porosity play important role for the applications exploiting surface functions. While the surface area of original melamine sponge is few tens of m^2g^{-1} , after coating with polypyrrole and of the same sponge after deposition of magnetite the surface area increases by one order of magnitude (Table 1). The pore volume increases slightly after polypyrrole coating but more after the magnetite deposition. This is a result of adhering polypyrrole and

magnetite nanoparticles (Figure 4). The corresponding adsorption/desorption isotherms are available in Supporting Information (Figure S4).

The determination of surface area was carried out at temperature of liquid nitrogen. It is interesting to note that the surface area of original sponge increased from $39 \text{ m}^2\text{g}^{-1}$ to $156 \text{ m}^2\text{g}^{-1}$, and even to $218 \text{ m}^2\text{g}^{-1}$ after repeated freezing, and with no increase after additional freezing cycles. Similar, but less pronounced behavior was visible for melamine coated with polypyrrole and only marginal increase after deposition of magnetite. This is explained by the gradual delamination of melamine microstructure.

Table 1. Specific surface area, S , and pore volume, V

Sponge	$S \text{ (m}^2\text{g}^{-1}\text{)}$	$V \text{ (cm}^3\text{g}^{-1}\text{)}$
Melamine	39.2 ± 0.5	0.071 ± 0.001
Melamine/PPy	118.9 ± 0.8	0.081 ± 0.002
Melamine /PPy/magnetite	121.8 ± 8.7	0.102 ± 0.011

2.5. Conductivity

The conductivity is a key parameter of materials based on conducting polymers. It is a material property, which is independent of sample size or shape, in the contrast to other electrical characteristics, such as resistance. Melamine sponge is non-conducting from the practical point of view. After the deposition of polypyrrole it acquired the conductivity $6.3 \times 10^{-3} \text{ S cm}^{-1}$, which further increased after the compression to maximum value 0.38 S cm^{-1} (Figure 6). This is close to the conductivity of neat globular polypyrrole, which is $\approx 1 \text{ S cm}^{-1}$.³⁶⁻³⁸ Conducting polypyrrole is deposited of the individual threads of the sponge (Figure 4) and the conducting pathways are thus connective. During the continuing compression, the number of pathways within the infinitesimal cross-section increases and conductivity does so accordingly (Figure 6).

After the deposition of magnetite, the conductivity decreased only moderately to $2.9 \times 10^{-3} \text{ S cm}^{-1}$ for the sponge in the absence of pressure and increased to 0.131 S cm^{-1} after compression. The original decrease is due to a partial deprotonation of polypyrrole under alkaline conditions (Figure 3) used for the generation of magnetite (Figure 2), which is associated with the decrease in conductivity.³⁴ This is partly compensated by the fact that magnetite is mildly conducting, with the conductivity of the order of $10^{-3} \text{ S cm}^{-1}$.³⁰

