Electrically conductive aluminosilicate/graphene nanocomposite

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Abstract

Highly electrically conductive ceramic material based on aluminosilicate/graphene nanocomposite has been prepared by high pressure (400 MPa) compaction of montmorillonite intercalated with polyaniline followed with the high temperature (1400 °C) treatment in argon atmosphere. Tablets pressed from polyaniline/montmorillonite intercalate exhibits strong texture due to the disc-shaped montmorillonite particles and, consequently, the high anisotropy in conductivity. The high temperature induced phase transformation of montmorillonite into cristobalite and mullite preserved the aluminosilicate layered structure and created good conditions for formation of graphene sheets from polyaniline layers intercalated in montmorillonite. Therefore, the texture and anisotropy in conductivity remains preserved in resulting aluminosilicate/graphene tablets, while the in-plane conductivity in aluminosilicate/graphene tablets is $23000 \times$ higher than the conductivity of uncalcined polyaniline/montmorillonite tablets. Simple fabrication method of aluminosilicate/graphene tablets is very promising for the manufacturing of the electrically conductive and tough ceramic material, which can be exposed to corrosive environment as well as to high temperatures.

Keywords: Aluminosilicate; Graphene; Polyaniline; Conductivity; Calcination

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1. Introduction

Graphene-based composite materials are of interest as a new class of materials usable in a large variety of applications [1]. In particular, much attention is paid to polymer-based composites [2,3,4], and, recently, also to graphene/metal nanoparticles composites due to the catalytic [5,6] and biosensing [7,8] properties. Graphene/metal oxides composites have been explored for electrode materials and tested for the electrochemical activity [9-13].

Graphene/non-oxide inorganic matrix composites are less common, although they offer a variety of options in preparation. One example how to use the structure and composition of inorganic matrix for a formation of graphene sheet is the thermal decomposition of SiC, leading to the growth of epitaxial graphene on 6H-SiC (0001) single crystals [14,15]. The main problem in manufacturing of nanocomposites with graphene is not to produce the graphene sheets but to make them homogeneously distributed in various matrices. Miranzo and co-workers [16] prepared electrically conducting graphene/SiC nanocomposites by spark plasma sintering of SiC powders. Using this technology, they reached a well dispersed graphene in nanocomposite and electrical conductivity ~100 S/m, which is relatively high for the robust ceramic composite.

In present work we solved the problem of homogeneous distribution of graphene sheets via intercalation of layer silicate matrix with polyaniline (PANI). PANI/silicate intercalate has been used as the precursor for aluminosilicate/graphene nanocomposite. Montmorillonite (MMT) as easy expandable layer silicate has been chosen as the most convenient silicate matrix for the preparation of PANI/MMT intercalate. This intercalate has been subsequently transformed (via high pressure and high temperature treatment) to aluminosilicate/graphene nanocomposite with N-doped graphene sheets adherent to aluminosilicate layers. To the best of our knowledge, the fabrication of graphene/aluminosilicate nanocomposite based on layer silicate matrix has not been reported hitherto.

It is well known, that layered structure of MMT is very easy expandable and, therefore, very convenient matrix for easy intercalation of various organic species [17] including polymers. Simple one-step preparation method of PANI/MMT has been described by Bober et al. [18] and Kulhánková et al. [19]. The structure analysis using combination of X-ray diffraction and molecular modeling revealed that MMT was fully and homogeneously intercalated with PANI, where one layer of flat-lying PANI chains is in the MMT interlayer space [19]. Recently, it has been reported that PANI/MMT nanocomposite powder pressed into tablets
exhibits strong texture due to the disk shaped MMT particles and, consequently, high anisotropy in electrical conductivity. The in-plane conductivity of pellets (8.4 S/m) is 1000× higher than the transversal conductivity (8·10^{-3} S/m) [20]. All the previous experiments focused on PANI/MMT nanocomposite have shown strong adhesion of PANI cationic chains to silicate layers of MMT and good dispersion of PANI in the nanocomposite. The PANI network confined in the interlayer space of MMT structure and adherent to the external surface of flat MMT particles offered a good chance to form N-doped graphene sheets by high temperature treatment of PANI/MMT pressed tablets.

