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Tailoring the properties of polyanilines/SiC nanocomposites by engineering monomer and chain substituents

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Abstract

Hybridization of nanomaterials constitutes an interesting approach to boost and develop novel properties and applications. In this work, different polyaniline (PANI)-derived polymer-SiC nanocomposites have been successfully synthesized by facile surface-initiated polymerization of aniline (ANI) and/or 4-Anisidine (4ANS) on HCl-functionalized SiC. The obtained materials were characterized by different analytical techniques as well as solubility, conductivity and electrochemical tests. The effect of the nature and combination of the substituents in the polymer was analyzed. XRD; thermogravimetry; and vibrational FTIR spectroscopy revealed effective polymerization and interaction between the polymers and the SiC nanoparticles to form PANI-SiC, poly(ANI-co-4ANS)-SiC and P4ANS-SiC nanocomposites. The presence of electron-donating (*para*) -OCH₃ substituents was found to hinder this interaction and/or to retard the polymerization, decreasing the content and crystallinity of the polymer in the nanocomposite. However, the dispersibility of the nanocomposites in different solvents greatly increased, and the electroactive and optical properties were affected. As a result, the poly(ANI-co-4ANS)-SiC nanocomposite exhibits higher dispersibility, lower band gap, similar conductivity and richer electroactivity than PANI-SiC, and an intermediate polymerization yield. Then, engineering the substituents of polymer chains is demonstrated to be an efficient approach to tailor the properties of (PANI)-derived polymer-SiC nanocomposites.

Keywords: Nanocomposites; polymer-SiC; Optical properties; Electrochemical properties.

1. Introduction

Organic-inorganic hybrid materials represent the natural interface between two worlds of chemistry each with very significant contributions to the field of materials science, and each with characteristic properties that result in diverse advantages and limitations. The main idea when developing hybrid materials is to take advantage of the best properties of each component that forms the hybrid, trying to decrease or eliminate their drawbacks getting in an ideal way a synergic effect; which results in the fabrication of hybrid materials with new properties for advanced energy transportation/storage [1-3].

SiC nanoparticles exhibit unique mechanical, thermal and optical properties for various applications [4, 5], due to its wide band gap, optical and electrical properties, SiC holds great potential for high-temperature, high-speed, high-power, surface acoustic wave (SAW) devices, and substrates for light emitters and radiationhard devices [6-9]. However, their low solubility and conductivity restrict their potential utilization in several fields [10]. SiC-based hybrid materials offer an attractive avenue to simultaneously harness the eminent properties of SiC. In this vein, SiC has been already combined with different conducting polymers (CPs), such as polypyrrole [11], polyaniline [12] and polythiophene [13]. polyaniline is particularly attractive, because of its versatile redox behavior, excellent chemical and electrochemical stability, large capacitance, and electrochromic properties [14, 15].

In this paper, we present the preparation and characterization of novel polymer-SiC nanocomposites by oxidative polymerization of aniline and/or 4-anisidine. The properties of the nanocomposites, morphology, thermal stability and electrical conductivity of the prepared materials were investigated using a number of different techniques.

2. Experimental

2.1. Materials

The monomers aniline (ANI) and 4-Anisidine (4ANS), silicon carbide (99%); ammonium persulfate (APS), N-methyl-2-pyrrolidone (NMP), ethanol, dimethyl sulfoxide (DMSO) and ammonia solution (NH_4OH) were all of analytical purity (Sigma-Aldrich) and used as received without further purification. Hydrochloric acid (Merck) was suprapur quality and all the solutions were freshly prepared with distilled-deionised water was obtained from an Elga Labwater Purelab Ultra system.

2.2. Chemical synthesis of hybrid materials

The samples of polymer-SiC nanocomposites were prepared by a surface initiated polymerization (SIP) method by adding 1 g of HCl-functionalized nanoparticles to 0.22 mol ANI and/or 4-ANS solution in 25 mL of HCl 0.1M with stirring for 1 hour. The functionalization of SiC with HCl was reported before [16-18], as illustrated in Fig. 1.

Next, for oxidative polymerization, an aqueous solution of APS (0.22 mol) was added drop wise maintained at ambient temperature, and the mixture was stirred for 24 hours. The precipitated polymer-SiC nanocomposites were collected on a filter paper and subsequently washed, first, with 1 M HCl, and ethanol till the filtrate became colorless; second, with water for three times; and finally, with NH_4OH . The precipitates were dried in air and then in vacuum at 60 °C prior characterizations [18-20]. Through this procedure, three different samples of polymer-SiC nanocomposites, named as PANI-SiC, poly(ANI-co-4ANS)-SiC and P4ANIS-SiC, were synthesized.

2.3. Physicochemical Characterization

The X-ray diffraction analysis of the powder nanocomposites was performed using a Bruker CCD-Apex equipment with a X-ray generator (Cu K_{α} and Ni filter) operated at 40 kV and 40 mA. Fourier transform infrared (FT-IR) spectra were recorded using a Bruker Alpha. Thermogravimetric analysis (TGA) was performed with a Du Pont thermogravimetric analyzer. In these assays, about 10 mg of sample was heated up to 900 °C at a heating rate of 25 °C/min under nitrogen.