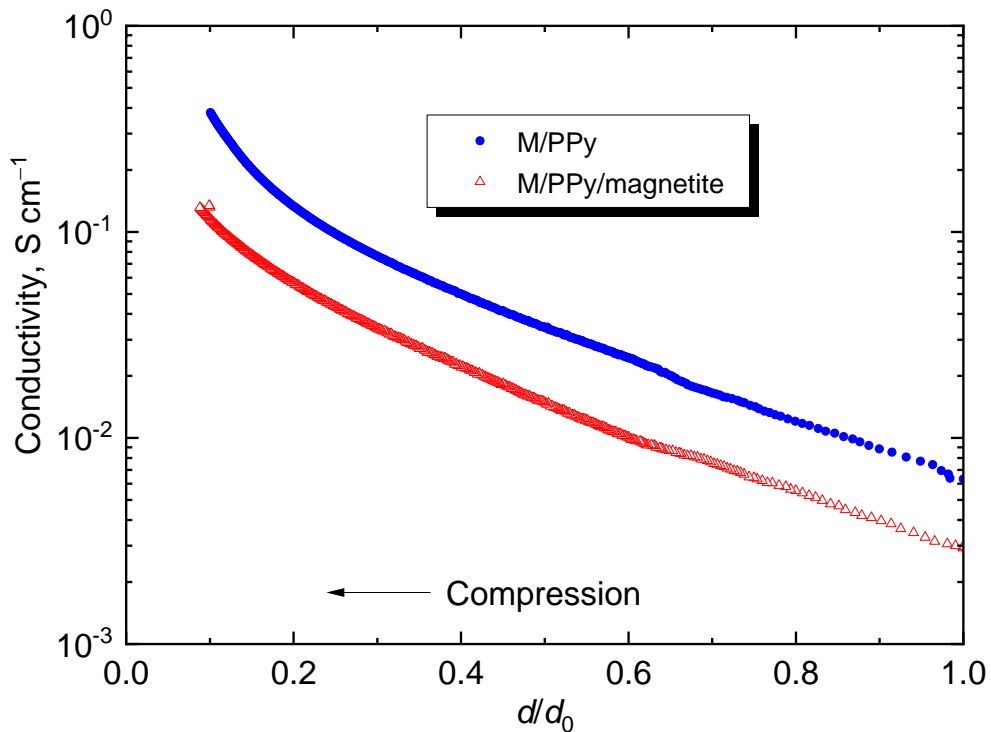


Figure 6. Conductivity as a function of compression, i.e. the reduction of the relative height of cylindrical sample d/d_0 , for melamine sponge coated with polypyrrole (M/PPy) and this sponge after deposition of magnetite (M/PPy/magnetite). The starting height was $d_0 \approx 8$ mm.

2.6. Compressibility

Melamine sponge is a macroporous material that is easily deformed by applied pressure. The setup for the conductivity determination allows also to follow the compression of the sample in dependence on applied pressure (Figure 7). The dependences are close to linear in double-logarithmic presentation. The steeper they are, the easier the sponge deforms. The slopes of the dependences do not significantly change after the coating with polypyrrole and deposition of magnetite. This means that the mechanical properties of the melamine sponge have not been affected by the deposition of components, which includes the treatment of sponges both under acidic and alkaline conditions. The moderate shift of the dependences to higher pressures illustrates some mechanical reinforcement of sponges, especially with magnetite, which acts as a filler.

