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► To cite this version:

H Kebiche, Fabienne Poncin-Epaillard, N Haddaoui, Dominique Debarnot. A route for the synthesis of polyaniline-based hybrid nanocomposites. *Journal of Materials Science*, 2020, 55 (14), pp.5782-5794. 10.1007/s10853-020-04406-y . hal-03015936

HAL Id: hal-03015936

<https://hal.science/hal-03015936>

Submitted on 20 Nov 2020

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A route for the synthesis of polyaniline-based hybrid nanocomposites

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J. Mat. Sci. **55**, 5782–5794 (2020)

Abstract

In this study, we present a new method of metal incorporation into polyaniline (PANI) nanostructures based on the use of palladium/tin colloidal solutions. This method allows controlling the size of metal particles inserted into the polymer matrix. The preparation of the PANI/Pd-Sn nanocomposites is done either with the *in-situ* method by addition of colloids during polymerization or with the *ex-situ* one by incorporation of colloids after polymerization. The results show that the *in-situ* addition of Pd/Sn colloids affects mainly the morphology of the nanostructures by increasing their surface area, whereas their *ex-situ* incorporation affects mainly the doping level of the nanostructures by increasing the concentration of positively charged nitrogen atoms in the polymer matrix. This work is supported by analysis techniques such as X-ray photoelectron spectroscopy, UV-Vis spectrometry and scanning electron microscopy.

Keywords: polyaniline nanostructures; polymer/metal nanocomposites; palladium/tin colloidal solution.

1. Introduction

Conducting polymer-metal nanocomposites are a new class of materials that combine mechanical, optical and electrical properties of conducting polymers with magnetic properties and high electrical conductivity of metallic inclusions. They offer new performance, which makes them particularly interesting for several applications such as electronics [1], sensors [2,3], photovoltaic cells [4], memory devices [5], protective coatings against corrosion [6] and supercapacitors [7]. Muraviev *et al.* [8] have shown that incorporating metals in conducting polymers enhances electron transfer through a direct or mediated mechanism with improved conductivity and enhanced stability. Moreover, better performance for the detection of reducing gases such as NH_3 , H_2 and CO is proved by Torsi *et al.* and Inoue *et al.* [9,10] using polypyrrole and poly-3-methylthiophene doped with copper and palladium inclusions. Polyaniline (PANI) is one of the most widely used conducting polymers due to its easy synthesis, low cost and also to its specific doping process via protonation or oxidation.

The methods reported in the literature for the preparation of polyaniline/palladium nanocomposites consist of adding a metallic salt either during the polymer synthesis or after its synthesis [11-19]. Athawale *et al.* [3,11] have incorporated the metallic salt ($\text{PdCl}_2 \cdot 5\text{H}_2\text{O}$) during the polymerization where aniline monomer acts as stabilizer for the Pd nanoparticles, prepared by thermal reflux and γ -irradiation methods. Other methods have treated polyaniline and its derivatives in their emeraldine base [12-19] or protonated forms [19], with a Pd salt (PdCl_2) in an aqueous acidic medium. Drelinkiewicz *et al.* [13,14], Hasik *et al.* [15,19] and Dhaoui *et al.* [16] showed that in highly acidic media (1 or 2 M HCl), PANI [13-16] and its derivatives [15,19] undergo a protonation with both HCl and H_2PdCl_4 with the incorporation of Pd(II) chloro-complexes acting as counter-ions [17,18]. However, in low acidic media (around 10^{-3} M HCl), some Pd^{2+} ions are reduced to Pd^0 with oxidation of PANI backbone which leads to a lower doping level [13].

In this work, the insertion of palladium nanoparticles in the PANI nanostructures is realized during (*in-situ* method) or after (*ex-situ* method) the polymerization thanks to an original method using a colloidal suspension of Pd/Sn [20]. The PANI nanostructures are synthesized by the rapid mixing oxidation method [21]. The advantage of the colloidal suspension is the ability to control the size of Pd nanoparticles by varying their synthesis parameters. The colloidal solution consists of a suspension of nanoparticles where each nanoparticle is composed of a nucleus covered by a stabilizing layer of tin. Debarnot *et al.* [20] suggested that the nucleus is formed by a mixture of palladium and tin.

The objectives of this study are to describe the chemical and the morphological structures of the nanocomposites elaborated by the two methods (*in-situ* or *ex-situ* one), and also to determine the mechanisms of interaction between the colloidal particles and the PANI nanostructures.