2.4. Optical, dispersibility and conductivity measurements

A Hitachi U-3000 spectrophotometer was used for recording the UV-Vis spectra. The dispersibility of the polymer-SiC nanocomposites was tested in Acetone, DMSO, Chloroform and Toluidine. About 10 mg of the samples was added into 5 ml of each solvent and a picture of the system was taken after.

Electrical conductivity measurements were carried out by using a Lucas Lab resistivity equipment with four probes in-line. The samples were dried under vacuum for 24 h and shaped into pellets (0.013 m diameter) by using a FTIR mold and applying a pressure of 7.4×10^8 Pa

2.5. Electrochemical characterization

The electrochemical properties of the investigated samples were studied at room temperature using a potentiostat-galvanostat. A conventional one compartment three electrode electrochemical cell was used with a reversible hydrogen electrode (RHE) and a platinum wire as the reference and counter electrodes, respectively. For the fabrication of working electrodes, an amount of each nanocomposite was mixed with NMP solvent. Then, 10 μ L of the suspension was transferred onto a glassy carbon (GC) rod and the solvent was evaporated under an infrared lamp. After drying, a mechanically-stable thin layer of the samples remained on the

GC surface. The electrodes prepared by this method were transferred to the electrochemical cell containing 1M perchloric acid solution. The cyclic voltammetry (CV) was proceeded at a scan rate of 50 mV.s^{-1} with a potential window between -0.1 V and 1.0 V.

3. Results and discussion

3.1. X-ray diffraction (XRD) studies

The prepared HCl-functionalized SiC nanoparticles and PANI-SiC, poly(ANI-co-4ANS)-SiC and P4ANS-SiC nanocomposites were examined using X-ray diffraction (XRD) (Fig. 2). The SiC nanoparticles display several diffraction peaks at $2\theta = 34.05^\circ$, 35.67° , 38.19° , 41.42° , 45.27° , 54.66° , 59.91° , 65.57° , 71.73° and 73.32° . The position (2θ) and relative intensity of these peaks coincide, respectively, with those of the (101), (111), (103), (200), (220), (311), (220), (400), (311) and (222) crystallographic planes of the moissanite structure of SiC nanoparticles (JCPDS 00-027-14029) [18].

The same diffraction pattern of SiC dominated also in the case of all the synthesized nanocomposites. Apart from that, the magnification of these diffractograms between $2\theta = 15-30^\circ$ enabled to distinguish additional features. The PANI-SiC nanocomposite showed three characteristic peaks. The most intense, centered at $2\theta = 18.43^\circ$, is ascribed to the (100) reflection of PANI, regarding the parallel and perpendicular periodicity of its polymer chains [19, 20]. The diffraction peak centered at $2\theta = 26.31^\circ$ is ascribed to the (200) plane of the orthorhombic unit cell of PANI [20, 21]. Moreover, a less intense peak was discerned at $2\theta = 23.92^\circ$. This diffraction has been attributed to the (020) crystallographic planes of the partially crystallized PANI [22]. All these results indicate that the polymer in the PANI-SiC nanocomposite exhibits relatively high crystallinity.

On the other hand, the pattern of P4ANS-SiC displayed only one characteristic broader peak at $2\theta = 25.58^\circ$, which is assigned to the (200) crystallographic plane of polymer. Compared to PANI, this lower crystallinity may be explained by the present of (-OCH₃) substituents in the 4ANS monomer, leading to branched and irregular polymer chains difficult to ordered in crystalline-like periodic arrangements. Finally, the diffractogram of the poly(ANI-co-4ANS)-SiC nanocomposite was characterized by the features of both PANI and P4ANS. Thus, the intensity of the (100) PANI-reflection decreases, and the same seems to occur with the intensity of the (200) and (020) reflections, which overlap with the (111) reflection of P4ANS to form an asymmetric broad peak. These results confirm the formation of the polymers around the SiC nanoparticles.

The interplanar distance (d -spacing) and the mean crystallite size (D) of SiC crystalline domains in the pure nanoparticles and the nanocomposites were calculated by the using the Bragg's law (eq. 1) and the Debye-Scherrer formula (eq. 2), respectively:

$$d = \frac{\lambda}{2 \sin \theta} \quad (1)$$

$$D = \frac{k \cdot \lambda}{\beta \cdot \cos \theta} \quad (2)$$

where λ is the wavelength of incident X-ray radiation (0.15406 nm); k is the dimensionless shape factor (0.9); β is the full width at half the maximum intensity (FWHM) of the diffraction peaks (rad); and θ is the (Bragg) scattering angle.

The calculated data for the main intense nanocomposites (200) reflection in the different polymer-SiC and SiC (111) reflection in the nanoparticles are collected in Table 1. For the

PANI-SiC, poly(ANI-co-4ANS)-SiC, P4ANS-SiC nanocomposites and SiC nanoparticles, the average crystallite size was 8.3 nm, 4.9 nm, 4.8 nm and 41.7 nm, respectively.