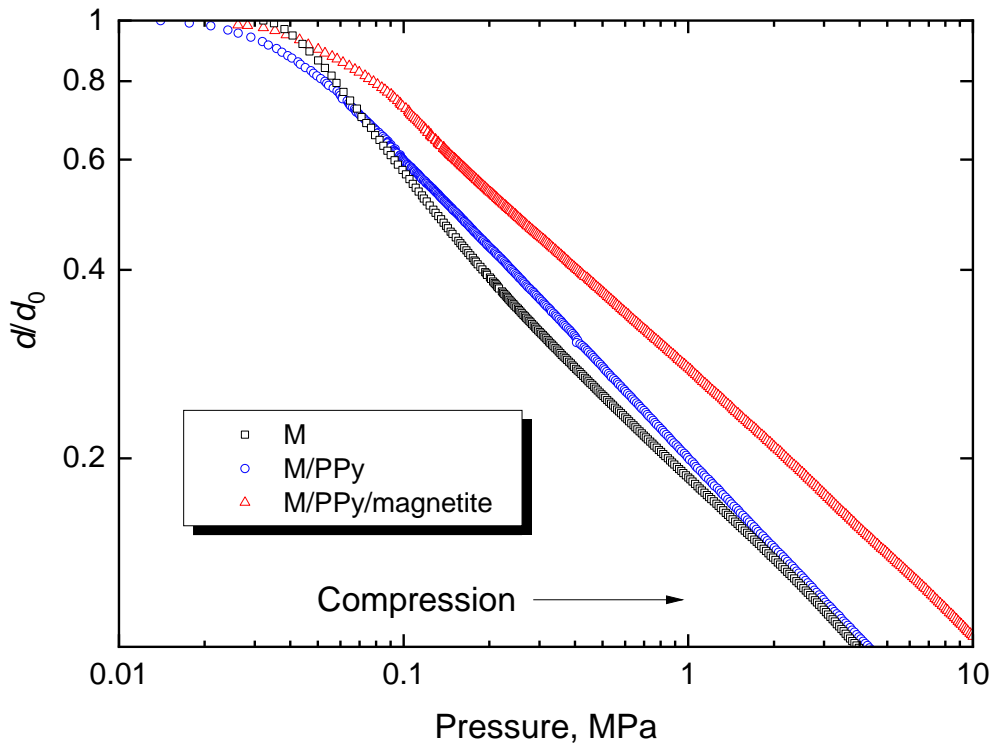


Figure 7. The dependence of the relative height of cylindrical sample, d/d_0 , on pressure for original melamine sponge (M), the sponge coated with polypyrrole (M/PPy), and finally the sponge after deposition of magnetite (M/PPy/magnetite). $d_0 \approx 8$ mm.

2.7. Magnetic Properties

The composite melamine/polypyrrole/magnetite sponge is attracted to a permanent magnet (Figure 8) and can therefore be regarded as a ferrosponge.¹ Original melamine sponge alone or the sponge coated with polypyrrole do not display any marked magnetic properties, except for those caused by the traces of iron compounds in the latter case (Figure 9). Melamine/polypyrrole has the saturation magnetization $M_s = 0.29$ emu g^{-1} (Figure 9), remanent magnetization $M_r = 1.78 \times 10^{-3}$ emu g^{-1} , and coercivity $H_c = 2.67$ Oe. Melamine/polypyrrole/magnetite sponge had saturation magnetization of $M_s = 12.3$ emu g^{-1} which is significantly higher and remanent magnetization $M_r = 0.076$ emu g^{-1} with coercivity $H_c = 2.40$ Oe. The presence of magnetite endows the sponge with superparamagnetic properties as demonstrated by notable saturation magnetization and marginal remanent magnetization. On the other hand, the sponges do not exhibit ferromagnetic behavior as follows from low coercivity.

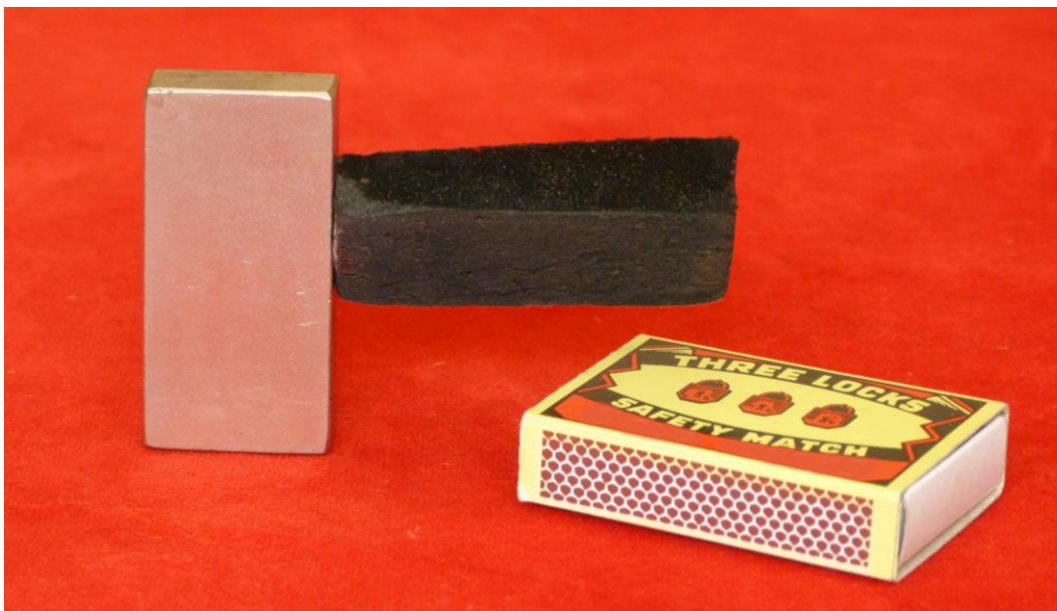


Figure 8. Black melamine/polypyrrole/magnetite sponge is attracted to the permanent magnet. A matchbox is shown for the size comparison.

