Poly(p-phenylene vinylene) incorporated into carbon nanostructures

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Abstract Composites of poly(p-phenylene vinylene) (PPV) and different carbon nanostructures, such as fullerene C_{60}, multi-walled carbon nanotubes (MWCNTs), single-walled carbon nanotubes (SWCNTs), graphene oxide (GO), and graphene nanoplatelets (GNPLs), were produced by Wittig’s soluble precursor procedure in solutions containing dispersed particles of carbon nanomaterials. These composites were investigated using infrared and Raman spectroscopy, scanning and transmission electron microscopy, thermogravimetry analysis, adsorption/desorption of N\textsubscript{2} measurement, and electrochemistry. Composites are produced in the form of nanostructural porous materials. A significant increase in the BET (Brunauer–Emmett–Teller) surface is observed for composites in comparison to unmodified PPV. The highest BET surface area of 125 m\textsuperscript{2}\cdot g\textsuperscript{-1} was obtained for the PPV/SWCNT composite. Compared to pristine PPV, composites also exhibit higher thermal stability. The effect of the content of composite components on their electrochemical properties was also investigated. The electronic interaction between components of composite significantly affects their electrochemical properties, particularly in the case of oxidation processes. PPV incorporated into network of carbon nanostructures exhibit two well separated oxidation steps. The carbon component is responsible for the shift of the PPV reduction and oxidation processes toward less negative and less positive potentials, respectively, significantly lowering the energy of the band gap.

Keywords Poly(p-phenylene vinylene) · Carbon nanostructures · PPV composites · Electrochemistry of PPV-based materials · Nanocomposites · Wittig’s soluble precursor procedure

Introduction

Modern technologies, especially focused on searching for new energy sources, storing energy or processing it, require the creation and research of new materials, cheaper, more durable and exhibiting desirable physicochemical properties. These new electro-technically useful materials include covalent organic frameworks [1, 2], metal–organic frameworks [3–5] or transition metal MXenes [6–8]. Traditional materials that have been used for many years in devices for generating,
storing and converting energy, such as transition metal oxides [9–11] conductive polymers [12–15], are also tested. Many of today’s advanced technologies are based on the use of conjugated conducting polymers [16]. Materials containing these polymers are applied in charge storage devices [17, 18], solar energy conversion [19, 20], light-emitting diodes [21], electrochromic devices [22], and chemical and biochemical sensors [23]. Most of these applications are based on their electrochemical and photochemical properties. Poly(α,α,α’,α’-tetrabromo-p-xylene) (PPV) and its derivatives have been commonly used in the construction of optoelectronic devices [24–29]. Understanding the mechanism of operation of these systems and improving their photochemical parameters requires knowledge about the distribution of energy levels in the photoactive material and the influence of electrochemical doping processes on their photochemical properties.

The PPV-based materials exhibit both $p$ and $n$ doping properties. They can be oxidized in the positive potential range. In the formed polaron, the positive charge is delocalized over the average of four monomer units. It was also postulated that oxidized PPV units undergo disproportionation processes leading to the formation of localized dications separated by four neutral monomer moieties [30]. The process of PPV oxidation is accompanied by the incorporation of supporting electrolyte anions into the polymeric network. PPV and its derivatives can also be reduced at negative potentials to form negative polarons and doping the polymeric phase with the cations of the supporting electrolyte.

The electrode processes of PPV-based materials depend on many parameters, such as the polymerization process, the structure of the polymerization monomer, the structural and morphological properties of polymeric materials, and the nature of doping ions. Wittig’s soluble precursor procedure is the most frequently used method in PPV and its derivative formation [31]. These polymers can also be formed under electrochemical conditions by electroreduction of α,α,α’,α’-tetrabromo-p-xylene [32]. Another method for PPV film formation by electrorereduction of 1,4-dibromobenzene-nickel complexes was reported by Fauvarque and coworkers [33]. The electrochemical properties of PPV films deposited on different electrode surfaces have been investigated for both chemically and electrochemically prepared materials. The electrochemically formed PPV films exhibit irreversible redox behavior for both the oxidation and reduction steps [34]. Poly(phenylene vinylene) substituted by electron-withdrawing and electron-donating groups exhibits partial electrochemical reversibility in both $n$-doping and $p$-doping processes [35, 36]. The covalent modification of the phenyl ring results in a change in the HOMO and LUMO energy levels and the energy gap between these orbitals. Additional variations in the energetic position of these levels are caused by conjugation disturbing by bulky substituents incorporated into the polymer structure [37].

The electrochemical properties of PPV-based polymeric materials can also be controlled by the structure of the electroactive film deposited at the electrode surface and the morphology of the polymeric material. Homogeneous and dense films formed under electrochemical conditions exhibit irreversible oxidation and reduction processes [34]. It has also been postulated that only a small part of the material undergoes electrode processes. Such problems can be overcome by the use of layers formed of nanoparticle materials. However, the thermal PPV synthesis process generates many effects in the formed polymeric material and leaves impurities from the solvent and side products of synthesis. Under such conditions, the formation of high-quality PPV nanoparticles is very difficult. Porous alumina and polycarbonate filters have been used as templates for the fabrication of PPV nanotubes and nanorods by the CVD polymerization method [38]. Deposition of PPV on carbon nanoparticles is another method of formation PPV-containing nanocomposite materials. To date, composites of PPV and its derivatives with C$_6$O [39–44], multi-walled carbon nanotubes [45], single-walled carbon nanotubes [40, 46], and graphene oxide [47] have been studied. These investigations were mainly focused on the photochemical properties of these materials. A significant electronic interaction between the two components of the composite was reported [48]. Carbon nanomaterials act as quenching agents in the photoluminescence of PPV [45]. In most cases, composites of PPV and carbon nanoparticles were fabricated by mechanical mixing of two components of composite. Alternatively, such composites can be produced during thermal conversion of the PPV precursor in solutions containing dispersed carbon material nanoparticles.

The ability to control photo and electrochemical properties of conducting polymers is extremely important and determines the directions of their application in electronics, electrotechnology, and optoelectronics.
In conducting polymers, the energy of electron levels depends on size and the structure of polymeric backbone, substituents incorporated into the polymeric chain and interchain interactions. In composites, the electronic interaction between components additionally results in the significance changes of the energy levels at the interphase. The structure of this interphase, which depends on the method of composite formation, affects the interaction energy between the components. In this work, a variety of composites containing PPV and different carbon nanostructures were formed by Wittig’s soluble precursor procedure in solutions containing dispersed particles of carbon nanomaterials (Scheme 1). Under these conditions, PPV was deposited at the surface of carbon nanostructures, allowing us to harvest the full potential of both composite components. The morphology, composition, and selected physicochemical properties of the formed materials were investigated. Many practical applications of such structures, including energy storage devices and solar cells, depend on their electrochemical properties. Therefore, special attention was given to electrochemical properties of formed composites.