3.2. FTIR Spectroscopy

The nature of the organic products formed after the oxidative polymerization process was studied by FTIR spectroscopy. Fig. 3. shows the FTIR spectra of the SiC nanoparticles and the synthesized composite materials. For SiC nanoparticles, the absorption bands at 799 cm^{-1} and 987 cm^{-1} can be attributed to the Si–C stretching of SiC, in addition, the bands at 1970 and 2024 cm^{-1} is due to Si-H stretching vibrations [23, 24], the band at 2159 cm^{-1} is due to SiH_2 stretching vibrations [25]. These bands are also observed to a lesser or greater extent in the spectra of the different nanocomposites. Particularly, the maximum of band at 987 cm^{-1} shifts to 982 for PANI-SiC sample, and further to 973 cm^{-1} for poly(ANI-co-4ANS)-SiC and P4ANS-SiC. This may be due to the emerge of the C–H out of plane band in the polymers at 982 cm^{-1} [26], which may overlap with that of the SiC. On the other hand, the relative intensity of the band at 799 cm^{-1} remarkably decreases in the composite materials, and mainly in the case of PANI-SiC. This suggests a higher covering of the SiC surface with the polymer.

Respect to the other bands, in the case of PANI-SiC several vibrational features can be observed. The bands at 1526 and 1452 cm^{-1} are characteristic of the C=C stretching of quinoid/benzenoid rings of PANI chains. The band at 1364 cm^{-1} corresponds to the C–N stretching of secondary amines, whereas that at 1196 cm^{-1} indicates the C–H in plane bending of quinoid rings; the intense bands at 2159 cm^{-1} are assigned to C=N stretching; and this at 1626 cm^{-1} may be due to aromatic ring (C=C), stretching vibrations [27]. The observance of all these bands would confirm the successful formation of PANI. Table 2. shows the band assignment of the FTIR spectra.

The same bands were observed for P4ANS-SiC and poly(ANI-co-4ANS)-SiC, although (compared to PANI-SiC) their relative intensity generally decreased, mainly in the former case. This is again in line with the lower amount of polymer observed in these samples. Nevertheless, some new bands appeared for these materials. For P4ANS-SiC, the absorption peak at 1633 cm^{-1} is characteristic of the electronic-like absorption of the $\text{N}=\text{Q}=\text{N}$ vibration that Q denotes the quinoid ring [28]. The peak at 1519 cm^{-1} is assigned to the benzenoid ring [29]. The absorption bands appear at 1267 and 1196 cm^{-1} , indicating the presence of a methoxy group on a benzene ring [15].

Finally, this results indicate that the efficiency of polymer formation/attachment onto the SiC nanoparticles significantly increases in the order: PANI-SiC > poly(ANI-co-4ANS)-SiC > P4ANIS-SiC.

A clear conclusion of this characterization is, then, that the presence of $-\text{OCH}_3$ substituents has a negative effect on the yield of these nanocomposites. On the other hand, it has been previously proposed that the formation of PPy-polymer/HCl-functionalized-ZrO nanocomposites may occur through $-\text{Zr}-\text{Cl}(\delta^-)-\text{N}(\delta^+)$ -like electrostatic interactions [18]. In this respect, the observed decrease in the positive formal charge in nitrogen atoms ($\text{C}(\text{Ar})-\text{N}^+$), caused by the presence of electron-donating (*para*) $-\text{OCH}_3$ substituents, may weaken the electrostatic interaction between these ammonium groups of the polymers and the $\text{Si}(\delta^+)\text{C}-\text{Cl}(\delta^-)$ nanoparticles (HCl-functionalized SiC nanoparticles).

3.3. Thermogravimetric analysis

Thermogravimetric analysis (TGA) was employed to assess the stability of the various nanocomposite samples (Fig. 4) The SiC nanoparticles experienced practically no weight loss

when heated up to 800 °C, demonstrating the high thermal stability of this compound. The results indicate that the initial mass loss of PANI at temperature ranges of 150-180°C is due to release of water and removal of solvent or dopant anions. Also, the weight loss occurring around 280-310°C is due to the decomposition of the PANI chains. The curve for P4ANS show that the weight losses are observed at the temperature above 260°C, these results also indicates that the starting decomposition temperature of the polymer depends of the monomer and structure chains. A comparison of the TGA graph of the copolymer with the TGA graph of the homopolymers shows that the weight loss pattern is similar to PANI and is a little stable.

The nanocomposites generally showed two main different thermal decomposition processes, which have been associated to (from lower to higher temperatures) (i) the liberation of water molecules; and (ii) the pyrolysis of the polymers [30]. For the PANI-SiC nanocomposite, the first step (25°C to 188°C) involved a weight loss of 2.36%, while the pyrolysis process (200°C to 650°C), entailed a weight loss of 31.95%. For the P4ANS-SiC nanocomposite, the pyrolysis started at considerably lower temperatures (at ca. 300°C), reflecting a lower thermal stability than PANI-SiC; and the weight losses associated to the release of H₂O and the polymer pyrolysis, 1.97% and 4.44%, respectively, were both remarkably lower than for PANI-SiC. For the poly(ANI-co-4ANS)-SiC nanocomposite, the release of water supposed a 3.05% weight loss and the pyrolysis started at even lower temperatures (ca. 180°C), involving a more complex process with various steps and a total weight loss of around 11.42% (up to 800°C) attributed desorption and vaporization of water [31].