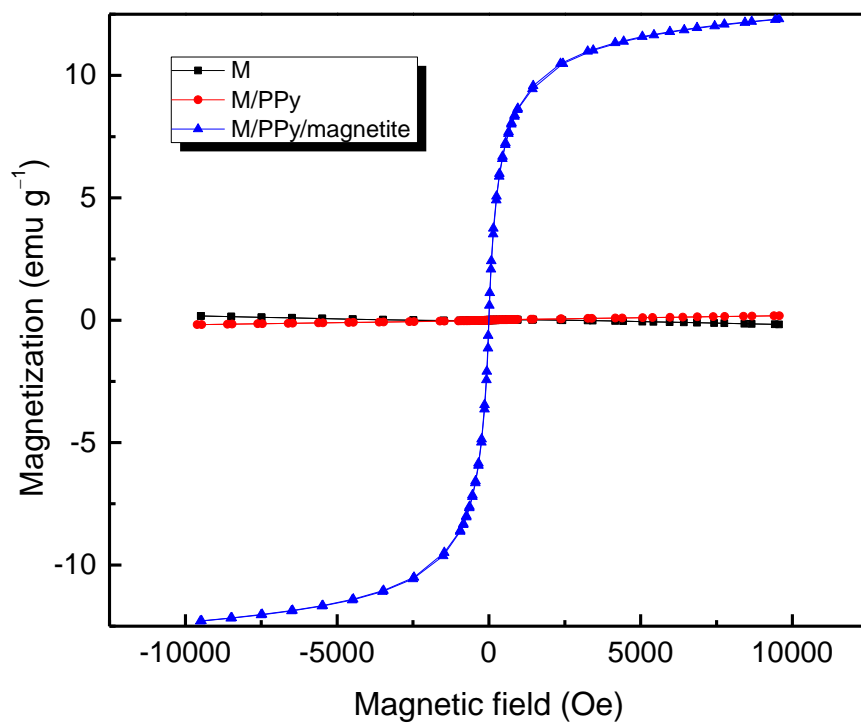


Figure 9. Magnetic hysteresis curves of the melamine sponge coated with polypyrrole (M/PPy) and the sponge after deposition of magnetite (M/PPy/magnetite). Original melamine sponge (M) does not display any magnetic properties.

2.8. Electromagnetic Radiation Shielding

The sponges filled with conducting polypyrrole of moderate conductivity and modified with magnetite could be potentially utilized as shielding materials for electromagnetic radiation in GHz frequency range. The total shielding effectiveness SE_T for shielding materials is given as:^{39,40}

$$SE_T(\text{dB}) = SE_A(\text{dB}) + SE_R(\text{dB}) + SE_M(\text{dB}) \quad (2)$$

where SE_A , SE_R , and SE_M are the partial shielding efficiencies related to absorption, reflection, and multiple reflections, respectively. The term related to multiple reflections and scattering SE_M can be usually neglected:

$$SE_T(\text{dB}) = SE_A(\text{dB}) + SE_R(\text{dB}) \quad (3)$$

The total efficiency SE_T is evaluated by using scattering parameters determined from a vector network analyzer, S_{11} a forward reflection coefficient and S_{21} a reverse transmission coefficient (Figure 10). They provide the quantitative assessment of the applicability of the individual materials in electromagnetic radiation and refer to a specific thickness, here 20 mm. The transmittance T and the reflectance R are related as:

$$T = |S_{12}|^2 = |S_{21}|^2 \quad (4)$$

$$R = |S_{11}|^2 = |S_{22}|^2 \quad (5)$$

and the absorbance is $A = (1-R-T)$. The efficiencies SE_A and SE_R are linked to the transmittance T and reflectance R , $SE_A(\text{dB}) = 10 \log[T/(1-R)]$ and $SE_R(\text{dB}) = 10 \log(1-R)$.