2. Experimental

2.1. Materials

Aniline monomer (Aldrich, 99.5%) was distilled under vacuum prior to use, ammonium persulfate (APS) ((NH₄)₂S₂O₈ Sigma-Aldrich, 98%) and all other reagents purchased from Aldrich were used as received without further purification.

2.2. Elaboration and deposition of polyaniline nanostructures

The polyaniline nanostructures have been synthesized by the rapid mixing polymerization method.

In a typical synthesis, 0.46 g (0.1 mol.L⁻¹) of aniline was dissolved in 50 mL of 1 mol.L⁻¹ HCl aqueous solutions. 1.16 g of APS, corresponding to an oxidant-to-monomer mole ratio

equals to 1, was also dissolved in 50 mL of 1 mol.L⁻¹ aqueous hydrochloric acid solution. These two solutions were then kept at a temperature of 4-5°C for 30 minutes.

The substrates (Si/SiO₂ wafer or glass) were introduced in the monomer solution. APS solution was then added rapidly, under a vigorous dynamic stirring. After about 30 minutes of reaction, uniform thin layers of PANI nanostructures were obtained on the surface of the substrates. They were then rinsed with distilled water, dried under air flow and immersed in 1 mol.L⁻¹ HCl solution for 10 minutes then dried under air flow at room temperature.

2.3. Preparation of Pd/Sn colloidal solutions

The colloidal solutions were prepared by mixing two aqueous hydrochlorhydric solutions of PdCl₂ and SnCl₂ (1.06 g.L⁻¹ PdCl₂; 4.25 g.L⁻¹ SnCl₂, 2H₂O; 0.34 L.L⁻¹ HCl 37%) at a given temperature T . In this work, two temperatures T have been studied: 25°C and 40°C. In this step, the formed nucleus of the colloidal particle grew during a time t_g (1 h or 6 h) at each temperature T . When the reaction time is higher than t_g , the nucleus growth was stopped by the addition of an excess of a SnCl₂ solution (575 g.L⁻¹ SnCl₂, 2H₂O; 0.5 L.L⁻¹ HCl 37%), which stabilizes the solution. Therefore, the colloidal solution consists of a suspension of nanoparticles where each nanoparticle is composed of the nucleus covered by a stabilizing layer of tin. The colloidal solutions were freshly prepared and stored in the dark, at around 4°C and under nitrogen atmosphere.

The colloidal solution prepared at $t_g = 1$ h and $T = 25^\circ\text{C}$ is so-called solution A; the one prepared at $t_g = 6$ h and $T = 25^\circ\text{C}$ is so-called solution B and finally the solution elaborated at $t_g = 1$ h and $T = 40^\circ\text{C}$ is so-called solution C. The solution prepared at $t_g = 6$ h and $T = 40^\circ\text{C}$ is not studied here due to its low stability leading to a rapid precipitation of the colloids.

2.4. Elaboration of polyaniline/Pd-Sn nanocomposites

The nanocomposites have been elaborated by two methods. One of them, called the *in-situ* method, consists of adding 9 mL of the colloidal solution into the polymerization reaction during polyaniline synthesis at room temperature. Concerning the *ex-situ* method, after ANI polymerization, the thin layers of PANI nanostructures were introduced into the colloidal solution for 10 minutes at room temperature.

Whatever the method, the next step consisted of rinsing the films with deionised water and drying them under air flow. Then, the films were immersed into 1 M HCl aqueous solution during 5 min in order to remove the tin layer. The films were again rinsed with deionised water and dried under air flow.

2.5. Characterization of PANI/Pd-Sn nanocomposites

The layers have been analyzed by different characterization techniques like Ultraviolet-Visible (UV-vis), X-ray photoelectron (XPS) spectroscopies and scanning electron microscopy (SEM) in order to characterize the chemical and morphological structure of the layer.

UV-vis spectra of thin films, deposited onto glass substrates, have been recorded using Cary 100 spectrophotometer (Varian). Windows-based Cary software was used for data acquisition and analysis.