The decrease in the onset temperature of the pyrolysis process, i.e. in thermal stability, in the order PANI-SiC > P4ANS-SiC > poly(ANI-co-4ANS)-SiC is associated a to an

increasing number of defects or heterogeneities in the polymer chains, by presence of (-OCH₃) groups and the random alternation of substituted with unsubstituted aromatic rings, and/or a lower crystallinity respect to that of PANI (Fig. 4). On the other hand, the remarkable variation (decrease) in the pyrolysis weight loss, in the order PANI-SiC > poly(ANI-co-4ANS)-SiC > P4ANS-SiC, is assigned to a decreasing amount of the polymer in these nanocomposites. In agreement with XRD and vibrational spectroscopies, this characterization confirms that the polymerization of aniline is much more effective than that of substituted units.

3.4. Optical properties

The UV-Vis absorption spectra of PANI-SiC, poly(ANI-co-4ANS)-SiC and P4ANS-SiC nanocomposites dissolved in DMSO are shown in Fig. 5. The absorption spectrum of PANI-SiC shows two characteristic bands with maxima at 381 and 577 nm, respectively. On the basis of the earlier studies on PANI, the first band is assigned to the π - π^* transition of the benzenoid ring and it is related to the extent of conjugation between the adjacent phenyl rings in the polymer chain [32]. The second absorption band is attributed to the quinoid ring transition (charge transfer from HOMO of the benzenoid ring to LUMO of the quinoid ring) [33]. This band is dependent on the overall oxidation state of the polymer [33].

On the other hand, the absorption spectrum of the SiC shows band at 390 nm and we observe in the case of P4ANS-SiC, the first band red shifts to 399 nm and the second one blue shifts to 528 nm. This may be due to the small amount of P4ANS formed onto SiC surface or the small interaction between aggregated SiC and P4ANS chain or an increase in the conjugated saturated bonds

For the poly(ANI-co-4ANS)-SiC nanocomposite, the π - π^* transitions of aromatic ring give an absorbance band at around 390 nm, whereas inter-band π - π^* transition of excitation in the aromatic ring demonstrates a band at 600 nm [34]. Both peaks show red shift of about 9 nm and 23 nm respectively, if compared to PANI-SiC spectra. A red shift usually occurs due to a change in π - π^* transitions and may be caused by the strong interaction between copolymer and SiC nanoparticles, as was reported in the case of the PANI-SnO₂ nanocomposite [35].

For further understanding the optical properties of the synthesized nanocomposites, the optical energy gap (E_g) was determined from the UV-vis spectra by using the Einstein formula (eq. 3) [36]:

$$E_g = \frac{h.c}{\lambda_{onset}} \quad (3)$$

where E_g is the band gap energy, h is Planck's constant, c is the speed of light (m.s⁻¹), and λ_{onset} is the onset value of the absorption spectrum for the second band in the long wavelength region (nm).

The observed λ_{onset} and calculated E_g values are collected in Table 3. It can be clearly observed, that the value of optical energy gap, which comes out to be 2.53 eV for PANI-SiC, has been found to decrease for poly(ANI-co-4ANS)-SiC at 2.49 eV and finally, attains a value of 2.59 eV for P4ANS-SiC.

From a physics point of view, when brought into contact with two semiconductors (p -type and n -type) may extracts some electrons from the valence band (HOMO) and adds some electrons to the conducting band (LUMO) of conducting polymer and thus increases its conductance [37]. The electronic structure of polymer then is modified by the interaction between SiC and polymer in the nanocomposite. In addition, such a reduction in the values

of optical energy gap may be explained in terms of the change in the structure of polymer due to the formation of some kinds of bonding between the SiC nanoparticles and polymer chains. This may, in turn, results in the formation of localized states between the HOMO and LUMO bands of nanocomposites, which modifies their extended electronic states, thus, contributing towards the formation of charge transfer complexes that are responsible for the feasibility of lower energy transitions leading to the observed change in optical energy gap [38].

3.5. Electrical conductivity of the polymer-SiC nanocomposites

The conductivity of PANI-SiC, poly(ANI-co-4ANS)-SiC and P4ANS-SiC nanocomposites was measured and compared (Table 3). It was found that the conductivity of PANI-SiC is higher than that P4ANS-SiC. This is assigned to (i) the higher content of conductive polymer in the PANI-SiC nanocomposite, as discussed in sections 3.1-3.3; and/or (ii) the presence of (-OCH₃) groups in para position in P4ANS, which may hinder the formation of linear polymer chains and/or crystalline domains, in agreement with XRD results (Fig. 2), thus, blocking the conductive pathway of P4ANS in the nanocomposite [15].

Interestingly, despite the lower polymer content and crystallinity, the copolymer poly(ANI-co-4ANS)-SiC nanocomposite shows quite similar conductivity than PANI-SiC. This is attributed to the presence of defects in the copolymer contributing to the delocalization of polarons [39].

3.6. Dispersibility of the polymer-SiC nanocomposites

The dispersibility of nanomaterials is very important for their handling and processing in different applications. Fig. 6. shows the aspect of the different nanocomposites in acetone,

DMSO, chloroform and toluidine. As indicated by the transparent color of the solvent and/or the two separated phases, the PANI-SiC nanocomposite (Fig. 6a) was not generally well-dispersed in the different solvents, showing only a poor dispersibility in chloroform. On the contrary, the poly(ANI-co-4ANS)-SiC and P4ANS-SiC nanocomposites (Fig. 6b and 6c) apparently well-dispersed in all the tested solvents. This good dispersibility is assigned to the presence of -OCH₃-substituents in the poly(ANI-co-4ANS) and P4ANS polymer rings, which can effectively interact with the polar organic solvents.