The experimental data describing the sponges are little dependent on the radiation frequency (Figure 10). On a relative basis, they can be presented as the analysis of the individual contributions to the shielding, which are, consequently, qualitatively similar for the individual frequencies (Figure 11).

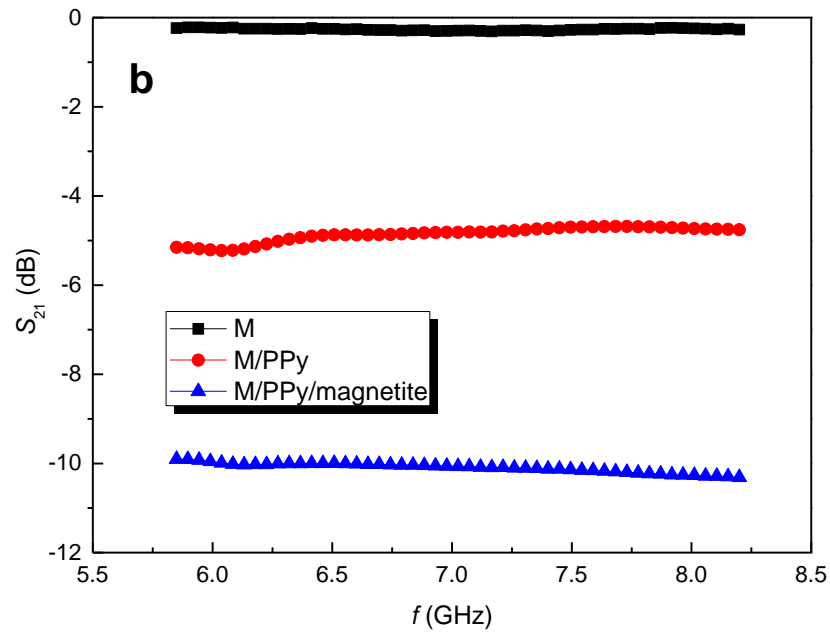
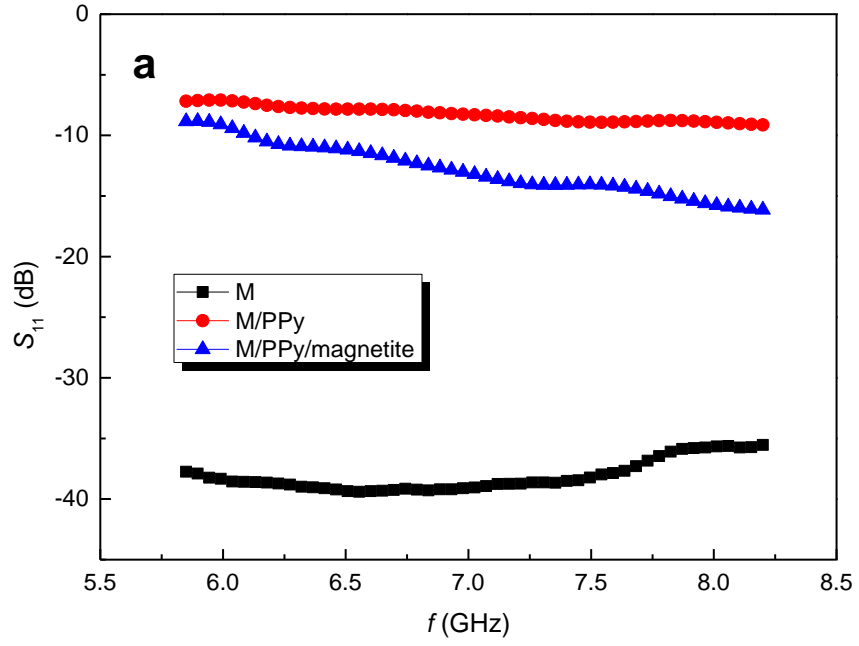
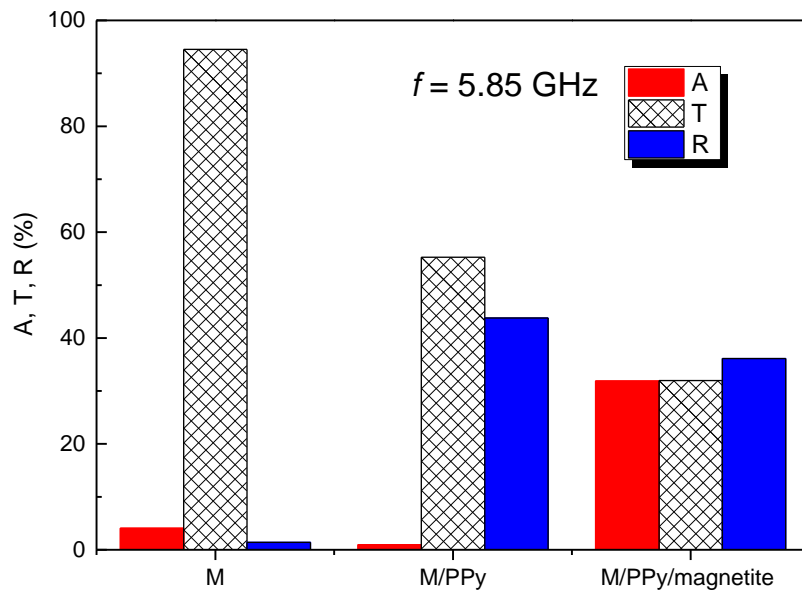