The chemical nature of the layers deposited onto Si/SiO₂ wafers was also determined by XPS using ESCA LHS 12 instrument (Leybold) at the Laboratoire de Physique des Couches Minces (Institut des Matériaux de Nantes, France). The photoemission was excited by a monochromatic Mg K α beam at 1253.6 eV. The spectra were taken with the electron emission angle at 90° relative to the sample surface, yielding a maximum sampling depth around 10 nm due to the mean free path of the electrons. Calibration was conducted on the C 1s peak of the C–C and C–H bonds at 285 eV. The binding energy error was 0.1 eV. The

curve fitting was performed using CasaXPS software (Casa Software Ltd.). The peak shape was chosen with Gaussian (70%) / Lorentzian (30%) curve fitting. The elemental quantification accuracy was 5%.

The morphology of the nanocomposites was obtained using a XL30-FEG (field emission gun) SEM microscope (Philips).

3. Results and Discussion

3.1. Study of Pd/Sn colloidal solutions

Figure 1 shows UV-Vis spectra of PdCl₂ and SnCl₂ solutions prepared in strongly HCl acidic medium, before (Figure 1a and 1b respectively) and after (Figure 1c) their mixing to prepare the colloidal solution.

The PdCl₂ solution shows an absorption maximum at 475 nm, a wide band at about 220-290 nm and a last one at 300-310 nm. The two first bands are attributed to Pd²⁺ ions whereas the last one is assigned to different ionic palladium complexes that may co-exist in the PdCl₂ acidic solution [3,13,15,22-24]. In particular, Hasik *et al.* [13,15] have studied the effect of HCl concentration on the formation of ionic palladium complexes in PdCl₂/HCl solutions. They have shown that in a strong acid medium (1-2 M), the concentration of anionic complexes ([PdCl₄]²⁻, [PdCl₃(H₂O)]⁻) increases, but in a weakly acid environment (~10⁻³ M), neutral and positively charged complexes ([PdCl₂(H₂O)₂] and [PdCl(H₂O)₃]⁺) predominate.

The SnCl₂/HCl solution presents a single absorption band centered at a wavelength lower than 280 nm that corresponds to Sn²⁺ ions.

For the preparation of colloids, the above two solutions are mixed during the chosen time t_g at the temperature T .

The UV-visible analysis of the mixed solution (Figure 1c) shows that the band at 475 nm decreases in intensity and is shifted to lower wavelengths whereas the broad band at 220 - 290 nm disappears. This result indicates the reduction of palladium ions (Pd²⁺) to their metallic state (Pd⁰) ($E^0(\text{Pd}^{2+}/\text{Pd}) = 0.99 \text{ V}$) by Sn²⁺ ions ($E^0(\text{Sn}^{4+}/\text{Sn}^{2+}) = 0.14 \text{ V}$), leading to the formation of the nucleus of the nanoparticle according to the following reaction [20]:

This is confirmed by the appearance of shoulders at 330-355 nm attributed to Pd⁰ absorption [11,25]. The intensity of these bands increases with t_g and T indicating the rise of the nucleus

size with that of t_g and T . Indeed, by referring to the results obtained by Froment *et al.* [16], the average nucleus size when the mixed solution is prepared at 25°C ($t_g = 1$ h) is evaluated at around 1 nm, and that obtained when the mixed solution is fabricated at 40°C ($t_g = 1$ h) is evaluated at around 3 nm. Furthermore, Gaikwad *et al.* [25] also observed broad shoulders at 370-390 nm assigned to Pd^0 where the mean size of palladium nanoparticles has been estimated at 3 nm. In the case of Athawale *et al.* [11] who studied the elaboration of palladium nanoparticles by thermal reflux and γ -irradiation methods, metallic palladium shows UV-Vis absorption bands at about 320 and 317 nm, with an average size of about 24 nm and 28 nm respectively.

Finally, Figure 1c shows the presence of absorption bands situated between 291 and 303 nm. They indicate the presence of ionic complexes of Pd and Sn in the colloids.

3.2. Study of PANI / Pd-Sn nanocomposites elaborated by the *in-situ* method

Chemical structure of the nanocomposites

The XPS wide scan (not shown here) of HCl-doped PANI nanostructures shows the presence of carbon, nitrogen and chlorine, whereas the nanocomposites present in addition, palladium and tin. The elemental composition of PANI nanostructures and PANI/Pd-Sn nanocomposites prepared with the different colloidal solutions is presented in Table 1.

According to Table 1, the amount of Pd and Sn in the nanocomposites is low, independently of the synthesis conditions of colloidal solutions. It may be due to the addition of a low amount of colloidal solution in the reaction medium.