Experimental

Chemicals

Unless otherwise stated, all reagents and chemicals, such as α,α'-dibromo-p-xylene (97%, Acros Organics), triphenylphosphine (≥95%, Sigma–Aldrich), N,N-dimethylformamide (DMF) (POCH), terephthaldehyde (99%, Sigma–Aldrich), sodium methoxide (≥98% POCH), methanol (POCH), acetone (100%, Chempur), tetrabutylammonium hexafluorophosphate (TBAPF6), ≥99%, Sigma–Aldrich, fullerene C60 (99.5%, Sigma–Aldrich), graphene oxide (GO) (dry platelets, Graphene Supermarket), graphene nanoplatelets (GNPLs) (Sigma–Aldrich), single-walled carbon nanotubes (SWCNTs) (>70%, Sigma–Aldrich), and multi-walled carbon nanotubes (MWCNTs) (Sigma–Aldrich), were purchased from commercial sources and used without further purification.

Synthesis of PPV

Triphenylenphosphine (0.0167 mol; 4.37 g) was mixed with α, α'-dibromo-p-xylene (0.008 mol; 2.11 g) and dissolved in 16.67 mL of DMF. The resulting solution was then refluxed for 5 h. After cooling to room temperature, the white precipitate of phosphonium salt was collected and washed several times with DMF and ether. In the final step, the obtained phosphonium salt (0.0027 mol; 1 g) and terephthaldehyde (0.001 mol; 0.129 g) were mixed in methanol (10 mL) with the addition of sodium methoxide (0.007 mol; 400 μL). The mixture was heated at 62 °C for 2 h. The resulting yellow product was washed three times with methanol, acetone, and water and then dried in an oven overnight at 80 °C. The yield of PPV synthesis was to 86%.

Synthesis of PPV and carbon nanostructure composites

The previously synthesized phosphonium salt (0.00134 mol; 0.05 g) was mixed with the same mass of the selected carbon material, terephthalaldehyde (0.0005 mol; 0.00645 g) and sodium methoxide (0.0035 mol; 200 μL), and then dissolved in methanol (5 mL). The solution was heated at 62 °C for 2 h. The obtained dark gray–yellow precipitate was washed three times with methanol, acetone, and water and then dried in an oven overnight at 80 °C.

Apparatus

Fourier transformation infrared (FTIR) spectra were recorded in the range between 4000 and 400 cm⁻¹ with a Nicolet 6700 Thermo Scientific spectrometer at room temperature in reflection mode. The spectra were collected with a resolution of 4 cm⁻¹. All the spectra were corrected with OMNIC software to normalize the spectra and utilize atmospheric correction. The room-temperature Raman spectra were recorded using a Renishaw spectrometer. As the excitation source, an argon laser with a wavelength of 514 nm was employed. The Raman spectra were registered at a spectral resolution of 2 cm⁻¹ and wavelengths between 100 and 3200 cm⁻¹.

The structure of the composites was characterized by powder X-ray diffraction using a SuperNova X-Ray diffractometer (Agilent Technologies) operating at 50 kV and 0.8 mA equipped with a CCD detector (158 mm sample-to-detector distance) working with a CuKα 1 (λ = 1.54056 Å) radiation source.
Thermogravimetric (TG) analyses were performed using a Mettler Toledo Star TGA/DSC unit (Greifensee, Switzerland). A sample (approx. 2 mg) was placed in an aluminum oxide crucible and heated from 50 to 800 °C at a rate of 10 °C min⁻¹ under an argon or oxygen flow rate of 40 mL min⁻¹. An empty pan was used as a reference. Transmission electron microscopy (TEM) images were recorded using an TEM FEI Tecnai T20 G2 X-TWIN Instrument operating at 200 kV. The SEM images were recorded using an INSPECT S50 microscope (FEI). The accelerating voltage of the electron beam was 20 keV. The solutions of the tested materials were placed on copper foil, and after the solvent was evaporated, the surface of the obtained layers was sputtered with 5 nm Au to obtain better image quality. Voltammetric measurements were performed using a PGSTAT 302 N potentiostat (AUTOLAB) with a three-electrode system consisting of a glassy carbon electrode (GCE) (ϕ 2 mm) as the working electrode, Pt wire as the counter electrode, and Ag/AgCl as the reference electrode. The surface of the GCE was modified by applying 10 µL of the obtained solution (2 mg of the synthesized material was dissolved in 1 mL of hexane) and evaporating the solvent. The experiments were carried out at room temperature. Nitrogen adsorption/desorption isotherms were obtained using an ASAP2020 automatic sorption system at −196 °C. All samples were degassed at 100 °C for 24 h under vacuum.

Results and discussion

Structure and morphology of PPV composites

PPV was synthesized based on the Wittig reaction according to a procedure published elsewhere [49]. The synthesis of composite materials was analogous to the procedure for the preparation of unmodified
PPV, except that in the second step, selected carbon nanomaterials, such as fullerene C_{60}, graphene oxide (GO), graphene nanoplatelets (GNPLs), single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs), were added (Scheme 1). Consequently, five different composites containing PPV and selected carbon material (PPV/C_{60}, PPV/GO, PPV/GNPLs, PPV/SWCNTs, PPV/MWCNTs) were obtained.

The composition of the formed composites containing PPV and carbonaceous materials was investigated by FTIR and Raman spectroscopy. Figure 1 shows FTIR spectra recorded in ATR mode for all studied materials. For comparison, the spectrum of PPV is also presented. The spectrum of pristine PPV (Fig. 1a) shows bending vibrations at 832, 962, and 1110 cm\(^{-1}\) corresponding to C-H out-of-plane deformation of phenylene units, out-of-plane angular deformation for the trans-vinylene unit and C-H in-plane deformation of the phenylene ring, respectively [32]. The stretching vibrations of phenyl groups are associated with bands between 1417 and 1598 cm\(^{-1}\) (Table 1) [50]. Two characteristic bands confirming polymer formation, trans-vinylene C-H stretching at 3017 cm\(^{-1}\) and trans-vinylene C-H deformation at 962 cm\(^{-1}\), are also observed [32].

