Influence of pH on the Specific Surface Area of Polyaniline Matrices

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ABSTRACT: We report the successful measurement of the specific surface area of chemically synthesized and treated polyaniline (PANI) and its composite PANI/silica (SiO₂). PANI was synthesized chemically from an aqueous solution of aniline and hydrochloric acid (HCl) in the presence of an oxidant, ammonium peroxydisulfate [(NH₄)₂S₂O₈]. In the synthesis of PANI/SiO₂, SiO₂ was incorporated from its colloidal solution contained in the solution for the polymerization of PANI. PANI and PANI/SiO₂ thus synthesized were pretreated with double-distilled water (pH = 6.95), aqueous HCl (pH = 1.09), and aqueous ammonia (pH = 10.15) solutions to control their pH levels. Surface morphologies of the treated PANI and PANI/SiO₂ matrices were investigated with scanning electron micro-

INTRODUCTION

Over the past decades, a great deal of information has been published about conducting polymers.¹ Scientific interest in polyaniline (PANI) originates from the fact that this conjugated polymer is unique among conducting polymers. Its electrical properties are reversibly controlled both by changes in the oxidation state of the main chain and by protonation of the imine nitrogen atoms.² Its excellent environmental and thermal stability and low cost make PANI an attractive material for applications in several areas such as rechargeable batteries, light-emitting diodes, antistatic packaging and coatings, photonics, and chemical and biochemical sensors.^{3–8}

Meanwhile, the synthesis and characterization of various polymer/inorganic oxide composite materials have also been reported in the literature.^{9–11} Of these, a composite made of PANI and silica (SiO₂) is worth mentioning. This composite can be successfully obtained by the surface-induced polymerization of aniline in the presence of colloidal SiO₂ in an

scopy. The successful incorporation of SiO₂ into the PANI/SiO₂ composite was confirmed by the characteristic infrared absorption band at 1096 cm⁻¹. The adsorption of methylene blue, which was found to follow the Langmuir isotherm, onto the prepared materials was probed to estimate the real surface area. The base-treated PANI matrix showed a higher surface area than the acidic and neutral ones. The incorporation of SiO₂ into the PANI matrix yielded a larger surface area. However, the treated PANI/SiO₂ showed the same trend as the treated PANI matrices. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 109: 1764–1771, 2008

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acidic medium. It is thought that the presence of SiO_2 in the polymeric component could develop a useful surface property (e.g., luminescence, effective surface area, or surface hardness) for the matrix.^{12–14}

Among the many studies concerning conducting polymers and their composites, only a few reports^{11,15-17} are available that deal with the surface phenomena of these materials. In our previous work,¹⁶ organic dyes were successfully removed by PANI matrices that were prepared at different protonation levels. The adsorption capacity of different matrices for dyes was found to differ, and this indicated dissimilar effective surface areas. This result made us interested in examining the surface area of these matrices.

It is known that the protonation level, that is, doping, can be used to progressively transform the morphology of PANI,¹⁸ and this protonation plays an important role in its final properties and may have a large impact on the possible applications. For some conjugated polymers, doping occurs via oxidationreduction reactions. For PANI, protonation is usually carried out by the exposure of the polymer to acidic substances. PANI can present multiple oxidation states and different degrees of protonation.¹⁹ The interconversion of different oxidation states of PANI is summarized in Scheme 1. As can be seen in Scheme 1, there are three stable insulating forms of PANI having three different oxidation states: fully

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Scheme 1 Interconversion of different forms of PANI depending on the variation of the pH of the solution.

reduced leucoemeraldine base, partially oxidized emeraldine base, and fully oxidized pernigraniline. Each oxidation state can exist in the protonated form after treatment with an acid.

In this work, PANI and PANI/SiO₂ were prepared chemically and pretreated with solutions of different pHs. An attempt was made to investigate the variation in the specific surface areas of PANI and PANI/SiO₂ matrices. The measurement of the specific surface area involved an adsorption process using dye methylene blue (MB) as an adsorbate. Meanwhile, the adsorption capacities of some dyestuff on clay materials have already been examined by other workers.²⁰ However, in this study, the adsorption of MB was performed onto polymeric matrices. MB, which is cationic in nature, was chosen in this study because of its known strong adsorption behavior onto different materials as well as PANI matrices with a monolayer Langmuir-type isotherm.^{16,21} The surface morphologies of the matrices were characterized with scanning electron microscopy (SEM) and infrared (IR) spectroscopy. Adsorption patterns of MB on different substrates were monitored with ultraviolet-visible (UV-vis) spectroscopy measurements, and the specific surface areas of the prepared matrices were determined with the Langmuir isotherm.