Figure 10. Frequency dependence of (a) forward reflection coefficient S_{11} and (b) reverse transmission coefficient S_{21} .

Concerning the original melamine sponge, there is practically no radiation absorption and reflection (Figure 11). Polypyrrole coating introduces a marked increase in reflection, as might be expected from the conducting material, and fraction of transmitted radiation decreases accordingly. Magnetite is generated under alkaline condition where polypyrrole salt converts to polypyrrole base, and the conductivity is reduced but not lost³⁴ and the reflectance decreases accordingly. The presence of magnetite in the composite sponge clearly adds to the absorption. The combination of the conducting and magnetic component is thus beneficial for the shielding efficiency, and the transmission substantially decreases.



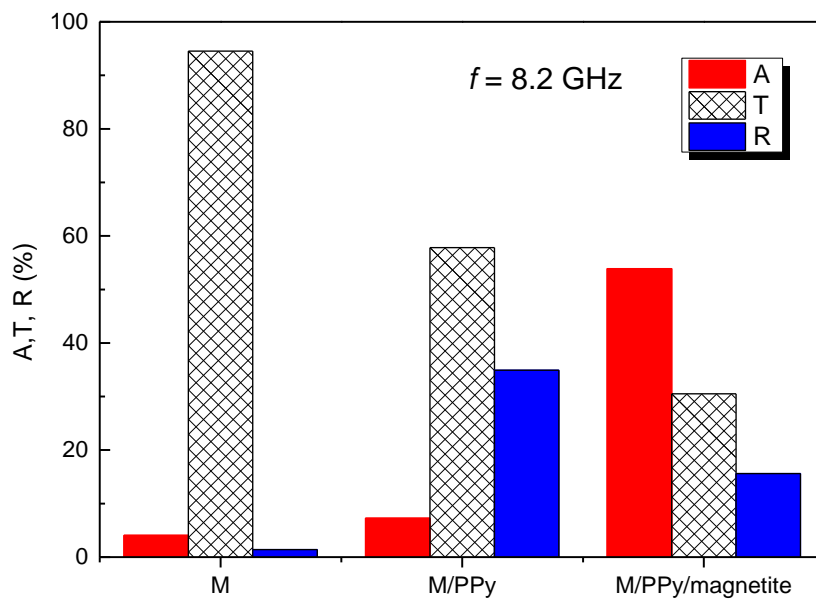
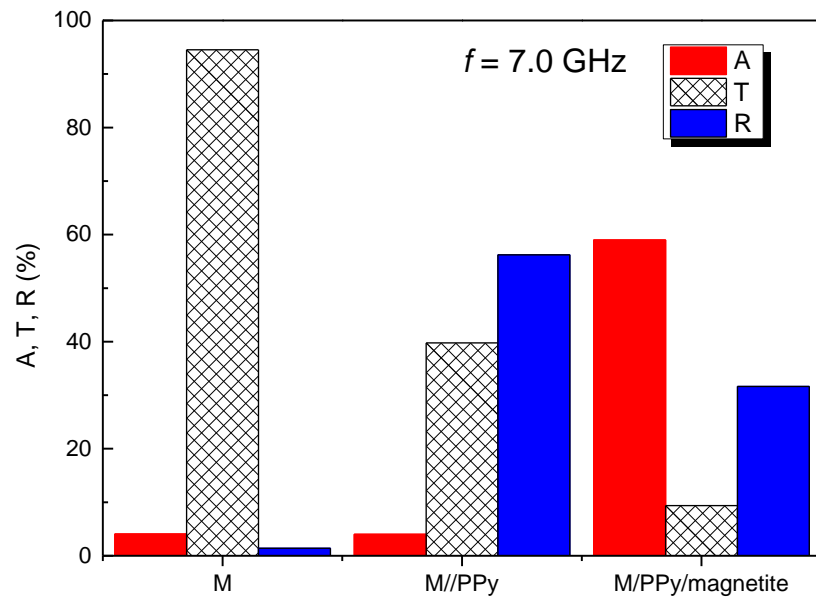


Figure 11. Absorbance A , transmittance T , and reflectance R of melamine sponge (M), the sponge coated with polypyrrole (M/PPy) and after deposition of magnetite (M/PPy/magnetite) at 5.85, 7.0, and 8.2 GHz.

3. CONCLUSIONS

The macroporous open-cell melamine sponge was used as substrate for the in-situ coating with conducting polymer, polypyrrole. The oxidant of pyrrole, iron(III) chloride, was used in stoichiometric excess, and its residual part was converted in the same reaction mixture to magnetite after addition of ammonium hydroxide. A resulting melamine/polypyrrole/magnetite ferrosponge