2. Materials and methods

Na-montmorillonite Portaclay® (The mineral company Ankerpoort NV, Nederland) with basal spacing of 1.245 nm, structural formula (Si₈) (Al₂₋₄,₃₅Mg₀.₇₁ Ti₀.₀₂ Fe³⁺₀.₄₂) O₂₀ (OH)₄ with layer charge ~ 0.7 el. per unit cell was used as a substrate for PANI intercalation. PANI/MMT nanocomposite was prepared using oxidation of aniline in the presence of ammonium persulfate. In the first step, the aniline solution in sulfuric acid (0.2 M) was mixed with ammonium persulfate and previously dried MMT in weight ratio 1 : 0.05 : 0.04. In the second step, the reaction mixture was stirred for 1h at laboratory temperature using an electromagnetic stirrer. The synthesis process was accomplished by separation of solid portion by the filtration, whereas the filter cake was washed several times using distilled water and finely dried 72 h at 40 °C in laboratory oven. Dried composite was gently homogenized using mortar and pestle.

Pure PANI was prepared similarly. In the first step, the aniline solution in sulfuric acid (0.2 M) was mixed with ammonium persulfate in weight ratio 1 : 0.05. In the second step, the reaction mixture was stirred for 1h at laboratory temperature, then the solid portion was separated by the filtration, the filter cake was washed using distilled water and finely dried 72 h at 40 °C in laboratory oven. Dried PANI was gently homogenized using mortar and pestle.

Powdered samples were pressed into square shaped tablets using Zwick 1494 press and molds made of steel. Course of the pressing is shown in Fig. 1.

As a result of pressure the disc shaped MMT particles in PANI/MMT composites become strongly preferentially oriented with the basal plane perpendicular to the direction of pressure (see Fig. 2).
Tablets pressed from PANI and PANI/MMT powders have been heat treated at temperatures: 900 °C, 1200 °C and 1400 °C in the furnace of the DIL 402C/7 dilatometer (Netzsch GmbH, Germany). The heating and cooling rate was 15 K·min⁻¹ with 60 min long delay at the maximum temperature. The treatment was preceded in protective argon atmosphere (99.999 % Ar) with the constant gas flow rate 20 ml·min⁻¹.

The prepared samples were denoted as PANI-900, PANI-1200, PANI-1400, PANI/MMT-900, PANI/MMT-1200 and PANI/MMT-1400. Non-calcined samples were denoted as PANI-d and PANI/MMT-d, where d means dried.

Determination of the total content of carbon, nitrogen, and sulfur was performed using microanalyzer Thermo Finnigan Flash FA 1112. X-ray diffraction measurements have been carried out in reflection mode using Bruker D8 Advance diffractometer (Bruker AXS GmbH, Germany) equipped with cobalt tube (Kα = 1.78897 Å) and fast position sensitive detector VÅNTEC1. Raman microspectroscopy was performed using Raman microscope XploRA™ (HORIBA Jobin Yvon, France) equipped with 532 nm excitation laser source, with 50× objective and using 1200 g/mm grating. Observation of the dried as well as calcined samples was performed in BSE mode using scanning electron microscope Philips XL30. Surface topography was studied using SolverNext atomic force microscope (NT MDT Co.) operated
in semi-contact mode, whereas DCP 11A probes (NT MDT Co.) were used for the measurement. For DC conductivity measurements we used special measuring cell designed especially for the pressed tablets [20]. Conductivity was measured in two perpendicular directions (Fig. 2), i.e. perpendicular to the tablet plane ($\sigma_{\perp}$) and in the tablet plane ($\sigma_{\parallel}$).

3. Results and discussion

3.1 Structure analysis of samples

X-ray diffraction patterns of all PANI/MMT samples are shown in Fig. 3.