EXPERIMENTAL

Materials

Before use, aniline was distilled twice under a nitrogen atmosphere and stored in a bottle. The dye MB was obtained from Fluka (Poole, England). All other chemicals used in this work were purchased from E. Merck (Darmstadt, Germany). All aqueous solutions were prepared with double-distilled water.

Synthesis and pretreatment of PANI and PANI/SiO₂ matrices

On the basis of a previously reported work,²² PANI was prepared by the chemical oxidative polymerization of aniline with ammonium peroxydisulfate $[(NH_4)_2S_2O_8]$ as an oxidant in an aqueous solution of hydrochloric acid (HCl). In brief, 2.5 mL of aniline, 5.0 mL of concentrated HCl (32%), and 3.0 g of (NH₄)₂S₂O₈ were added to water in a beaker, the total volume of the mixture being maintained at 400 mL. The reaction mixture was turned into a deep blue polymeric sediment instantaneously. The content was left overnight for the completion of polymerization. The deep blue sediment was then filtered and washed several times. The obtained PANI was treated separately with aqueous solutions having pHs of 1.09, 6.95, and 10.15. The substrates were then dried initially in air, and this was followed by vacuum drying. The dried mass was ground and then sieved with 100-mesh sieves and was stored in a vacuum desiccator. The PANI matrices, treated with aqueous solutions of pHs 1.09, 6.95, and 10.15, are hereafter called acidic PANI, neutral PANI, and basic PANI, respectively.

The synthetic procedure for the preparation of PANI/SiO₂ composites was followed as described in detail elsewhere.¹¹ In this study, an aqueous colloidal suspension of SiO₂ was prepared by the addition of 2.0 g of SiO₂ powder (mesh size = 100) to water followed by beating of the mixture for 2 h. The

resultant dispersion was then allowed to settle for 2 h. During this span of time, bigger SiO_2 particles were found to settle at the bottom of the container. The smaller SiO₂ particles remained in the supernatant water as colloidal particles. The colloidal solution was then decanted and used for PANI/SiO₂ composite preparation. Aniline (2.5 mL), 5.0 mL of concentrated HCl (32%), and 3.0 g of (NH₄)₂S₂O₈ were added to 400 mL of the prepared aqueous suspension of colloidal SiO2. The polymerization was allowed to proceed overnight. The reaction mixture was then centrifuged for 30 min, and the resulting deep blue sediment was redispersed in water. The centrifugation-redispersion cycle was repeated three times to completely remove the free SiO₂ particles from the PANI/SiO₂ composite. The PANI/ SiO_2 composite was then treated with water (pH = 6.95), an acid (pH = 1.09), and a base (pH = 10.15) and was dried and sieved as described previously for the PANI matrix. The obtained matrices are termed hereafter acidic PANI/SiO₂, neutral PANI/ SiO₂, and basic PANI/SiO₂.

Characterization of PANI and PANI/SiO₂

The physical appearances of the synthesized and pretreated PANI matrices were noted. The surface morphologies of the PANI matrices thus prepared were examined with an XL 30 scanning electron microscope (Philips, Eindhoven, Holland). IR spectral analysis was performed with an IR spectrophotometer (IR-470, Shimadzu, Tokyo, Japan).

Adsorption of MB and determination of the specific surface area

The adsorption of cationic MB onto all PANI and PANI/SiO₂ composites was studied spectroscopically by the change in the concentration of the aqueous MB solutions with time. UV-vis spectral analysis of MB was performed with a UV-vis spectrophotometer (UV-1601 PC, Shimadzu). A stock solution of MB was made separately in double-distilled water (pH = 6.95), aqueous HCl (pH = 1.09), and aqueous NH_3 (pH = 10.15) solutions having concentrations of 2.02×10^{-4} M each. Intermediate MB solutions of 1×10^{-5} , 2×10^{-5} , 3×10^{-5} , 4×10^{-5} , 5×10^{-5} , 6×10^{-5} , and 7×10^{-5} *M* were prepared with the appropriate dilutions. The calibration curves of the concentration of MB versus the absorbance were determined for three solutions of pHs 1.09, 6.95, and 10.15, and the molar extinction coefficients were 0.110, 0.100, and 0.105, respectively.