The FTIR spectra of the second component of composites, carbon nanomaterials are shown in Figure S1. Carbon nanoparticles are usually partially oxidized particularly at their edges and surface defects. The spectra of carbon nanomaterials are dominated by two large peaks at ca 1630 and 3340 cm\(^{-1}\). The peak at ca.1630 cm\(^{-1}\) is related to the stretching of ketone C=O ketone groups at vacancy edges of carbon nanostructures. The vibrations of the C=C double bonds are responsible for the band at ca. 1580 cm\(^{-1}\) [51]. The presence of water in the hygroscopic carbon material surface results in formation intense absorption band at ca. 3430 cm\(^{-1}\) [52]. This signal overlaps with bands corresponding to the vibration of hydroxide and carboxyl groups [51]. In the case of carbon nanotubes (SWCNTs and MWCNTs), two bands at around 1110 and 1070 cm\(^{-1}\) are associated with stretching of ether type groups [53]. These signals are better developed for MWCNTs due to the higher degree of oxidation.

The FTIR spectra recorded for the PPV composites are shown in Fig. 1b-f. As expected, all bands characteristic of PPV are present in these spectra. For the studied composites, a blueshift of most bands is observed. Such behavior indicates a weak interaction between both components of the composite material. The most evident shift was observed for the band associated with the C-H bending vibrations at a wavenumber of ca. 830 cm\(^{-1}\) (Table 1). Signals related to vibrations of carbon nanostructures overlap with bands associated to PPV vibrations. Intensity of the bonds associated with the carbon nanostructures is much lower in comparison to polymeric materials. Therefore, spectra presented in Fig. 1 are dominated by the signals corresponding to PPV vibrations. The signals observed in this are the result of PPV aromatic ring vibrations of and aromatic rings of carbon nanostructures.

Raman spectra of PPV and PPV-based composites are presented in Fig. 2. The PPV band characteristic of the PPV (Fig. 2a) at 1174 cm\(^{-1}\) (marked as field circles) is assigned to the C-C stretching and C-H bending of the phenyl ring vibrational mode [47, 54]. A triplet located at 1549, 1586, and 1628 cm\(^{-1}\) (Fig. 2a), assigned to the vibrational modes of the C=C stretching of the phenyl ring, C=C stretching of the phenyl ring, and C=C stretching of the vinyl group, respectively, is also characteristic of PPV [47, 54]. The small peak located at 1325 cm\(^{-1}\) is assigned to the C=C stretching and C–H bending of the vinyl unit. In the Raman spectrum for carbonaceous material, two characteristic modes, namely, D and G, located at approximately 1320 and 1590 cm\(^{-1}\), which correspond to the breathing mode of the carbon hexagonal ring and the E2 g phonon mode at the center of the Brillouin zone, respectively, are observed [47]. For all hybrid materials (Fig. 2c, e, g, i, k), the aforementioned band and triplet, typical modes for PPV films, overlap with the D and G bands characteristic of carbon nanostructures used in composites. Moreover, an intensification of the peak located at nearly 1600 cm\(^{-1}\) due to the imposition of band G from carbon materials and triplets from PPV is observed. Such behavior indicates the effective modification of carbon materials by polymers. Furthermore, the characteristic band for PPV at 1174 cm\(^{-1}\) is shifted toward shorter wavelengths.

The phase components of the various PPV/carbon nanostructure composites together with polymer are confirmed by X-ray diffraction (XRD) patterns as displayed in Fig. 3. In the case of PPV/C_{60} composite, the XRD pattern is dominated by the signals
that can be indexed to the face-centered cubic structure of fullerene phase with lattice parameter 14.24 Å [55]. The XRD spectrum of PPV/GO composite shows dominant (002) diffraction peak at 20 of 9.97° (interlayer distance of 0.89) and (100) diffraction peak at 20 of 42.69° indicating a short range order in stacked graphene layers [56, 57]. The presence of polymeric phase within the composite material is manifested by the increase of background signal in the 20 range of ca. 17.97° (inset in Fig. 3). Broad signals in the 20 range of ca. 17.5–20.5° corresponding to diffraction from PPV are also observed in the case of other composites. Additionally, diffraction peaks at 20 of 26.53° (interlayer distance of 0.34) and 25.66° (interlayer distance of 0.35) corresponding to (002) plane of graphene layers stacks are observed for PPV/GNPLs [58] and PPV/MWCNT [59] composites, respectively. The greater interlayer distance for GO compared to GNPLs or MWCNTs, calculated from Bragg’s law for the (002) plane, indicates incorporation of many oxygen functional groups between the carbon layers in GO.

The thermal stability of the PPV and PPV/carbon nanostructure composites was studied using
The carbon nanomaterials decompose continuously over the entire applied temperature range (50–800 °C). However, the observed total weight losses are relatively small (< 10%), except for the loss recorded for SWCNTs, which is equal to 17% (Fig. S2, Table S1). It is worth mentioning that weight losses observed in the temperature range up to 150/200 °C are most likely due to the removal of the absorbed moisture. PPV starts to degrade at approximately 200 °C, whereas its composites with nanomaterials show slightly higher thermostability (Fig. 4). The TG curves of PPV and its composites show few consecutive and overlapping decomposition steps over broad temperature ranges, with the maxima of the degradation rates collected in Table S1. All tested materials do not decompose completely; the residues observed at 800 °C are between 40 and 90% (Table S1). These residues are associated with the presence of carbon fractions that do not decompose in the applied temperature range. Different amounts of residues indicate different compositions of the tested materials. However, a precise determination of the PPV/carbon material weight ratio based on the TG data is impossible. The TG analyzes performed in oxygen (Fig. S3) show that under oxidizing conditions PPV is slightly more stable than its composites, which begin to undergo oxidizing processes below 200 °C. These processes are manifested as an increase in mass above 100% on the TG curves and exothermic peaks present on the DSC curves. Generally, PPV and its composites degrade totally in several steps over a wide temperature range, which depends on the type of carbon nanomaterial used. The TG results taken in oxygen confirm formation of materials of different compositions.

In Fig. 5, the TEM images obtained for various carbon nanomaterials and their PPV composites are compared. Additionally, the image obtained for unmodified PPV has been inserted into the photos of composites. Due to the small particle size of C₆₀, the PPV/C₆₀ composite forms a compact and strong aggregated mass. This tendency reduces the active surface area of synthesis material. The most effective polymer coating with the most developed surface area was obtained for GO and GNPLs composites. PPV forms a thin, quite compact, not completely uniform layer on the graphene flakes, which does not significantly affect their size. In the PPV/SWCNT and PPV/MWCNT samples, heterogeneous polymer coatings were observed with different layer thicknesses. Coating of SWCNTs with PPV led to the strong aggregation of the nanotubes. The coating process of MWCNTs was not completely effective, and pristine nanotubes were observed in the images (Fig. 5). Morphological studies of PPV-based composites were carried out using SEM microscopy (Fig. 6). SEM images of the synthesized pristine PPV (Fig. 6a) confirmed the fine graininess and high degree of porosity of the tested material. The use of carbon nanostructures in the polymerization process resulted in the formation of larger agglomerates and lower homogeneity of the material compared to unmodified PPV. Moreover, the morphology of the obtained composites was strongly dependent on the shape, size, and dimensions of the selected carbon nanostructures.