Table 1. Elemental composition of PANI nanostructures and PANI/Pd-Sn nanocomposites (XPS data).

Element (relative %)	C	N	Cl	Pd	Sn
PANI nanostructure	84.1±4.2	11.2±0.6	4.7±0.2	-	-
PANI/Pd-Sn nanocomposite <i>Solution A</i>	82.9±4.1	12.1±0.6	4.7±0.2	0.20±0.01	0.10±0.01
PANI/Pd-Sn nanocomposite <i>Solution B</i>	83.8±4.2	12.1±0.6	3.9±0.2	0.10±0.01	0.10±0.01
PANI/Pd-Sn nanocomposite <i>Solution C</i>	85.2±4.3	9.9±0.5	4.6±0.2	0.30±0.01	0

Figure 2 presents the N 1s XPS core-level spectra of PANI nanostructures and nanocomposites. The N 1s spectra can be decomposed into four components at 397.9 eV attributed to imines ($-N=$), at 399.2 eV assigned to amines ($-NH-$), at 400.7 eV and 402.3 eV due to positively charged nitrogen ($-NH^{+}-$ and $-NH^{+}=$). Most authors [26,27] attribute the component at 400.7 eV to oxidized amine ($-NH^{+}-$) and the other one at 402.3 eV to protonated imine ($-NH^{+}=$) since the doping occurs either through the protonation of imines or the oxidation of amines. The positively charged nitrogen allows then evaluating the doping level of the polymer.

Table 2 summarizes the binding energy and percentage of each N 1s component determined from Figure 2.

Figure 2. N 1s XPS core-level spectra of (a) PANI nanostructures, (b, c, d) PANI/Pd-Sn nanocomposites elaborated with colloids prepared at (b) $t_g = 1$ h, $T = 25^\circ\text{C}$, or (c) $t_g = 6$ h, $T = 25^\circ\text{C}$, or (d) $t_g = 1$ h, $T = 40^\circ\text{C}$.

Table 2. Binding energy and percentage of each N 1s component of PANI nanostructures and PANI/Pd-Sn nanocomposites (XPS data).

	-N=		-NH-		-NH ⁺⁺ - and -NH ⁺ =					-NH-/-N=
	Position (eV)	%	Position (eV)	%	Position (eV)	%	Position (eV)	%	Total (%)	
PANI nanostructure	397.9	14.2	399.15	58.65	400.7	20	402.3	7.2	27.2	4.1

PANI/Pd-Sn nanocomposite <i>Solution A</i>	398.5	11.9	399.8	61	401.3	19.6	402.9	7.5	27.1	5.1
PANI/Pd-Sn nanocomposite <i>Solution B</i>	398.4	11.4	399.85	61.15	401.3	18.95	402.95	8.5	27.45	5.35
PANI/Pd-Sn nanocomposite <i>Solution C</i>	398.7	14.85	399.85	64.15	401.4	15.2	402.95	5.8	21	4.3

After addition of Pd-Sn colloids in PANI nanostructures, no significant differences appear in the chemical structure of the composites. The doping level remains constant except for the composite synthesized with colloidal solution C where the amount of positively charged nitrogen decreases slightly. Moreover, for composites prepared from colloidal solutions A and B, the imine proportion decreases whereas that of amine increases. It means that PANI goes to its reduced form after addition of colloids. This result shows the redox reaction of the imines of the polymer ($E^0(-N=/-NH- = 0.7 - 0.75 \text{ V [28]}$) with Sn^{2+} ions ($E^0(\text{Sn}^{4+}/\text{Sn}^{2+}) = 0.14 \text{ V}$). This reaction is not possible for nanocomposites prepared at $T = 40^\circ\text{C}$ since no tin is detected (Table 1).

Morphological structure of the nanocomposites

Figure 3. SEM micrographs of (a) PANI nanostructures and (b) *in-situ* PANI/Pd-Sn nanocomposites.

As reported in our previous work [21], the morphology of the PANI nanostructures obtained by the rapid mixing oxidation method (Figure 3a) corresponds to a cauliflower-like structure with two levels of topography: nanoparticles with dimensions of about 200-300 nm, and on these particles, a divided surface. As seen on figure 3b, the morphology of PANI nanostructures seems to be affected by the *in-situ* addition of colloids. The diameter of the nanostructures is more important and can reach 500 to 600 nm. The surface seems to be more divided leading then to an important developed surface area.