3.7. Electrochemical properties of the polymer-SiC nanocomposites

The voltammetric response of PANI-SiC, poly(ANI-co-4ANS)-SiC and P4ANS-SiC nanocomposites is shown in Fig. 7. In all cases, two broad electroactive redox couples are observed within the stability potential window of the polymers and electrolyte. For PANI/SiC, the maximums of the first redox pair (A_1/C_1) were found to be at 0.44/0.23 V (the peak-to-peak potential separation (ΔE_p) was 210 mV), whereas those of the second redox pair (A_2/C_2) were centered at 0.87/0.79 V ($\Delta E_p = 80$ mV). From the vast literature, the first process corresponds to the reversible transition between leucoemeraldine (reduced form of PANI) and emeraldine (half-oxidized form of the polymer) [40], whereas the second one is ascribed to reversible transition between emeraldine and pernigraniline (fully oxidized form of the PANI) [41].

In the case of P4ANS-SiC, these two peaks displayed some important changes: (i) the first couple (A'_1/C'_1) was found more asymmetric (with discernible coupled processes or humps before and after the maximums at 0.40/0.31 V), but more reversible ($\Delta E_p = 90$ mV) and slightly more intense; (ii) and the second pair (A'_2/C'_2) appeared at considerably lower potentials 0.74/0.64 V, showing lower reversibility ($\Delta E_p = 100$ mV) and intensity than for PANI/SiC.

Finally the copolymer poly(ANI-co-4ANS)/SiC presented a characteristic CV curve with electroactive processes generally showing higher intensity. Particularly, on the one hand, at least three contributions were easily distinguished in the first asymmetric broad process (A''_1/C''_1) at 0.18/0.12 V ($\Delta E_p = 60$ mV), at 0.35/0.29 V ($\Delta E_p = 50$ mV), and at 0.49/0.46 V ($\Delta E_p = 30$ mV), which were remarkably more reversible (lower ΔE_p values) than those of the homopolymer-SiC nanocomposites. The marked asymmetry is attributed to the more heterogeneous structure of the copolymer nanocomposite, showing different possible combinations of unsubstituted and -OCH₃-substituted rings, whereas the higher reversibility observed for this sample (at least for the leucoemeraldine-emeraldine processes) may be related to its higher conductivity (Table 3). On the other hand, the second process (A''_2/C''_2) appeared at approximately the same electrode potentials (at 0.72/0.62 V) and with similar reversibility ($\Delta E_p = 100$ mV) to the case of P4ANS-SiC. This finding suggests that the emeraldine-pernigraniline transition in the poly(ANI-co-4ANS)/SiC seems to be governed by the electroactivity of the -OCH₃-substituted rings.

All these results indicate that the poly(ANI-co-4ANS)/SiC nanocomposite exhibits a richer electroactivity, with additional (discernible) higher-intense and -reversible redox processes, than the homopolymer-SiC materials.

In addition, as one can see, poly(ANI-co-4ANS) show than the two homopolymer-SiC. We believe that this improvement could be attributed to the better electrochemical conductivity (see Table 3).

4. Conclusions

This study reports the synthesis of polymer-SiC nanocomposites (PANI-SiC, poly(ANI-co-4ANS)-SiC and P4ANS-SiC) based of aniline and/or 4-anisidine with silicon carbide (SiC HCl-functionalized) by in-situ oxidative polymerization method. This facilitates charge transfer processes between the two components and results in enhanced electronic properties. On the other hand, the use of SiC with monomers under the same polymerization conditions only results in the synthesis of inhomogeneous mixtures. The results of spectroscopic methods such as XRD, FTIR and TGA have demonstrated the successful polymerization of the monomers on the SiC nanoparticles. In addition, these techniques enable to discern effective interactions between the ammonium groups ($C-N^{+}<$) in polymers and the $Si(\delta^{+})C-Cl(\delta^{-})$ nanoparticles to form truly PANI-SiC, poly(ANI-co-4ANS)-SiC and P4ANS-SiC nanocomposites. Furthermore, these techniques have revealed that the efficiency of polymer formation/crystallization/attachment onto the SiC nanoparticles significantly increases in the order P4ANIS-SiC < poly(ANI-co-4ANS)-SiC < PANI-SiC, what has been reasonably explained by steric and/or charge effects of electron-donating (*para*) -OCH₃ substituents.

Optical, solubility, conductivity and electrochemical tests show that the presence of -OCH₃ substituents in the (PANI)-derived polymers remarkably affect the properties of the nanocomposites. By combining substituted and unsubstituted units in the co-polymer chains, the poly(ANI-co-4ANS)-SiC nanocomposite exhibits higher dispersibility, lower band gap, similar conductivity and richer electroactivity than PANI-SiC, and an intermediate polymerization yield.