Fig. 2 Raman spectra (λ = 785 nm) of the films of (a) PPV, (b) C₆₀, (c) PPV/C₆₀, (d) GO, (e) PPV/GO, (f) GNPLs, (g) PPV/GNPL, (h) SWCNTs, (i) PPV/SWCNTs, (j) MWCNTs, and (k) PPV/MWCNTs.
For example, fullerene C$_{60}$ coated with PPV (Fig. 6b) formed mainly spherical aggregates with a wide range of diameters (2 to 7 µm). The PPV/GO composite (Fig. 6c), which exhibits a polymer-coated flake structure, is highly aggregated and much more porous than PPV/C$_{60}$. On the other hand, the material, which is a combination of PPV and GNPLs, shows a completely different morphology (Fig. 6d). In this case, the SEM images exhibit the formation of large spindle-shaped aggregates (even 20–25 µm long) glued together with a polymer material. Materials based on the combination of PPV with carbon nanotubes are also characterized by a high degree of aggregation but show much higher porosity than the PPV/GNPLs composite. The difference in the morphology of PPV/SWCNTs and PPV/MWCNTs suggests a different manner of deposition of PPV on the surface of the selected type of nanotubes. In the case of PPV/SWCNTs (Fig. 6e), polymeric material is observed both on the walls of the nanotubes and as a binder sticking them together. On the other hand, the walls of the MWCNTs (Fig. 6f) were covered with a thick, sponge-like layer of polymer, which resulted in the formation of characteristic agglomerates.

The non-covalent modification of PPV by carbon materials with different shapes and sizes induces alteration of the hybrid material surface and hence the size or/and distribution of pores. The nitrogen adsorption/desorption isotherms of the synthesized composite materials are presented in Fig. 7. According to the IUPAC classification, isotherms recorded for PPV/carbon materials represent type IV due to the characteristic shape and presence of hysteresis loops (type H3) [60, 61]. This result strictly indicates that mesoporous materials with slit pores are formed. In the inset of Fig. 7, linear plots of $\frac{1}{[Q(P/P_0) - 1]}$ vs. the relative pressure (P/P$_0$) are shown. From this relationship, based on Brunauer–Emmett–Teller (BET) theory, specific surface areas (S$_{BET}$) were
calculated. The textural parameters of the studied materials are collected in Table 2. The pore volume, pore width and surface area of the pores were computed using Barrett–Joyner–Halenda (BJH) calculations. All studied composites exhibit higher specific surface areas than unmodified PPV. The specific surface areas were between 24.1 and 140.7 m²·g⁻¹, and the highest value was obtained for the PPV/SWCNT composite. According to the pore size distribution of the BJH calculation (Table 2), the PPV shows a mesoporous structure (pore size = 16.891 nm). The remaining composites show also mesoporous domains with pore widths between 16.144 and 41.396 nm. Moreover, other textural parameters, such as pore volume and surface area of pores, are the highest for PPV/SWCNT composite (Table 2).

To sum up adsorption/desorption research, isotherms of PPV GO composites on three different mass ratios were also measured. This was to test the effect of increasing the polymer amount in composite relative to the carbon material. As expected, as the mass of the polymer in the composite increases, the specific surface area of the BET decreases. The isotherms and values of BET for PPV GO composites with different mass ratios are shown in Figure S4.

Electrochemical properties

The electrochemical properties of PPV-based composite materials depend on the structure and morphology of the electroactive films deposited at the electrode surface. The possible electron transfer between the PPV phase and the carbon nanostructural component may influence the thermodynamics of the PPV-involved electron transfer processes. Additionally, an increase in the porosity of composite materials and their real surface areas significantly increases the amount of electroactive material that participates in the charge transfer processes.

The electrochemical performance of obtained composites was compared to the electrochemical properties of pristine PPV synthesized by Wittig reaction. The voltammetric response of PPV in acetonitrile solution containing different supporting electrolytes containing the same anion and different tetra(n-alkyl) ammonium cations is shown in Fig. 8. The polymeric material exhibits a large oxidation current peak, O₁,
at potentials more positive than ca. 0.8 V. At negative potentials, voltammetric signals corresponding to the PPV reduction processes are observed. The large density current of PPV reduction at potentials more negative than ca. 2 V is preceded by a small voltammetric signal R$_1$ at less negative potentials.

Fig. 6 SEM images of (a) PPV, (b) PPV/C$_{60}$, (c) PPV/GO, (d) PPV/GNPLs, (e) PPV/SWCNTs and (f) PPV/MWCNTs coated on Cu foil.

Fig. 7 Isotherms of adsorption/desorption of N$_2$ for PPV composites. Inset figure: BET surface area curves.
As can be expected for the \( p \)-doping process, the oxidation electrode reaction is practically independent of the cation type of the supporting electrolyte. Montilla and Malalavia reported that two PPV oxidation steps overlap in the potential range of \( O_1 \) peak [19]. The first oxidation process is partially reversible. However, further oxidation and doping of the polymer with anions of the base electrolyte leads to structural changes and loss of electrochemical activity of the polymeric material. In the case of polymeric material synthesized in this work, no electrochemical reversibility was observed for the oxidation step in whole potential range of PPV electrooxidation.

Complex redox behavior is also observed for PPV involved reduction processes. First of all, charge corresponding to PPV reduction processes in the potential range of \( R_1 \) reduction step is much lower than the charge corresponding to the oxidation processes. Such behavior indicates that the process of polymer doping with large cations of the basic electrolyte during material reduction is much less effective and limits the amount of material that can be reduced. In fact, the potentials of polymer reduction steps and the density of reduction current significantly depend on the size of supporting electrolyte cations as is shown in inset \( a \) of Fig. 8.