3.3. Study of PANI / Pd-Sn nanocomposites elaborated by the *ex-situ* method

Chemical structure of the nanocomposites

Figure 4 presents the elemental composition of PANI nanostructures and PANI/Pd-Sn nanocomposites elaborated by the *ex-situ* method with the different colloidal solutions and determined by XPS.

Figure 4. Elemental composition of PANI nanostructures and PANI/Pd-Sn nanocomposites (XPS data).

When the composites are elaborated with colloidal solutions B or C, the amount of Cl, Pd and Sn is high compared to composites elaborated by the *in-situ* method. Therefore, this method allows the incorporation of a higher amount of metallic particles. These results show the presence of both Pd and Sn in the nucleus of the colloidal particle. However, the proportion of Sn in the nucleus, compared to Pd, decreases when the nucleus size increases as shown by the Sn/Pd ratio. Furthermore, the concentration of adsorbed Pd and Sn is higher when t_g and T are high in accordance with bigger average nucleus size observed with the rise of t_g and T (see §3.1).

Figure 4 shows also the increase of Cl/N ratio in the nanocomposites with the raise of the growth time (t_g) or the temperature (T) chosen for the colloids' synthesis. This increase is due, in part, to anionic complexes ($[\text{PdCl}_4]^{2-}$, $[\text{PdCl}_3(\text{H}_2\text{O})]^-$) that predominate in strong acidic medium (1 M).

Figure 5 shows the N 1s XPS core-level spectra of PANI nanocomposites synthesized by the *ex-situ* method. Table 3 gives the binding energy and percentage of each N 1s component determined from Figure 5.

Table 3. Binding energy and percentage of each N 1s component of PANI nanostructures and PANI / Pd-Sn nanocomposites (XPS data).

	–N=		–NH–		–NH ⁺⁺ – and –NH ⁺ –					N ⁺ /N=	N ⁺ /NH–
	Position (eV)	%	Position (eV)	%	Position (eV)	%	Position (eV)	%	Total (%)		
PANI nanostructure	397.9	14.2	399.2	58.7	400.7	20	402.3	7.2	27.2	1.9	0.5

PANI/Pd-Sn nanocomposite <i>Solution A</i>	397.9	6.1	399.5	65.7	400.9	20.7	402.4	7.6	28.3	4.6	0.4
PANI/Pd-Sn nanocomposite <i>Solution B</i>	–	–	399.6	54.2	401	28.1	402.5	17.8	45.9	-	0.85
PANI/Pd-Sn nanocomposite <i>Solution C</i>	–	–	399.4	49.5	400.6	39	402.1	11.6	50.7	-	1.02

After *ex-situ* addition of colloids, the amount of imine groups decreases for solution A and goes to zero for solutions B and C. With these latter, the amount of amines decreases also. In the same time, the doping level rises, especially with the two last solutions where the doping occurs on both imine and amine groups. These results prove that palladium and Sn act as dopants by oxidation of the amines to give $-\text{NH}^{+*}-$ and protonation of the imines leading to $-\text{NH}^+=$. The protonation can occur thanks to the molecules of the anionic complexes: H_2PdCl_4 or $\text{HPdCl}_3(\text{H}_2\text{O})$ [13-16,19]. The doping by protonation is then not only due to HCl but can also be induced by the anionic complexes of Pd.

It seems that the doping occurs preferentially on the imine groups and then continues on the amine sites when imines groups are completely depleted.

Concerning the **morphological structure** of the nanocomposites, no change is observed compared to PANI nanostructures.

3.4. Mechanism of interaction of colloidal particles with PANI nanostructures

In order to understand the mechanism of interaction between the colloids and PANI chains, the nanocomposites elaborated by the *in-situ* and *ex-situ* methods are analyzed by UV-Vis spectroscopy (Figure 6).

Figure 6. UV-Vis spectra of (a) PANI nanostructures, *in-situ* and *ex-situ* PANI/Pd-Sn nanocomposites prepared at $t_g = 6$ h and $T = 25^\circ\text{C}$, and (b) PANI nanostructures and *ex-situ* PANI/Pd-Sn nanocomposite prepared at $t_g = 1$ h and $T = 40^\circ\text{C}$.