The adsorption isotherm and specific surface area were determined as follows. Typically, a dried PANI sample was put in seven reaction vessels (0.133 g each). Each vessel was charged with a 100-mL MB solution of a desired concentration (1 \times 10⁻⁵, 2 \times 10⁻⁵, 3 \times 10⁻⁵, 4 \times 10⁻⁵, 5 \times 10⁻⁵, 6 \times 10⁻⁵, and 7×10^{-5} M). Immediately after the addition of the MB solution to the container, it was kept in a shaking device, and mild shaking was allowed. The bottles were taken from the shaker in turn after 15, 30, 60, 90, and 120 min. After the shaking, the solutions were pipetted out for UV-vis measurements. The absorbance of the clear solution containing unadsorbed MB was measured. In each case, the absorbance was converted to the corresponding concentration of MB with the calibration curve. This procedure was followed for three matrices of acidic PANI, neutral PANI, and basic PANI and three matrices of acidic PANI/SiO₂, neutral PANI/SiO₂, and basic PANI/ SiO_2 with MB solutions with pH values of 1.09, 6.95, and 10.15. The values of the concentration of MB measured at any time subtracted from the initial concentration of MB were considered the amounts of MB adsorbed onto the PANI matrices at the corresponding time.

RESULTS AND DISCUSSION

Preparation and doping of PANI

The prepared deep-blue PANI powders had slightly different colors after the treatment with HCl (blue) and aqueous NH_3 (greenish yellow). Scheme 1 shows that the emeraldine base and leucoemeraldine base forms of PANI can be converted into emeraldine and leucoemeraldine salts, respectively, by a treatment with an aqueous solution of HCl. These two forms can be regenerated by a treatment with an aqueous solution state (y = 0.5) contains equal numbers of alternating reduced and oxidized repeat units, which can be protonated by HCl to produce the corresponding salt. Such a degree of color change of the matrices can be attributed to the structural change after the treatment.

When aniline was oxidized in the presence of colloidal SiO₂, a colloidal PANI/SiO₂ composite was produced. The sample color faded from blue (acidic PANI) with the incorporation of white SiO₂. Through the chemical doping process of PANI, it is possible to systematically vary the electrical conductivity of this material from the insulating state to the conducting state. The electrically conductive forms of the polymeric materials are best described as *p*-type doped polymeric charge transfer salts.²³ In this synthesis,¹¹ the precipitating PANI is adsorbed as an insoluble, thin layer onto SiO₂ particles. This outer layer of PANI is nonsolvated and acts as a binder, effectively gluing the SiO₂ particles together. The conjugated polymer supports positive charges that are delocalized over relatively short segments of the backbone, for example, over three to four repeat-



Figure 1 Morphologies of PANI and PANI/SiO₂ composites by SEM: (a) acidic PANI, (b) neutral PANI, (c) basic PANI, and (d) acidic PANI/SiO₂ (magnification, $100\times$).

ing units for a highly doped polymer. Charge neutrality is maintained by a negatively charged counterion, which is usually derived from the electrolyte anion. This variation in charge on the surface of the polymer may cause differences in the adsorption process. Most colloidal SiO₂ has a negative surface charge.¹⁵ Because PANI chains are polycations,²⁴ the attractive electrostatic interaction may play a certain role in the formation of a stable PANI/SiO₂ composite.