![Fig. 3. X-ray diffraction patterns of the PANI/MMT composites. A) PANI/MMT-d; B) PANI/MMT-900; C) PANI/MMT-1200; D) PANI/MMT-1400. 1 - MMT, 2 - $\alpha$-quartz, 3 - illite, 4 - cristobalite, 5 - mullite, 6 - graphite 3R-polytype.](image)

![Fig. 4. Top view on the arrangement of PANI chains in monolayer adherent to the silicate layers in the interlayer space of MMT structure. Result of molecular modeling using empirical force field [20].](image)
Diffraction pattern for tablet pressed from PANI/MMT-d shows the basal spacing $d = 1.285$ nm corresponding to the monolayer arrangement of flat laying PANI chains in the interlayer space of MMT (see Fig. 4).

The profile of PANI/MMT basal reflection $00l$ confirms the homogeneously intercalated structure while the intensity ratio $00l/hk$ indicates the strong texture caused by high degree of preferred orientation of MMT platy particles parallel with pellets plane (i.e. perpendicular to direction of pressure, see Fig. 2). Diffraction pattern of PANI/MMT-900 corresponds to the destruction of silicate layers at 900 °C and diffraction pattern of PANI/MMT-1200 shows the gradual formation of high temperature phases of MMT (cristobalite and mullite) at 1200 °C. Diffraction pattern of PANI/MMT-1400 shows, that in pellets calcined at 1400 °C these high-temperature phases cristobalite and mullite are well developed. In addition, graphite phase 3R-polytype has been observed well developed at 1400 °C (Fig. 3). Nevertheless, weak reflection corresponding to the graphite phase 3R-polytype is observable already at 1200 °C (Fig. 3). This graphite phase arises from the PANI located at the edges and between the MMT particles. This interparticle PANI material has no conditions to be transformed into graphene and, therefore, it is transformed into graphite. Analysis of the PANI/MMT diffraction patterns shows that cristobalite phase exhibits quite strong texture, i.e. $(101)$ planes of tetragonal cristobalite structure are preferentially oriented perpendicular to the direction of pressure. That means the texture type remains in the tablets because the MMT $(001)$ planes are transformed to cristobalite $(101)$ planes. This becomes understandable when we compare the structure of Si-O tetrahedral sheet in $00l$ plane of MMT structure and Si-O tetrahedral sheet in $10l$ plane of cristobalite structure. Both structures are compared in Fig. 5 and it is evident that Si-O tetrahedral sheet of cristobalite is in fact just slightly distorted Si-O sheet of MMT.

Fig. 5. Top and side view of (a) MMT $(001)$ plane, and (b) cristobalite $(101)$ plane explaining the mechanism of the phase transition and conditions for the formation of graphene sheets.
These MMT and cristobalite structures were built in Accelrys Materials Studio modeling environment using data published by Mering and Oberlin [21] and Dollase [22], respectively. It can be concluded that this phase transformation does not destroy PANI layers adherent to Si-O sheets in MMT and, therefore, there is a good chance for formation of graphene sheets. Diffraction pattern confirmed that the preferred orientation of MMT (001) planes is transformed into preferred orientation of cristobalite (101) planes parallel with the tablets plane. However, the degree of preferred orientation in tablets slightly decreased during the phase transformation. In addition, the formation of mullite phase does not disturb the layered aluminosilicate structure, as the orthorhombic mullite phase exhibits also the layered character [23,24].

Fig. 6. X-ray diffraction patterns of the PANI pellets. A) PANI-d; B) PANI-900; C) PANI-1200; D) PANI-1400. 1 – C₆N₆, 2 – C₃N₄.

X-ray diffraction patterns of all PANI samples are shown in Fig. 6. As one can see, presence of graphite and graphene was not confirmed. However, two different phases not observed in X-ray diffraction patterns of PANI/MMT samples were found: carbon nitride (C₃N₄) and 1,3,5-triazine-2,4,6-tricarbonitrile (C₆N₆). Comparison of Fig. 3 and Fig. 6 suggests that during calcination the phase transformation of pure PANI differs from the phase transformation of PANI in presence of MMT sheets.