displays paramagnetic behavior. When tested in electromagnetic radiation shielding, the conducting polypyrrole increased the reflection of electromagnetic radiation in GHz region, while magnetite contributed to radiation absorption.

4. EXPERIMENTAL SECTION

4.1. Preparation

The macroporous open-cell melamine sponge ($105 \times 62 \times 25 \text{ mm}^3$) produced by BASF AG (Germany) technology, distributed under the trade-mark Basotect, and advertised as "a miraculous sponge" or "a magic eraser sponge", was purchased from Drogerie ZDE (Czech Republic).

The melamine sponge was immersed in a freshly prepared aqueous mixture of 0.05 M pyrrole and 0.25 M iron(III) chloride hexahydrate pre-cooled to 5°C to slow down the reaction rate. The oxidation of pyrrole was thus carried out at oxidant/monomer mole ratio 5, i.e. with excess of oxidant compared with current preparations of polypyrrole using stoichiometric oxidant/monomer mole ratio 2.5. In practice, 1 L of reaction mixture thus contained 3.35 g of pyrrole and 67.6 g of iron(III) chloride hexahydrate. The sponge immersed in the reaction mixture was briefly gently squeezed to replace air in the pores with reactants solution and the polymerization of pyrrole was let to proceed for 30 min. The polypyrrole-coated melamine sponge was then removed, repeatedly washed in excess of 0.2 M hydrochloric acid until no coloration of acid solution was observed, followed by similar washing with ethanol. The composite melamine/polypyrrole sponge was left to dry in open air.