SEM characterization of the treated PANI and PANI/SiO₂ matrices

Typical SEM micrographs of the samples are depicted in Figure 1, which clearly presents different morphologies with respect to the distribution, size, and shape of the particles of the prepared matrices. The acidic PANI consists of agglomerates stacked over the surface to make a big deposit [Fig. 1(a)]. When PANI is treated with double-distilled water (neutral PANI), the aggregates seem to exhibit a granular morphology [Fig. 1(b)] in which grains seem to be aggregated into a stonelike body and distributed nonuniformly over the substrate. The treatment of PANI with a basic solution (basic PANI) also appears to lead to a granular morphology [Fig. 1(c)], but the grains are collected into a coral-like body with sharp edges. The surface morphology of the acidic PANI/SiO₂ substrate [Fig. 1(d)] looks different from that of acidic PANI [cf. Fig. 1(a,d)] as well as basic and neutral PANI. In this case, powdery and small stonelike, granular particles are found. These granules may be SiO₂ particles embedded in the PANI matrix. Modification of the PANI surfaces has also been reported by various workers^{16,25,26} by the variation of the synthesis conditions, and similar morphological changes have been reported. Thus, this SEM observation clearly suggests that the PANI surface is modified by the postsynthesis acid and base treatments and by the incorporation of SiO₂. The presence of SiO₂ particles in PANI/SiO₂ was further evidenced by the IR study (discussed later). From the observed dissimilar morphological features of the acidic, basic, and neutral PANI and PANI/SiO₂ studied in this work, it can be expected that their surface behaviors with respect to adsorption and the specific surface area will be different.



Figure 2 IR spectra of (a) acidic PANI, (b) basic PANI, (c) neutral PANI, and (d) acidic PANI/SiO₂.

IR spectral analysis

The IR spectra of PANI and PANI/SiO₂ presented characteristic features of the samples. A typical IR spectrum for PANI/SiO₂ is shown in Figure 2. The principal absorptions are 3385 (vw), 3230 (vw), 3090 (vw), 2348 (m), 2180 (vw), 1991 (vw), 1896 (vw), 1761 (vw), 1696 (m), 1558 (vs), 1487 (vs), 1393 (s), 1296 (s), 1096 (vs), 876 (w), 821 (s), 707 (w), 630 (w), and 461 (s) cm^{-1} . This spectrum is essentially identical to that of bulk PANI reported elsewhere,^{27,28} except for the appearance of the peaks at 1096 and 461 cm^{-1} . The peak that appears at 1296 cm^{-1} for the acidic PANI sample is found for the basic PANI; on the contrary, for the neutral one, the intensity of the peak is reduced considerably. The absorption at 1296 cm⁻¹ has been reported to be strengthened by the acid treatment.²⁹ Therefore, the observed band can be attributed to the --NH group appearing in the skeleton of acidic PANI (Scheme 1). In addition, when the PANI/SiO₂ composite is prepared, three prominent and well-defined peaks appear around 1096 (asymmetric Si-O-Si stretching), 821 (symmetric Si-O-Si stretching), and 461 cm⁻¹ (Si-O-Si bending) that clearly confirm the presence of SiO₂ particles in the composite. Thus, the presence of SiO₂ in the PANI matrix may show different degrees of affinity for the adsorption of MB.

Adsorption study

Figure 3 shows the change in the absorbance of the spectrum of $6 \times 10^{-5} M$ MB (pH = 10.15) with time

soon after it is charged to the basic PANI matrix. Figure 3(a) presents the initial absorbance of MB before adsorption, whereas for the progress of adsorption at 15, 30, 60, 90, and 120 min, the corresponding absorption spectra are presented in Figure 3(b–f), respectively. As soon as the MB solution was charged to the adsorbents, a decrease in its absorbance started. The decrease in the absorbance of MB gradually reached a constant value with the lapse of time. Similar spectral studies with each concentration of MB (1×10^{-5} , 2×10^{-5} , 3×10^{-5} , 4×10^{-5} , 5×10^{-5} , 6×10^{-5} , and 7×10^{-5} *M*) gave the equilibrium time (~ 2 h) at which the portion of MB



Figure 3 UV–vis absorption spectra of an MB solution (a) before adsorption and (b–f) during the course of adsorption [(b) 15, (c) 30, (d) 60, (e) 90, and (f) 120 min].