Results of AFM analysis can be seen in Fig. 7. Before calcination, the surface of tablet is relatively smooth and the PANI/MMT particles are closely packed to each other (Fig. 7a). The surface of PANI/MMT-1400 tablet (Fig. 7b) shows significantly different (glassy) character as a result of sintering of PANI/MMT particles.
3.2 Raman spectroscopy

Raman spectra of all calcined samples are shown in Fig. 8. Characteristic bands belonging to PANI were not observed, only the disorder band showing defects in the samples (~1350 cm\(^{-1}\)) and the graphitic band determining orderliness of the carbon structure (~1600 cm\(^{-1}\)) are present. Broadness of bands reveals the presence of amorphous carbon. Although these bands are a little bit sharper in spectra of PANI-1200, PANI-1400, and PANI/MMT-1400 samples (Figs. 8b,c,f), the higher intensities of disorder bands in these spectra suggest that defects in carbon structure still predominate [25,26].

![Raman spectra](image)

**Fig. 8.** Raman spectra of pure PANI and PANI/MMT samples. (a) PANI-900, (b) PANI-1200, (c) PANI-1400, (d) PANI/MMT-900, (e) PANI/MMT-1200, (f) PANI/MMT-1400.
Raman spectrum of the sample PANI/MMT-1400 (Fig. 8f) contains an additional intensive band with maxima centered at 2701 cm\(^{-1}\), which is generally ascribed to 2D (historically named G’) overtone band of graphite, but high intensity of this band is typical for graphene [26-29]. Therefore, it can be concluded that after calcination of PANI/MMT sample at 1400 °C the PANI layer intercalated in the interlayer space of MMT is transformed into graphene sheets.

3.3 Conductivity

Results of conductivity measurements are summarized in Table 1, where we compare the conductivities in two perpendicular directions: in-plane conductivity \(\sigma_{\perp}\), and conductivity in the direction of pressing \(\sigma_{\parallel}\) (see Fig. 2) in dependence on calcination temperature. Anisotropy factor \(\alpha = \sigma_{\perp}/\sigma_{\parallel}\) describes the anisotropy of conductivity.

<table>
<thead>
<tr>
<th>sample</th>
<th>calcination T (°C)</th>
<th>(\sigma_{\parallel}) (S/m)</th>
<th>(\sigma_{\perp}) (S/m)</th>
<th>(\alpha = \sigma_{\perp}/\sigma_{\parallel})</th>
</tr>
</thead>
<tbody>
<tr>
<td>PANI uncalcined</td>
<td>0</td>
<td>0.102</td>
<td>3.50</td>
<td>34</td>
</tr>
<tr>
<td></td>
<td>900</td>
<td>0.27</td>
<td>0.29</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>1200</td>
<td>1.22</td>
<td>1.24</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>1400</td>
<td>1.76</td>
<td>1.81</td>
<td>1</td>
</tr>
<tr>
<td>PANI/MMT uncalcined</td>
<td>0</td>
<td>0.0007</td>
<td>0.03</td>
<td>43</td>
</tr>
<tr>
<td></td>
<td>900</td>
<td>11.54</td>
<td>86.45</td>
<td>7</td>
</tr>
<tr>
<td></td>
<td>1200</td>
<td>34.42</td>
<td>272.69</td>
<td>8</td>
</tr>
<tr>
<td></td>
<td>1400</td>
<td>78.67</td>
<td>693.41</td>
<td>9</td>
</tr>
</tbody>
</table>