Polyaniline doped with HCl is characterized by three absorption bands. The one at 360 nm is attributed to the benzene ring system; the two other ones at 420 and 850 nm are assigned to polaron- π^* and π -polaron transitions respectively [21,29-32].

The presence of *ex-situ* deposited colloids on PANI leads to a shift of the π - π^* transition to a lower wavelength with an increase in its intensity. This shift indicates a possible interaction between ionic palladium and nitrogen atoms by protonation, oxidation or complexation. The increase in intensity shows the presence of metallic Pd. These spectra present also a shift of the π -polaron transition to a higher wavelength and a small shoulder centered at 300 nm. The red shift of the π -polaron transition to around 870 nm may be due to the increase of the degree

of delocalization of charge carriers, thus increasing the doping level. The presence of the shoulder at about 300 nm indicates the presence of palladium anionic complexes.

In the case of *in-situ* addition of colloids, no significant change in the UV-Vis spectrum is observed compared to the PANI nanostructures. The *in-situ* addition of the colloids does not seem to affect the doping level.

Figure 7 shows the Pd 3d and Sn 3d core-level XPS spectra of the PANI nanostructures *ex-situ* treated with colloids.

Figure 7. Pd 3d and Sn 3d core-level XPS spectra of PANI/Pd-Sn nanocomposites *ex-situ* prepared with (a) solution A, (b) solution B and (c) solution C.

Each of the Pd and Sn spectra presents a doublet corresponding to 3d_{5/2} and 3d_{3/2} with a binding energy difference of about 5.3 eV for Pd 3d and 8.5 eV for Sn 3d [33].

Each Pd spectrum ((a), (b) and (c)) can be fitted with three spin-orbit-split doublets. The doublet with the Pd 3d_{5/2} peak lying at around 336 eV is attributed to Pd(0), the one at around 337 eV is assigned to Pd(II) [20,33,34] and the last one at about 338.5 eV is due to the formation of coordination bonds between palladium ions and chlorine atoms to form the anionic complexes [33] but also with nitrogen atoms of the polymer chain [13,35]. Indeed, the complexation of silver and copper ions with PANI has also been reported to form PANI-Ag⁺ [36] and PANI-Cu²⁺ [37] systems.

The composites containing colloids prepared at $t_g = 1$ h and $T = 25^\circ\text{C}$ present a low level of doping since the quantity of adsorbed colloids is low (Cf. Figure 4, % of Pd and Sn).

The Sn 3d_{5/2} spectra (a) and (b) can be decomposed only into one peak at about 487 eV assigned to its ionic states, Sn⁴⁺ as a result of the reduction of Pd²⁺ to its metallic state, and Sn²⁺ coming from the SnCl₂ salt dissolved in HCl, and used in excess in the stabilization step

of colloids. The Sn 3d_{5/2} spectrum (c) presents an additional component at 485.5 eV attributed to metallic tin Sn(0).

Concerning the *in-situ* addition of colloids (Figure 8), all Pd and Sn XPS spectra of composites (except Figure 8c), show three components: a metallic one, an ionic one and a coordination one. The Sn coordination component can be explained by the complexation reactions either between PANI and SnCl₄, known as a Lewis acid [38], or between Sn²⁺ and chlorine atoms to form SnCl₃⁻ ions.

Figure 8. Pd 3d and Sn 3d core-level XPS spectra of PANI/Pd-Sn nanocomposites *in-situ* prepared with (a) solution A, (b) solution B and (c) solution C.

This study has thus shown the participation of colloids in the doping process. In the following, we propose different doping mechanisms of PANI/colloids nanocomposites elaborated either by the *in-situ* or by the *ex-situ* method.

1. Acidic doping with Brönsted acids by protonation of the imines with HCl, H_2PdCl_4 , $\text{HPdCl}_3(\text{H}_2\text{O})$ or HSnCl_3 according to the following mechanisms:

2. Doping by oxidation of the amines with Pd ions (Pd^{2+}) or Sn ions (Sn^{2+} and Sn^{4+}):

The doping with Pd^{2+} is favoured since the difference in standard potentials between PANI ($E^0(-\overset{+}{\text{N}}\text{H—}/-\text{NH—}) < -1 \text{ V}$ [39]) and palladium ($E^0(\text{Pd}^{2+}/\text{Pd}) = 0.99 \text{ V}$) is higher than that with tin ($E^0(\text{Sn}^{4+}/\text{Sn}^{2+}) = 0.14 \text{ V}$ and $E^0(\text{Sn}^{2+}/\text{Sn}) = -0.14 \text{ V}$).