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References

- [1] S. Repp, E. Harputlu, S. Gurgun, M. Castellano, N. Kremer, N. Pompe, J. Wörner, A. Hoffmann, R. Thomann, F.M. Emen, S. Weber, K. Ocakoglu, E. Erdem. Synergetic Effects of Fe^{3+} doped Spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$ Nanoparticles on Reduced Graphene Oxide for High Surface Electrode Hybrid Supercapacitors. *Nanoscale*. 10 (2018) 1877-1884.
- [2] R. Genc, M.O. Alas, E. Harputlu, S. Repp, N. Kremer, M. Castellano, S.G. Colak, K. Ocakoglu, E. Erdem. High-Capacitance Hybrid Supercapacitor Based on Multi-Colored Fluorescent Carbon-Dots. *Scientific Reports*. 7 (2017) 11222.
- [3] A. Kassiba, W. Bednarski, A. Pud, N. Errien, M.M. Janusik, L. Laskowski, M. Tabellout, S. Kodjikian, K. Fatyeyeva, N. Ogurtsov, Y. Noskov. Hybrid core-shell nanocomposites based on silicon carbide nanoparticles functionalized by conducting polyaniline: Electron paramagnetic resonance investigations. *J. Phys. Chem. C*. 111 (2007) 11544-11551.
- [4] E. Erdem, V. Mass, A. Gembus, A. Schulz, V.L. Kunzmann, C. Fasel, R. Riedelf, R.A. Eichel. Defect structure in lithium-doped polymer-derived SiCN ceramics characterized by Raman and electron paramagnetic resonance spectroscopy. *Phys. Chem. Chem. Phys.*, 11 (2009) 5628-5633
- [5] A. Peled, J.P. Lellouche. Preparation of a novel functional SiC-polythiophene nanocomposite of a core-shell morphology. *J. Mater. Chem*. 22 (2012) 2069-2073.

- [6] E. Kang, K. Neoh, K. Tan. Polyaniline: A polymer with many interesting intrinsic redox states. *Prog. Polym. Sci.* 23 (1998) 277-324.
- [7] C. Janaky, N.R. de Tacconi, W. Chanmanee, K. Rajeshwar. Electrodeposited polyaniline in a nanoporous WO₃ matrix: An organic/inorganic hybrid exhibiting both p-and n-type photoelectrochemical activity. *J. Phys. Chem. C.* 113 (2012) 4234-242.
- [8] G.F. Samu, K. Pencz, C. Janáky, K. Rajeshwar. On the electrochemical synthesis and charge storage properties of WO₃/polyaniline hybrid nanostructures. *J. Solid State Electrochem.* 19 (2015) 2741-2751.
- [9] S.A. Khan, E.A. de Vasconcelos, H. Uchida, T. Katsube. Gas response and modeling of NO-sensitive thin-Pt SiC schottky diodes. *Sensors Actuators B.* 92 (2003) 181-185.
- [10] E.A. de Vasconcelos, E.F.Jr. da Silva, T. Katsube, S. Yoshida, Y. Nishioka. X-Ray Radiation Response of Epitaxial and Non-epitaxial n-6H-SiC Metal-Oxide-Semiconductor Capacitors. *Japan. J. Appl. Phys.* 40 (2001) 2987-2990
- [11] M. Mičušík, M. Omastová, K. Boukerma, A. Albouy, M.M. Chehimi, M. Trchová, P. Fedorko. Preparation, surface chemistry, and electrical conductivity of novel silicon carbide/polypyrrole composites containing an anionic surfactant. *Polymer Engineering and Science.* 47 (2007) 1198-1206
- [12] J.F. Felix, E.A. de Vasconcelos, E.F.Jr. da Silva, W.M. Azevedo. Fabrication and electrical characterization of polyaniline/silicon carbide heterojunctions. *Journal of physics D: Applied physics.* 44 (2011) 205101-205105

- [13] A. Peled, J.P. Lellouche. Preparation of a novel functional SiC@polythiophene nanocomposite of a core-shell morphology. *Journal of Materials Chemistry*. 22 (2012) 2069-2073
- [14] N. Gospodinova, L. Terlemezyan. Conducting polymers prepared by oxidative polymerization: polyaniline. *Progress in Polymer Science*. 23 (1998) 1443-1484.
- [15] F. Chouli, I. Radja, E. Morallon, A. Benyoucef. A Novel Conducting Nanocomposite Obtained by p-Anisidine and Aniline With Titanium(IV) Oxide Nanoparticles: Synthesis, Characterization, and Electrochemical Properties. *Polymer Composites*. 38 (2017) 254-260.
- [16] S. Daikh, F.Z. Zeggai, A. Bellil, A. Benyoucef. Chemical polymerization, characterization and electrochemical studies of PANI/ZnO doped with hydrochloric acid and/or zinc chloride: Differences between the synthesized nanocomposites. *Journal of Physics and Chemistry of Solids*. 121 (2018) 78-84
- [17] A. Bekhoukh, A. Zehhaf, A. Benyoucef, S. Bousalem, M. Belbachir. Nanoparticles Mass Effect of ZnO on the Properties of Poly(4-Chloroaniline)/Zinc Oxide Nanocomposites. *Journal of Inorganic and Organometallic Polymers and Materials*. 27 (2017) 13-20.
- [18] H. Gu, H. Wei, J. Guo, N. Haldolaarachige, D.P. Young, S. Wei, Z. Guo. Hexavalent chromium synthesized polyaniline nanostructures: Magnetoresistance and electrochemical energy storage behaviors. *Polymer*. 54 (2013) 5974-5985.
- [19] A.R. Hopkins, R.A. Lipeles, S.J. Hwang. Morphology characterization of polyaniline nano- and microstructures. *Synth. Met.* 158 (2008) 594-601