The effect of an anion of the supporting electrolyte on the electrochemical behavior of PPV was also investigated. In this case, only the oxidation process depends on the nature of supporting electrolyte anion. The voltammograms of PPV oxidation recorded in solutions containing the same cation and different anions of supporting electrolyte are shown in inset \( b \) of Fig. 8. The sharp \( O_1 \) oxidation peak precedes the polymer oxidation current in the range of the more negative potentials. The current density observed in this range is much higher than the background current density obtained for the electrode not covered with the polymer. The charge reproducibility corresponding to the \( O_1 \) peak is low. It is probably related to the morphology of the polymer layer deposited on the surface of the glassy carbon. PPV deposited by the drop coating method forms amorphous particles. The surface of the layer is not uniform. It is very likely that the \( O_1 \) peak is responsible for the oxidation of that surface polymer layer in direct contact with the electrolyte solution. Problems related to the formation of a reproducible polymer layer on the electrode surface by the drop coating method can be responsible for the low reproducibility of the charge related to the \( O_1 \) peak. The oxidation of the polymer layers that are not in direct contact with the electrolyte solution takes place in the more positive potential range. The current density corresponding to this process correlates with the anion size of the supporting electrolyte, which varies in the series \( BF_4^- \) (ionic radius 0.229 nm) < \( ClO_4^- \) (0.237 nm) < \( PF_6^- \) (0.254 nm) [62].

The voltammetric responses of composites containing PPV and carbon nanostructures are shown in Fig. 9. Background current responses recorded at electrodes coated with appropriate carbon materials are also presented for comparison. In most of the cases, the two separated oxidation steps are recorded for the PPV oxidation process (voltammograms \( b-e \) in Fig. 9). Only for the composite consisting of \( C_{60} \) and PPV, a single signal of polymer oxidation is observed (voltammogram \( a \) in Fig. 9).

### Table 2 The textural parameters of PPV/carbon nanostructure composites based on adsorption/desorption studies

| Sample     | BET Surface Area \( (S_{BET}) \) \( [\text{m}^2 \cdot \text{g}^{-1}] \) | Pore volume \( [\text{cm}^3 \cdot \text{g}^{-1}] \)\(^{(a)} \) | Pore width \( [\text{nm}] \)\(^{(b)} \) | Surface area of pores \( [\text{m}^2 \cdot \text{g}^{-1}] \)\(^{(c)} \) |
|------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|
| PPV        | 24.1                        | 0.0311                      | 16.891                      | 7.372                       |
| PPV/\( C_{60} \) | 46.9                        | 0.0934                      | 19.785                      | 18.982                      |
| PPV/GO     | 92.2                        | 0.3104                      | 11.493                      | 57.356                      |
| PPV/GNPLs  | 70.3                        | 0.1295                      | 41.396                      | 12.518                      |
| PPV/SWCNTs | 140.7                       | 0.5081                      | 16.144                      | 125.902                     |
| PPV/MWCNTs | 121.0                       | 0.4312                      | 18.587                      | 92.799                      |

\(^{(a)}\) Calculated based on BJH adsorption cumulative volume of pores between 17,000 and 3000,000 Å diameter; \(^{(b)}\) Calculated based on BJH adsorption average pore diameter (4 V/A); \(^{(c)}\) Calculated based on BJH adsorption cumulative surface area of pores between 17,000 and 3000,000 Å diameter.
In Fig. 10, voltammograms recorded in different potential ranges for PPV/SWCNT composite are shown. Similar experiments were performed for other composites and results of these investigations are shown in Figures S5-S7. The first PPV oxidation process at less positive potentials (indicated by arrows in Fig. 9) is totally reversible (Fig. 10b). Voltammogram recorded in potential range from 0 to 1.4 V exhibits reversible behavior of charge transfer process with almost the same charge corresponding to oxidation and reduction process under cyclic conditions. The further oxidation of polymeric material results in losing of PPV electrochemical activity at positive potential. Such behavior is probably related to the irreversible doping of polymeric component with the counterions from the supporting electrolyte upon PPV oxidation. In the case of PPV/SWCNT and PPV/MWCNT composites, the separation of oxidation potentials of both oxidation steps is significantly higher in comparison to the PPV/GO and PPV/GNPL composites. At negative potentials, polymer reduction process is shifted toward the less negative potentials in comparison to the potentials of pristine PPV oxidation. All these results indicate a significant electronic interaction between components of described composites. A degree of separation between two polymer oxidation steps may suggest stronger electronic interaction between components in composites containing carbon nanotubes.

Also, the charge corresponding to pristine PPV electrode processes (Fig. 8) is significantly lower in comparison to charge of oxidation and reduction processes of composites containing the same amount of polymer. Such behavior indicates that the polymer layer within the composite material is more effectively doped with counterions of supporting electrolyte in companion to the electrode processes of pristine PPV. The presence of carbon nanostructures within the composite also affects the amount of electroactive material that undergoes electrode processes. The charge related to the PPV oxidation and reduction peak increases as the amount of carbon nanomaterial in the electrode material increases.
Only for PPV/C₆₀ composite, the voltammetric response of both polymeric and fullerene components resembles electrochemical behavior obtained for pristine material. In this case, PPV and fullerene exist in composite as separate components with no electronic interaction.

Voltammetric measurements allow to calculate electrochemical band gap between the LUMO and HOMO orbitals (E₁) in the composite materials. Results of these calculations are summarized in Table 3. For comparison, E₁ value obtained for pristine PPV is also presented. The electronic interaction between composite components results in significant reduction of E₁ value in comparison to pristine polymeric material. Only in the case of PPV/C₆₀ composite, the value of band gap is close to the one obtained for pristine polymer. So far, band gap energies were only reported for pristine PPV [63–65]. Values of band gap energies obtained from spectroscopic measurements are about 0.3 eV lower compared to the value obtained on the basis of electrochemical measurements in this work. However, the electrochemical band gap energies are elevated by a number of kinetic limitations, such as overpotential of counter-ion transport, overpotential of polymer chain reorganization, or overpotential of charge transfer between electrode and electroactive material. These effects can be responsible for observed differences between

![Fig. 9 Cyclic voltammograms of GCE coated with composites of PPV and different carbon nanostructures (1:1 mass ratio of both components) recorded in acetonitrile containing 0.1 M (C₄H₉)₄NClO₄ at a scan rate of 50 mV s⁻¹. Broken curve represents background current](image)

![Fig. 10 Cyclic voltammograms of GCE coated with PPV/SWCNT (1:1 mass ratio) composite recorded in acetonitrile containing 0.1 M (C₄H₉)₄NClO₄ at a scan rate of 50 mV s⁻¹ in different potential ranges. Broken curve represents background current](image)
electrochemical band gap energies obtained in this work and reported in literature for band gap energies determined from spectroscopic measurements.

The effect of the amount of polymeric phase within the composite material was also investigated. This charge of polymer-involved electrochemical processes increases with an increase in the amount of polymeric material within the composite. However, the increase of PPV amount in composite material results in change of the shape of voltammetric response at positive potentials. At higher mass ratio of PPV to carbon nanostructure, the voltammograms resemble the shape of voltammograms obtained for pure polymeric phase. For example, in the case of PPV/SWCNT and PPV/GO composites, such behavior was observed for PPV to carbon nanostructure ratio higher than 6:1 and 4:1, respectively.