Another piece of polypyrrole-coated sponge still swollen with the solution of residual reaction mixture containing iron(II) and iron(III) chlorides was transferred to excess 1 M ammonia solution and left for 1 h to allow for the formation of magnetite nanoparticles. The composite melamine/polypyrrole/magnetite sponge was rinsed with water, immersed in ethanol in order to remove soluble low-molecular-weight residues and any free magnetite, and dried as above.

Polypyrrole and polypyrrole/magnetite powders produced in both syntheses outside the sponges were separated and treated in the same manner.

4.2. Characterization

Morphology was observed with a scanning ultra-high-resolution electron microscope MAIA3 Tescan. FTIR spectra were recorded using a Nicolet 6700 (Thermo-Nicolet, USA) spectrometer equipped with a reflective ATR extension GladiATR (PIKE Technologies, USA) with diamond crystal in the 4000–400 cm^{-1} wavenumber region with a deuterated L-alanine doped triglycine sulfate detector at 4 cm^{-1} resolution with 64 scans and Happ-Genzel apodization. Specific surface area and pore volume were determined from nitrogen adsorption and desorption isotherms with a NOVA3200 (Quantachrome Instruments) using NovaWin software. Samples were degassed for 24 h at 100°C. Brunauer-Emmett-Teller (BET) analysis has been applied for the total surface area determination and Barrett-Joyner-Halenda (BJH) model for pores volume.

The sponges have been characterized also by van der Pauw method when compressed in a lab-made cylindrical glass cell with 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 set-up used the current source Keithley 220, a Keithley 2010 multimeter and a Keithley 705 scanner with a Keithley 7052 matrix card. The pressure was controlled with L6E3 load cell (Zemic Europe BV, The Netherlands). Magnetic characteristics of prepared nanocomposites were investigated by vibrating sample magnetometer (VSM, Model 7407, USA). Electromagnetic radiation shielding parameters of sponges were studied with the PNA-L Network Analyzer Agilent N5230A (Agilent Technologies, Santa Clara, CA, USA) in the frequency range 5.85–8.2 GHz.

Supporting Information

Scanning electron microscopy of accompanying powders; Transmission electron microscopy of magnetite nanoparticles; EDAX of powders; Adsorption/desorption isotherm of sponges

Notes

The authors declare no competing interests.

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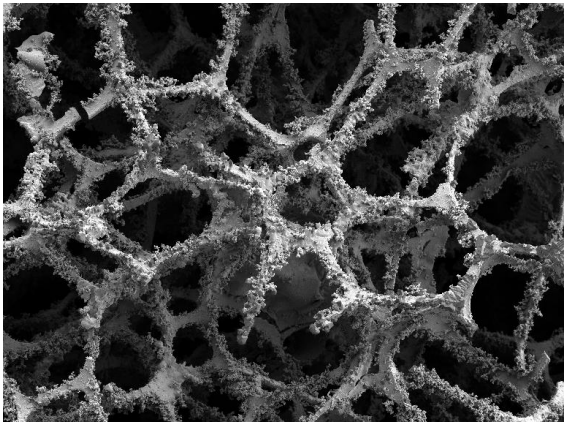
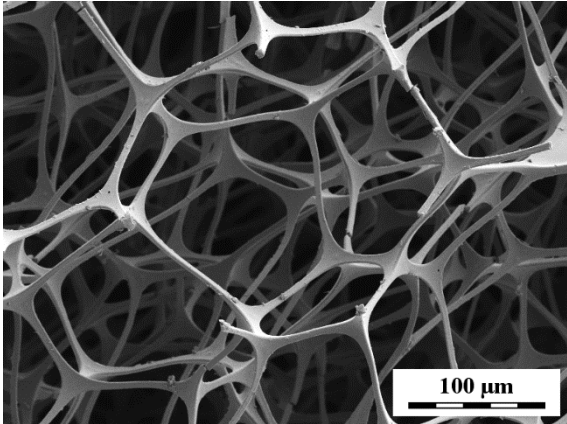
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Table of Contents Graphic:



Melamine



**+ polypyrrole
+ Fe₃O₄**