Table 1 shows that the uncalcined PANI sample exhibits 100\(\times\) higher in-plane conductivity \((\sigma_{\perp})\) than the uncalcined PANI/MMT sample. However, the degree of preferred orientation and, consequently, the anisotropy factor is, of course, higher in the uncalcined PANI/MMT sample. Calcination led to the change in conductivity and in the anisotropy. In PANI samples, the calcinations caused the decrease of \(\sigma_{\perp}\) values and led to the isotropic conductivity and structure. In case of PANI/MMT, the calcinations result in dramatic increase of the in-plane conductivity from 0.03 S/m for uncalcined sample up to the 693.41 S/m for calcination at 1400 °C. The strong increase in conductivity \(\sigma_{\perp}\) is the result of formation of graphene sheets.
between the aluminosilicate layers, as revealed by Raman spectroscopy. This increase is accompanied with the decrease of anisotropy factor $\alpha$ from two reasons: (1) the MMT $\rightarrow$ cristobalite and mullite structural phase tranformations and (2) the transformation of the interparticle PANI material into graphite. The presence of interparticle graphite (see the diffraction pattern for 1200 °C and 1400 °C in Fig. 3) results in increase of conductivity in the direction of pressing ($\sigma_\parallel$).

In order to reveal the graphene content and the possible graphene dopants, the elemental analysis of the most conductive PANI/MMT-1400 sample has been performed. Results are compared with results obtained for the uncalcined PANI/MMT sample in the Table 2. While the amount of carbon remains unchanged (within the limit of experimental error 1%), the amounts of hydrogen, nitrogen, and sulfur significantly decreased after the calcination. Nitrogen can be present as a dopant in graphene, but only in a very low concentration.

<table>
<thead>
<tr>
<th>Table 2</th>
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<tbody>
<tr>
<td>Total content of carbon, hydrogen, nitrogen and sulfur before and after calcinations.</td>
</tr>
<tr>
<td>sample</td>
</tr>
<tr>
<td>-------------------------</td>
</tr>
<tr>
<td>PANI/MMT-d</td>
</tr>
<tr>
<td>PANI/MMT-1400</td>
</tr>
</tbody>
</table>

Present conductivity values are much higher those published so far for graphene-based nanocomposites. Graphene/polystyrene nanocomposite prepared by Stankovich et al. exhibits the conductivity $\sigma = 9$ S/m [1]. Fan et al. reported a combination of graphene/polystyrene nanocomposite with latex and usage of layer-by-layer assembly approach but the conductivity decreased to $\sigma = 0.1$ S/m [4]. Even smaller conductivity value ($\sigma = 0.01$ S/m) was reached by Rozlívková et al. [30] via carbonization of granular PANI at 800°C. Relatively high conductivities can be found for systems of graphene-crystalline anorganic matrix type. Thus, for graphene/alumina ceramics [31], graphene/silica [32], graphene/Au [33], and graphene/SiC [16] nanocomposites the conductivities 11 S/m, 45 S/m, 49 S/m, and 100 S/m, respectively, were reported.
4. Conclusions

Ceramic material with anisotropic conductivity has been prepared in three steps: (1) intercalation of layered silicate (montmorillonite) with polyaniline, (2) pressing powder intercalate into tablet using high pressure 400 MPa, and (3) calcination of pressed tablet. In the first step, layered structure of montmorillonite has been homogeneously intercalated with conducting polyaniline. Structural phase tranformation in montmorillonite during high temperature (1400 °C) treatment of tablet does not change the layered character of aluminosilicate matrix and enables carbonization of polyaniline layers into graphene sheets accompanied with dramatic increase of the in-plane conductivity from 0.03 to 693.41 S/m. Anisotropy factor for graphene/aluminosilicate tablets is lower than for starting polyaniline/montmorillonite uncalcined tablets, probably due to a creation of additional percolation pathways also in the transversal direction.

Using furnace with appropriate volume it is possible to prepare any amount of this material if there will be sufficient flow of argon ensuring a sufficiently quick renewal of inert atmosphere and if the carbonization fumes will be continuously removed from the volume of furnace. The main advantage of this technology is the low cost of all input materials, i.e. clay mineral and polyaniline.

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