In Fig. 11, the dependence of anodic and cathodic peak currents on the scan rate recorded in the range from 25 to 400 mV·s⁻¹ for the PPV/SWCNT 1:1 w/w composite is shown. The oxidation and reduction peak currents linearly depend on the sweep rate (inset a in Fig. 11). Such behavior indicates that the rate of PPV/SWCNT composite oxidation and reduction electrode processes is controlled by the rate of electrode process that involved electroactive material

| Sample     | \( E_{\text{ox}} \) (a) [V] | \( E_{\text{HOMO}} \) (b) [eV] | \( E_{\text{red}} \) (c) [V] | \( E_{\text{LUMO}} \) (d) [eV] | \( E_g \) (e) [eV] | Ref.   |
|------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|----------------|-------|
| PPV        | 1.040                       | -5.440                      | -1.670                      | -2.730                      | 2.71            | This work |
| PPV/C₆₀    | 0.920                       | -5.320                      | -1.580                      | -2.820                      | 2.50            | This work |
| PPV/SWCNTs | 0.765                       | -5.165                      | -0.885                      | -3.515                      | 1.65            | This work |
| PPV/MWCNTs | 0.715                       | -5.115                      | -0.955                      | -3.445                      | 1.67            | This work |
| PPV/GO     | 0.850                       | -5.250                      | -0.760                      | -3.640                      | 1.61            | This work |
| PPV/GNPLs  | 0.780                       | -5.180                      | -1.665                      | -2.735                      | 2.45            | This work |
| PPV        |                            |                            |                             |                             | 1.76*           |       |
| PPV        |                            |                            |                             |                             | 2.38**          | [63]  |
| PPV        |                            |                            |                             |                             | 2.40**          | [64]  |
| PPV        |                            |                            |                             |                             | 2.42***         | [65]  |

Fig. 11 Cyclic voltammograms of GCE coated with PPV/SWCNT (1:1 mass ratio) composite recorded in acetonitrile containing 0.1 M (C₆H₅)₄NClO₄ at a scan rate of (1) 400 mV·s⁻¹, (2) 200 mV·s⁻¹, (3) 100 mV·s⁻¹, (4) 50 mV·s⁻¹, and (5) 25 mV·s⁻¹. Inset (a) shows linear relation between oxidation and reduction peak currents and the sweep rate. Inset (b) shows anodic part of voltammogram recorded at 25 mV·s⁻¹ with well separated oxidation steps.
coffined at the electrode surface. At lower sweep rates, the two electron transfer steps observed in positive potential range are well separated as is shown in inset $b$ of Fig. 11.

**Conclusions**

Composites of PPV and different carbon nanostructures were synthesized by Wittig’s soluble precursor procedure in solutions containing dispersed particles of carbon nanomaterials. The formation of nanocomposites was confirmed by FTIR spectroscopy, Raman spectroscopy, and thermogravimetry. During the synthesis, carbon material nanoparticles were coated with the polymeric phase. The morphology of the obtained composites was strongly dependent on the shape, size, and dimensions of the carbon nanostructures. The PPV/GO composite exhibits a porous, polymer-coated flake structure. The composite of PPV and GNPLs forms large spindle-shaped aggregates that are glued together. In the case of composites containing carbon nanotubes, the polymeric phase is deposited within the network of carbon nanotubes both on the walls and in the empty spaces of the network to form a sponge-like porous structure. Such a structure of composite materials provides them with a relatively large surface area. The highest BET surface area, calculated from the nitrogen adsorption/desorption isotherms, was obtained for the PPV/SWCNT composite (141 m$^2$·g$^{-1}$). This value is much higher than the value of 24 m$^2$·g$^{-1}$ obtained for unmodified PPV.

Carbon nanostructural components significantly enhance the electrochemical performance of polymeric materials in composites. The results obtained for the studied composites indicate a significant increase in the polymer reduction and oxidation current of the polymeric component due to the increase in the real surface area of the electroactive material. The electronic interaction between both composite components is responsible for redox processes accelerating in the polymer material and shifting the potentials of reduction and oxidation peaks toward less negative and less positive potentials, respectively. This leads to a significant reduction in the gap energy in the polymer incorporated in the composite compared to unmodified PPV. Such behavior is particularly advantageous for the application of composites in solar energy conversion and optoelectronic devices. In organic solar cells, the optimum band gap of a single photoactive material is ca. 1.4 eV [66]. The most commonly used electron-acceptor layer in such cells is [6, 6]-phenyl-C$_{61}$-butyric acid methyl ester (PCBM). In combination with this material, the optimal band gap of 1.3 to 1.9 is expected for the solar energy harvesting polymers [67]. For pristine PPV, band gap energy above 2 eV was obtained in this work and reported in literature [63–65]. Much lower values of this energy obtained for the tested composites locate these materials among good candidates for layers absorbing solar radiation in organic cells. Additionally, the electronic interaction of composite components results in better separation of two electron transfer steps upon polymer oxidation. The electronic interaction between carbon nanostructures and PPV was also confirmed by FTIR spectroscopy. The reversible behavior of electron transfer processes within the polymeric component of the composite is particularly advantageous in the analytical and bioanalytical use of these systems. It enables the mediation of the charge exchange through the polymer layer leading to the amplification of the electroanalytical signal. It should be mentioned that the issues related to the electroanalytical use of PPV have not been the subject of research so far. It was shown that the electrochemical performance of composites is affected by the amount of carbon nanoparticles within the composite.