- [20] Z. Zehang, Z. Xinxing, L. Canhui, L. Lidan, Y. Guiping. Polyaniline-decorated cellulose aerogel nanocomposite with strong interfacial adhesion and enhanced photocatalytic activity. *RSC Adv.*, 4 (2014) 8966-8972.
- [21] T.M. Wu, Y.W. Lin, C.S. Liao. Preparation and characterization of polyaniline/multi-walled carbon nanotube composites. *Carbon*. 43 (2005) 734-740.
- [22] Z.C. Feng, A.J. Mascarenhas, W.J. Choyke, J.A. Powell. Raman scattering studies of chemical vapor deposited cubic SiC films of (100)-Si. *J. Appl. Phys.* 64 (1998) 3176-3186.
- [23] C. Hu, Y. Qing, Y.L.N. Zhang. Preparation of poly(o-ethoxyaniline)-nano SiC composite and evaluation of its corrosion resistance properties. *Journal of Alloys and Compounds*. 717 (2017) 98-107
- [24] S. Chaudhari, P.P. Patil, Corrosion protective poly(o-ethoxyaniline) coatings on copper, *Electrochimica Acta* 53 (2007) 927-933.
- [25] W. Daves, A. Krauss, N. Behnel, V. Häublein, A. Bauer, L. Frey. Amorphous silicon carbide thin films (aSiC:H) deposited by plasma-enhanced chemical vapor deposition as protective coatings for harsh environment applications. *Thin Solid Films* 519 (2011) 5892-5898.
- [26] D. Kar. D. Das. Conducting wide band gap nc-Si/a-SiC:H films for window layers in nc-Si solar cells. *Journal of Materials Chemistry A*. 1 (2013) 14744-14753

- [27] Y. Xia. Electrical and optical polymer systems. Marcel Dekker, Inc., 1nd Ed., New York, USA (1998) pp. 339-386.
- [28] X.G. Li, L.X. Wang, M.R. Huang, Y.Q. Lu, M.F. Zhu. Synthesis and characterization of pyrrole and anisidine copolymers. *Polymer*. 42 (2001) 6095-6103.
- [29] F. Cataldo, P. Maltese. Synthesis of alkyl and Nalkyl-substituted polyanilines: a study on their spectral properties and thermal stability, *Eur Polym J*, 38 (2002) 1791-1803.
- [30] C.B. Hu, Y. Li, Y.Z. Kong, Y.S. Ding. Preparation of poly (otoluidine)/nano ZnO/epoxy composite coating and evaluation of its corrosion resistance properties. *Synthetic Metals*. 214 (2016) 62-70
- [31] W. Hu, S. Chen, Z. Yang, L. Liu, H. Wang. Flexible Electrically Conductive Nanocomposite Membrane Based on Bacterial Cellulose and Polyaniline. *J. Phys. Chem. B*. 115 (2011) 8453-8457.
- [32] P.S. Khiew, N.M. Huang, S. Radiman, M.S. Ahmad. Synthesis and characterization of conducting polyaniline-coated cadmium sulphide nanocomposites in reverse microemulsion. *Materials Letters*. 58 (2004) 516-521.
- [33] A.I. Kuestan. Synthesis and characterization of polyaniline and poly(aniline-co-o-nitroaniline) using vibrational spectroscopy. *Arabian Journal of Chemistry*. 10 (2017) S2668-S2674
- [34] B. Qiu, Z. Li, X. Wang, X. Li, J. Zhang. Exploration on the microwave-assisted synthesis and formation mechanism of polyaniline nanostructures synthesized in different

- hydrochloric acid concentrations. *Journal of polymer science, part A: Polymer chemistry*. 55 (2017) 3357-3369
- [35] M. Alam, A.A. Ansari, M.R. Shaik, N.M. Alandis. Optical and electrical conducting properties of Polyaniline/Tin oxide nanocomposite. *Arabian J. Chem.* 6 (2013) 341-345.
- [36] X. Sun, C. Bruckner, M.P. Nieh, Y. Lei. A fluorescent polymer film with self-assembled three-dimensionally ordered nanopores: preparation, characterization and its application for explosives detection. *J. Mater. Chem. A*. 2 (2014) 14613-14621.
- [37] D.N. Huyen, N.T. Tung, N.D. Thien, L.H. Thanh. Effect of TiO₂ on the Gas Sensing Features of TiO₂/PANi Nanocomposites. *Sensors* 11 (2011) 1924-1931.
- [38] S. Ebrahim, A.H. Kashyout, M. Soliman. Ac and Dc conductivities of polyaniline/poly vinyl formal blend films. *Current Applied Physics*. 9 (2009) 448-454.
- [39] R. Steyrleuthner, Y. Zhang, L. Zhang, F. Kraffert, B.P. Cherniawski, R. Bittl, A.L. Briseno, J.L. Bredas, J. Behrends. Impact of morphology on polaron delocalization in a semicrystalline conjugated polymer. *Phys.Chem.Chem.Phys.*, 19 (2017) 3627-
- [40] Y.G. Wang, H.Q. Li, Y.Y. Xia. Ordered Whisker-like Polyaniline Grown on the Surface of Mesoporous Carbon and Its Electrochemical Capacitance Performance. *Advanced Materials*. 18 (2006) 2619-2623.
- [41] C.C. Hu, C.H. Chu. Electrochemical and textural characterization of iridium-doped polyaniline films for electrochemical capacitors. *Materials Chemistry and Physics*. 65 (2000) 329-338.