Figure 4 Amount of MB adsorbed onto the treated PANI matrices versus the time. The initial concentration of MB before adsorption was $6 \times 10^{-5} M$.

adsorbed became saturated. This may indicate the saturation of MB onto the PANI matrix. To ensure complete adsorption onto each matrix, MB was allowed to be adsorbed onto the matrix for 2 h. The result shows that MB can be adsorbed efficiently onto the treated PANI matrices under the experimental conditions employed. The absorbance data for all the matrices were converted to concentrations as before with the calibration curve. The concentration at the saturation point is the equilibrium concentration of MB. These equilibrium concentration data were used to calculate the amount of MB adsorbed onto the PANI matrices as discussed previously. Figure 4 presents the amount of MB adsorbed (mg/g) versus time. Here, an MB solution having an initial concentration of $6 \times 10^{-5} M$ was used in each case. In all cases, the progress of MB adsorption was fast, and PANI was nearly saturated within 60 min. The adsorption isotherms thus obtained were found to follow the Langmuir isotherm¹⁶ (discussed later). The extent of adsorption seems to be different for different matrices. The cationic dve MB showed significant adsorption on the base-treated PANI and PANI/SiO₂. The effect of the solution pH provided the most dramatic evidence for the interaction of the PANI matrix and MB in the adsorption process. That the high pH conditions resulted in maximum attraction between PANI and MB may have been due to the net negative surface charge acquired by PANI¹⁶ and the positive charge on MB. At a solution of pH 1.09, the PANI matrix developed a net positive charge resulting in reduced attractive forces with the cationic MB followed by a reduced rate of adsorption of MB onto the PANI matrix. The negative surface charge of SiO_2 likely enhanced the attraction between PANI/SiO₂ and MB, and this might have influenced the adsorption behavior.

Similarly, curves of the amount of MB versus time were determined for all PANI matrices with seven different MB solutions $(1 \times 10^{-5}, 2 \times 10^{-5}, 3 \times 10^{-5}, 4 \times 10^{-5}, 5 \times 10^{-5}, 6 \times 10^{-5}, \text{ and } 7 \times 10^{-5}$ *M*). From that, the amount of MB adsorbed onto each matrix at the equilibrium time [x/m (mg/g)] was calculated. Finally, the plot of x/m versus the equilibrium concentration gave the monolayer capacity, which was obtained from the plateau region of each curve. The results are shown in Figure 5.

Determination of the specific surface area of the substrates

The specific surface areas of the various PANI substrates studied were determined with the monolayer capacity, which was obtained from the plateau of each curve of Figure 5. The equation used for the calculation is as follows³⁰:

$$S = (\chi_m/M) \times N \times A_m \times 10^{-20} \tag{1}$$

where χ_m is the monolayer capacity (g/g), *M* is the molecular mass of MB (355.89 g/mol), *N* is Avogadro's constant (6.023 × 10²³ mol⁻¹), A_m is the cross-sectional area of MB (130 Å²),³¹ and *S* is the specific surface area (m²/g).

With the relation shown in eq. (1), the areas of all PANI and PANI/SiO₂ matrices were estimated from the monolayer capacity, and the obtained results are tabulated in Table I. The surface area measurements showed higher areas for basic PANI (29 m²/g) than for acidic (15 m²/g) and neutral PANI (11 m²/g) substrates. On the other hand, the PANI/SiO₂ matrix showed rather more surface area (basic PANI/SiO₂, 33 m²/g; acidic PANI/SiO₂, 21 m²/g; and neutral



Figure 5 Amount of MB adsorbed onto the treated PANI matrices versus the equilibrium concentration.

Comparison of the Specific Surface Areas of PANI and PANI/SiO ₂ Matrices			
Substrate	Monolayer capacity (×10 ⁻³ g/g)	Specific surface area (m²/g)ª	Adsorption coefficient (×10 ⁵ L/mol)
Neutral PANI	4.95	11	0.490
Acidic PANI	6.95	15	0.502
Basic PANI	13.00	29	1.390
Neutral PANI/SiO ₂	8.00	18	0.980
Acidic PANI/SiO ₂	9.50	21	1.070
Basic PANI/SiO ₂	15.00	33	5.300

TABLE I

^a Cross-sectional area of MB = 130 Å².