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**Declarations**

**Conflict of interest** The authors declare no competing interests.

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References

1. Ibrahim M, Abdelhamid HN, Abueltooh AM, Mohamed SG, Wen Z, Sun X (2022) Covalent organic frameworks (COFs)-derived nitrogen-doped carbon-reduced graphene oxide nanocomposite as electrodes materials for supercapacitors. J Energy Storage 55:105375
2. Lohse MS, Bein T (2018) Covalent organic frameworks: structures, synthesis, and applications. Adv Funct Mater 28:1705553
3. Al Kiey SA, Abdelhamid HN (2022) Metal-organic frameworks (MOFs)-derived Co3O4@N-doped carbon as an electrode materials for supercapacitor. J Energy Storage 55:105449
4. Wang H, Zhu Q-L, Zou R, Xu Q (2017) Metal-organic frameworks for energy applications. Chem 2:52–80
5. Qiu T, Liang Z, Guo W, Tabassum H, Gao S, Zou R (2020) Metal–organic framework-based materials for energy conversion and storage. ACS Energy Lett 5:520–532
6. Pang J, Mendes RG, Bachmatiuk A, Zhao L, Ta HQ, Gemming T, Liu H, Liu Z, Rummeli MH (2019) Applications of 2D MXenes in energy conversion and storage systems. Chem Soc Rev 48:72–133
7. Sun S, Liao C, Hafez AM, Zhu H, Wu S (2018) Two-dimensional MXenes for energy storage. Chem Eng J 338:27–45
8. Su T, Ma X, Tong J, Ji H, Qin Z, Wu Z (2022) Surface engineering of MXenes for energy and environmental applications. J Mater Chem A 10:10265–10296
9. Lei Z, Lee JM, Singh G, Sathish CI, Chu X, Al-Muhtaseb AH, Vinu A, Yi J (2021) Recent advances of layered-transition metal oxides for energy-related applications. Energy Storage Mater 36:514–550
10. Yuan C, Wu HB, Xie Y, Lou XW(David) (2014) Mixed transition-metal oxides: design, synthesis, and energy-related applications. Angew Chem Int Ed 53:1488–1504
11. Meyer J, Hamwi S, Kröger M, Kowalsky W, Riedl T, Kahn A (2012) Transition metal oxides for organic electronics: energetics, device physics and applications. Adv Mater 24:5408–5427
12. Bryan AM, Santino LM, Lu Y, Acharya S, D’Arcy JM (2016) Conducting polymers for pseudocapacitive energy storage. Chem Mater 28:5989–5998
13. Yang J, Liu Y, Liu S, Li L, Zhang C, Liu T (2017) Conducting polymer composites: material synthesis and applications in electrochemical capacitive energy storage. Mater Chem Front 1:251–268
14. Grądzka E, Wysocka-Zolopa M, Winkler K (2020) Fullerene-based conducting polymers: n-dopable materials for charge storage application. Adv Energy Mater 10:2001443
15. Shi Y, Peng L, Yu G (2015) Nanostructured conducting polymer hydrogels for energy storage applications. Nanoscale 7:12796–12806
16. Sekhar KN, Rout C (2021) Conducting polymers: a comprehensive review on recent advances in synthesis, properties and applications. RSC Adv 11:5659–5697
17. Chen K, Zhao S, Sun J, Zhou J, Wang Y, Tao K, Xiao X, Han L (2021) Enhanced capacitance performance by coupling 2D conductive metal–organic frameworks and conducting polymers for hybrid supercapacitors. ACS Appl Energy Mater 4:9534–9541
18. Jia P, Lu M, Sun S, Gao Y, Wang R, Zhao X, Sun G, Colvin VL, Yu WW (2021) Recent advances in flexible perovskite light-emitting diodes. Adv Mater Interfaces 8:2100441
19. Li X, Li P, Wu Z, Luo D, Yu H-Y, Lu Z-H (2021) Review and perspective of materials for flexible solar cells. Mater Rep Energy 1:100001
20. Sun Y, Liu T, Kan Y, Gao K, Tang B, Li Y (2021) Flexible organic solar cells: progress and challenges. Small Sci 1:2100001
21. Kee S, Kim N, Park B, Kim BS, Hong S, Lee J-H, Jeong S, Kim A, Jang S-Y, Lee K (2018) Highly deformable and see-through polymer light-emitting diodes with all-conducting-polymer electrodes. Adv Mater 30:1703437
22. Howard EL, Österholm AM, Shen DE, Panchumarti LP, Pinheiro C, Reynolds JR (2021) Cost-effective, flexible, and colorful dynamic displays: removing underlying conducting layers from polymer-based electrochromic devices. ACS Appl Mater Interfaces 13:16732–16743
23. Ramanavicius S, Ramanavicius A (2021) Conducting polymers in the design of biosensors and biofuel cells. Polymers 13:49
24. Abdel-Aziz MH, Zwawi M, Al-Hossainy AF, Zoromba MSh (2021) Conducting polymer thin film for optoelectronic devices applications. Polym Adv Technol 32:2588–2596
25. Lee JS, Oh EJ, Park JY, Shin MW, Cho IH (2001) Synthesis of carbazole-containing PPV and its application to the electroluminescent devices. Mater Sci Eng B 2–3:186–189
26. Damlin P, Östergärd T, Ivaska A, Stubb H (1999) Light-emitting diodes of poly(p-phenylene vinylene) films electrochemically polymerized by cyclic voltammetry on ITO. Synth Met 102:947–948
27. Khokhar D, Jadoun S, Arif R, Jabin S (2021) Functionalization of conducting polymers and their applications in optoelectronics. Polym-Plast Technol Mater 60:465–487
28. Lee H, Jiang Z, Yokota F, Fukuda K, Park S, Someya T (2021) Stretchable organic optoelectronic devices: design of materials, structures, and applications. Mater Sci Eng R Rep 146:100631
29. Liu L, Cao K, Chen S, Huang W (2020) Toward see-through optoelectronics: transparent light-emitting diodes and solar cells. Adv Opt Mater 8:2001122
30. Yu G, Zhang C, Heeger AJ (1994) Dual-function semiconducting polymer devices: light-emitting and photodetecting diodes. Appl Phys Lett 64:1540–1542
31. McDonald RN, Campbell TW (1960) The wittig reaction as a polymerization method1a. J Am Chem Soc 82:4669–4671
32. Peres LO, Varela H, Garcia JR, Fernandes MR, Torresi RM, Nart FC, Gruber J (2001) On the electrochemical polymerization of poly(p-phenylene vinylene) and poly(o-phenylene vinylene). Synth Met 118:65–70
33. Fauvarque J-F, Digua A, Petit M-A, Savard J (1985) Electrolysis of poly(1,4-phenylene) catalyzed by nickel complexes. Makromol Chem 186:2415–2425
34. Montilla F, Mallavia R (2006) In situ electrochemical fluorescence studies of PPV. J Phys Chem B 110:25791–25796
35. Gruber J, Wu Chia Li R (1997) Electrochemical syntheses of poly(4,7-benzofuran vinylene) (PBFV) and poly(4,7-benzothiophene vinylene) (PBTV). Synth Met 88:201–204