Figure Captions

Fig. 1. Scheme of nanocomposites preparation and the general chemical structure of the polymer-SiC synthesized.

Fig. 2. XRD diffraction patterns of HCl-functionalized silicon carbide nanoparticles and nanocomposites (polyaniline-silicon carbide, poly(aniline-*co*-4-anisidine)-silicon carbide and poly(4-anisidine)-silicon carbide). Inlet: magnification of the spectra showing the diffraction peaks of the different samples polymers.

Fig. 3. FT-IR adsorption spectra of HCl-functionalized silicon carbide nanoparticles and nanocomposites (polyaniline-silicon carbide, poly(aniline-*co*-4-anisidine)-silicon carbide and poly(4-anisidine)-silicon carbide).

Fig. 4. Thermogravimetric analysis of HCl-functionalized silicon carbide nanoparticles and nanocomposites (polyaniline-silicon carbide, poly(aniline-*co*-4-anisidine)-silicon carbide and poly(4-anisidine)-silicon carbide) obtained in nitrogen atmosphere at with a heating rate of 10°C/min.

Fig. 5. UV-vis spectra of nanocomposites (polyaniline-silicon carbide, poly(aniline-*co*-4-anisidine)-silicon carbide and poly(4-anisidine)-silicon carbide) dispersed in DMSO.

Fig. 6. The photo images obtained after dispersing the nanocomposites: polyaniline-silicon carbide (a), poly(aniline-*co*-4-anisidine)-silicon carbide (b) and poly(4-anisidine)-silicon carbide (c) into the acetone, DMSO, chloroform and toluidine solvents.

Fig. 7. Steady-state cyclic voltammograms of nanocomposites (polyaniline-silicon carbide, poly(aniline-*co*-4-anisidine)-silicon carbide and poly(4-anisidine)-silicon carbide) in 1M HClO₄ solution. Scan rate 50 mV.s⁻¹.

Highlights

- New materials hybrid for PANI-derived on SiC has been studied.
- Adhesion of PANI-derived on SiC was followed by chemical oxidative in-situ.
- The materials hybrid was analyzed by XRD, TGA, Raman and FTIR.
- The nanocomposite is more thermal stability than the PANI-derived.
- Good electrochemical response has been observed for samples of PANI-derived/SiC.

P4ANS-SiC

(b)

poly(ANI-co-4ANS)-SiC

PANI-SiC

SiC

Samples in Acetone Solvent

Samples in DMSO solvent

Samples in Chloroform solvent

Samples in Toluidine Solvent

Table 1. Crystallite sizes of polymer-SiC and SiC nanoparticles.

Samples	Braggs angle	<i>d</i> -spacing (Å)	FWHM	Size (nm)
HCl-SiC nanoparticles	35.65 (±0.1)	2.51 (±0.01)	0.20 (±0.05)	41.7 (±0.2)
PANI-SiC	26.31 (±0.1)	3.38 (±0.01)	0.98 (±0.05)	48.3 (±0.2)
poly(ANI-co-4ANS)-SiC	25.68 (±0.1)	3.46 (±0.01)	1.66 (±0.05)	44.9 (±0.2)
P4ANS-SiC	25.58 (±0.1)	3.48 (±0.01)	1.68 (±0.05)	44.8 (±0.2)

Table 2. FTIR bands of SiC nanoparticle, PANI-SiC, poly(ANI-co-4ANS)-SiC and P4ANS-SiC nanocomposites.

Band Assignment	SiC/ cm ⁻¹	PANI-SiC/ cm ⁻¹	poly(ANI-co-4ANS)-SiC/ cm ⁻¹	P4ANS-SiC/ cm ⁻¹
C–H in plane bending	//	1196	1196	1196
C–H out of plane bending	//	982	973	973
C=C quinonoid ring	//	1530	1532	1633
C=C benzenoid ring	//	1454	1452	1558
C–N stretching of aromatic ring	//	1364	1377	1371
C=C=N Quinonoid	//	2159	2159	2160
–NH ₂ stretching	//	1626	1633	1634
–OCH ₃ groups	//	//	1270	1267
1,2,4 Trisubstituted benzene ring	//	1196	1196	1196
Si–C (LO)	799	799	791	797
Si–C (TO)	987	982	973	973

Table 3. The UV-vis absorption spectra properties (λ_1 , λ_2 and λ_{onset}) optical band gap energy (E_g) and electrical conductivity values of PANI-SiC, poly(ANI-co-4ANS)-SiC and P4ANS-SiC nanocomposites.

Samples	λ_1 (nm)	λ_2 (nm)	λ_{onset} (nm)	E_g (eV)	Conductivity (S.cm ⁻¹)
PANI-SiC	381	577	487	2.53	1.46
poly(ANI-co-4ANS)-SiC	390	600	500	2.47	1.47
P4ANS-SiC	399	528	480	2.59	0.82
PANI	335	625	750	1.66	2.24
poly(ANI-co-4ANS)	319	595	757	1.64	2.25
P4ANS	315	613	736	1.69	2.18
SiC	//	390	476	2.61	0.98