 $PANI/SiO_2$, 18 m²/g) than all PANI matrices. The observed results directly reflect the presence of different active surfaces of different PANI or PANI/ SiO₂ matrices. On the contrary, the larger surface areas obtained in the case of PANI/SiO2 versus those of the corresponding PANI matrices can be ascribed to SiO₂ incorporated into PANI. This variation in the specific surface area is also supported by the consideration of the adsorption equilibrium of the MB dye onto the PANI and PANI/SiO₂ matrices [Scheme 2(a)]. To investigate the adsorption capacities of MB onto all PANI and PANI/SiO₂ matrices, the isotherms for the adsorption processes were studied. The adsorption data were analyzed with the following linearized equation¹⁶ for the Langmuir adsorption isotherms:

$$\frac{C_{\rm e}}{x/m} = \frac{1}{K_L k_L} + \frac{C_{\rm e}}{k_L} \tag{2}$$



Scheme 2 (a) Probable equilibrium and (b) adsorption orientation of MB onto the PANI matrix.

where C_e is the concentration of the dye (MB) after the adsorption equilibrium is attained on the PANI and PANI/SiO₂ matrices, x is the mass (g) of dye adsorbed onto *m* grams of substrate, k_L is the proportionality constant, and K_L is the adsorption coefficient (which should indicate the affinity of the dye to the adsorbents).^{16,32} From the results, it was found that the adsorption data of MB closely fit the Langmuir equation [eq. (2)].

 K_L was determined from the slopes and intercepts of the Langmuir plots of $C_e/(x/m)$ versus C_e (Fig. 6). For all the substrates, a linear nature (R^2 values were in the range of 0.93-0.95 for all the substrates) of the plots of $C_e/(x/m)$ versus C_e was observed. The K_L values thus predicted from the slope and intercept of each straight line are listed in Table I. For basic PANI and basic PANI/SiO₂, the K_L values were evaluated to be 1.39 \times 10^5 and 5.3 \times 10^5 L/mol, respectively, whereas its values were 0.50×10^5 , 0.49 \times 10⁵, 1.07 \times 10⁵, and 0.98 \times 10⁵ L/mol for acidic PANI, neutral PANI, acidic PANI/SiO₂, and neutral PANI/SiO₂, respectively. The values of K_L showed a trend (basic PANI and PANI/SiO₂ > acidic PANI



Figure 6 Langmuir plot of $C_e/(x/m)$ versus C_e for the evaluation of K_L .

and PANI/SiO₂ > neutral PANI and PANI/SiO₂) similar to that of the surface areas of the substrates investigated. Thus, the predicted K_L values clearly demonstrate that both the basic PANI and PANI/SiO₂ adsorbents have a considerably higher capacity to bind dye, which could be the result of the higher number of active sites for the adsorption in comparison with other PANI and PANI/SiO₂ matrices studied.

The observed trend of specific surface areas of PANI or PANI/SiO₂ matrices may be further understood by the consideration of the adsorption equilibrium and orientation of MB molecules on the polymer matrices. Scheme 2(a) shows the two possible equilibriums that can be established during the adsorption process of MB onto PANI matrices, one between the PANI matrix and MB (equilibrium constant K_L) and the other between the protonated and deprotonated MB (equilibrium constant K_a). In this study, the occurrence of protonation equilibrium of MB may not have been possible in the experimental pH range (1.09–10.15) because the pK_a value of MB³³ is very low (-0.258). Thus, the adsorption orientation of MB onto PANI matrices [Scheme 2(b)] would be the same and is assumed to be vertical because only one positive center of MB should be available for the adsorption. A similar argument for the adsorption orientation of MB containing a positive charge on the side $-N(CH_3)_2$ group²¹ was also made by Hahner et al.³⁴ From Scheme 1, it can be statistically calculated that when PANI is treated with a basic solution (i.e., basic PANI), four N-centers in the unit structure of PANI become electronrich, and through this, MB can be adsorbed (as shown in Scheme 2). This number is double that of acidic PANI (where two sites possess a positive charge). This analogy directly reflects the results of the surface areas of basic and acidic PANI (29 $m^2/g : 15 m^2/g = 2 : 1$). On the other hand, the incorporation of SiO₂, which has a negative surface charge, may provide more active sites for MB adsorption, and this may influence the higher surface area; for example, basic PANI/SiO₂ has a higher surface area (33 m²/g) than basic PANI (29 m²/g).

CONCLUSIONS

This study demonstrates that the pretreatment of PANI matrices results in excellent surface properties with respect to the specific surface area. The adsorption of MB was successfully employed to determine the specific surface area of PANI matrices. Surface modification of PANI can be achieved by a postsynthesis treatment with an acid and base. Surface modification by the incorporation of SiO₂ particles also leads to a significant increase in the surface area of PANI.

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