36. Gruber J, Li RWC (1999) Electrochemical synthesis of poly(4,4′-biphenylenevinylene)s (PBPVs). J Mater Chem 9:1461–1464
37. Liu B, Yu W-L, Lai Y-H, Huang W (2001) Blue-light-emitting fluorene-based polymers with tunable electronic properties. Chem Mater 13:1984–1991
38. Kim K, Jin J-I (2001) Preparation of PPV nanotubes and nanorods and carbonized products derived Therefrom. Nano Lett 1:631–636
39. Yoshino K, Yin XH, Muro K, Kiyomatsu S, Morita S, Zakhidov AA, Noguchi T, Ohnishi T (1993) Marked enhancement of photoconductivity and quenching of luminescence in Poly(2,5-dialkoxy-p-phenylene vinylene) upon C60 doping. Jpn J Appl Phys 32:L357
40. Yang C, Wohlgenannt M, Vardeny ZV, Blau WJ, Dalton AB, Baughman R, Zakhidov AA (2003) Photoinduced charge transfer in poly(p-phenylene vinylene) derivatives and carbon nanotube/C60 composites. Phys B Condens Matter 338:366–369
41. Wang S, Yang J, Li Y et al (2002) Composites of C60 based poly(phenylene vinylene) dyad and conjugated polymer for polymer light-emitting devices. Appl Phys Lett 80:3847–3849
42. Frolov SV, Lane PA, Ozaki M, Yoshino K, Vardeny ZV (1998) Picosecond to millisecond photoexcitation dynamics in blends of C60 with poly(p-phenylene vinylene) polymers. Chem Phys Lett 286:21–27
43. Liu Y, Fan L, Li Y, Xiao S, Li Y (2002) Electrochemistry of the films of a novel class C60 covalently linked PPV derivative: electrochemical quartz crystal microbalance study in acetonitrile solutions of tetra-n-butylammonium cations. J Appl Polym Sci 86:2737–2741
44. Xiao S, Wang S, Fang H, Li Y, Shi Z, Du C, Zhu D (2001) Synthesis and characterization of a novel class of PPV derivatives covalently linked to C60. Macromol Rapid Commun 22:1313–1318
45. Ago H, Shaffer MSP, Ginger DS, Windle AH, Friend RH (2000) Electronic interaction between photoexcited poly(p-phenylene vinylene) and carbon nanotubes. Phys Rev B 61:2286–2290
46. Mulazza E, Peregò R, Aarab H, Mihut L, Lefrant S, Faulques E, Wéry J (2004) Photoconductivity and optical properties in composites of poly(paraphenylene vinylene) and single-walled carbon nanotubes. Phys Rev B 70:155206
47. Baiabarac M, Ilie M, Baltog I, Lefrant S, Humbert B (2017) Infrared dichroism studies and anisotropic photoluminescence properties of poly(para-phenylene vinylene) functionalized reduced graphene oxide. RSC Adv 7:6931–6942
48. Nismy NA, Jayawarden KDG, Adikaari AADT, Silva SRP (2011) Photoluminescence quenching in carbon nanotube-polymer/fullerene films: carbon nanotubes as exciton dissociation centres in organic photovoltaics. Adv Mater 23:3796–3800
49. Khattab AF, Ahmad SM (2009) Studies on electrical conductivity of poly phenylene vinylene. Arab J Sci Eng 34:27–35
50. Jafari MJ, Liu J, Engquist I, Ederth T (2017) Time-resolved chemical mapping in light-emitting electrochemical cells. ACS Appl Mater Interfaces 9:2747–2757
51. Zhang C, Dabbs DM, Liu L-M, Aksay IA, Car R, Selloni A (2015) Combined effects of functional groups, lattice defects, and edges in the infrared spectra of graphene oxide. J Phys Chem C 119:18167–18176
52. McAllister MJ, Li J-L, Adamson DH et al (2007) Single sheet functionalized graphene by oxidation and thermal expansion of graphite. Chem Mater 19:4396–4404
53. Scheibe B, Borowiak-Palen E, Kalenczuk RJ (2010) Oxidation and reduction of multiwalled carbon nanotubes — preparation and characterization. Mater Charact 61:185–191
54. Mulazzi E, Ripamonti A, Wery J, Dulieu B, Lefrant S (1999) Theoretical and experimental investigation of absorption and Raman spectra of poly(paraphenylene vinylene). Phys Rev B 60:16519–16525
55. Murphy DW, Rosseinsky MJ, Haddon RC, Ramirez AP, Hebard AF, Tycko R, Fleming RM, Dabbagh G (1991) Superconductivity in alkali metal fullerenes. Phys C Supercond 185–189:403–408
56. Stobinski L, Lesiaik B, Malolepszy A, Mazurkiewicz M, Mierzwa B, Zemek J, Jiricek P, Bieloshapka I (2014) Graphene oxide and reduced graphene oxide studied by the XRD, TEM and electron spectroscopy methods. J Electron Spectrosc Relat Phenom 195:145–154
57. Suresh D, Nethravathi PC, Udayabhanu NH, Sharma SC (2015) Spinach assisted green reduction of graphene oxide and its antioxidant and dye absorption properties. Ceram Int 41:4810–4813
58. Wang Q, Wang Y, Meng Q, Wang T, Guo W, Wu G, You L (2017) Preparation of high antistatic HDPE/polyaniline encapsulated graphene nanoplatelet composites by solution blending. RSC Adv 7:2796–2803
59. Pedrosa MCG, Dutra Filho JC, Menezes LR de, Silva EO da (2020) Chemical surface modification and characterization of carbon nanostructures without shape damage. Mater Res23:e20190493
60. ALOthmanZA (2012) A review: fundamental aspects of silicate mesoporous materials. Mater 5:2874–2902
61. Breczko J, Grzeskiewicz B, Gradzka E, Bobrowska DM, Peres LO, Varela H, Garcia JR, Fernandes MR, Torresi RM, Nart FC, Gruber J (2001) On the electrochemical polymerization of poly(p-phenylene vinylene) and poly(o-phenylene vinylene). Synth Met 118:65–70
62. Xu K, Ding SP, Jow TR (1999) Nonaqueous electrolyte development for electrochemical capacitors. United States Department of Energy: DOE/ID/13451. https://doi.org/10.2172/15050
63. Voss KF, Foster CM, Smilowitz L, Mihailović D, Askari S, Srdanov G, Ni Z, Shi S, Heeger AJ, Wudl F (1991) Substitution effects on bipolarons in alkoxy derivatives of poly(1,4-phenylene-vinylene). Phys Rev B 43:5109–5118

64. Eckhardt H, Shacklette LW, Jen KY, Elsenbaumer RL (1989) The electronic and electrochemical properties of poly(phenylene vinylenes) and poly(thiénylene vinylenes): An experimental and theoretical study. J Chem Phys 91:1303–1315

65. Moses D, Wang J, Heeger AJ, Kirova N, Brazovski S (2001) Exciton binding energy in poly(phenylene vinylene). Synth Met 125:93–98

66. Shockley W, Queisser HJ (1961) Detailed balance limit of efficiency of p-n junction solar cells. J Appl Phys 32:510–519

67. Kroon R, Lenes M, Hummelen JC, Blom PWM, de Boer B (2008) Small bandgap polymers for organic solar cells (polymer material development in the last 5 years). Polym Rev 48:531–582

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