3. Imines acidic doping with Lewis acids (SnCl_4 and PdCl_2) to form acid-base complexes:

4. Amines acidic doping with Lewis acids (SnCl_4 and PdCl_2) to form acid-base complexes:

It has also been shown in the literature that polyaniline could be transformed to its conductive form using Lewis acids as dopants such as SnCl_4 [38] or BF_3 [40].

4. Conclusion

This work described a novel route to elaborate polymer / metal nanocomposites. The metallic nanoparticles have been introduced in the matrix from a Pd/Sn colloidal solution *via* two ways: the *in-situ* one where the monomer and the colloids are mixed and the *ex-situ* one where the colloids are added after polymerization.

The *in-situ* addition of colloids affects mainly the morphology of the nanocomposites with a rise of the surface area compared to PANI nanostructures. Concerning the *ex-situ* method, it influences the doping level of the polymer leading to a higher quantity of positively charged nitrogen. We proposed different doping mechanisms involving the protonation, the oxidation and the complexation of imine and amine groups by palladium and tin salts and complexes. This increase in the doping level is not observed with the *in-situ* method certainly due to the lower quantity of colloids introduced in the nanocomposites as proved by XPS analyses. The morphology of PANI nanostructures seems to remain unmodified after the *ex-situ* addition of colloids.

The amount of colloids adsorbed on the surface of PANI thin films, depends greatly on the elaboration conditions of the colloidal solutions.

Conflict of Interest

The authors declare that they have no conflict of interest.

References

- [1] Z. Peng, L. Guo, Z. Zhang, B. Tesche, T. Wilke, D. Ogermann, S. Hu, K. Kleinermanns, Micelle-assisted one-pot synthesis of water-soluble polyaniline-gold composite particles, *Langmuir* 22 (2006) 10915-10918.
- [2] Y. Xian, Y. Hu, F. Liu, Y. Xian, H. Wang, L. Jin, Glucose biosensor based on Au nanoparticles-conductive polyaniline nanocomposite, *Biosens. Bioelectron.* 21 (2006) 1996-2000.
- [3] A. Athawale, S.V. Bhagwat, P.P. Katre, Nanocomposite Pd-polyaniline as a selective methanol sensor, *Sensor. Actuat. B-Chem.* 114 (2006) 263-267.
- [4] R.J. Tseng, J. Huang, J. Ouyang, R.B. Kaner, Y. Yang, Polyaniline nanofiber/gold nanoparticle nonvolatile memory, *Nano. Lett.* 5 (2005) 1077-1080
- [5] M.A. Malik, M.T. Galkowski, H. Bala, B. Grzybowska, P.J. Kulesza, Evaluation of polyaniline films containing traces of dispersed platinum for protection of stainless steel against corrosion, *Electrochim. Acta* 44 (1999) 2157-2163.
- [6] C.C. Hu, E. Chen, J.Y. Lin, Capacitive and textural characteristics of polyaniline-platinum composite films, *Electrochim. Acta* 47 (2002) 2741-2749.
- [7] T. Amaya, D. Saio, T. Hirao, Template synthesis of polyaniline/Pd nanoparticle and its catalytic application, *Tetrahedron Lett.* 48 (2007) 2729-2732.
- [8] D. N. Muraviev, J. Macanàs, M. Farre, M. Munoz, S. Alegret, Novel routes for inter-matrix synthesis and characterization of polymer stabilized metal nanoparticles for molecular recognition devices, *Sensor. Actuat. B-Chem.* 118 (2006) 408-417.
- [9] L. Torsi, M. Pezzuto, P. Siciliano, R. Rella, L. Sabatini, L. Valli, P.G. Zambonin, Conducting polymers doped with metallic inclusions: New materials for gas sensors, *Sensor. Actuat. B-Chem.* 48 (1998) 362-367.

- [10] M.E. Inoue, K.W. Nebesny, Q. Fernando, M.M. Castillo-Ortega, M. Inoue, Complexation of electroconducting polypyrrole with copper, *Synth. Met.* 38 (1990) 205-212.
- [11] A.A. Athawale, S.V. Bhagwat, P.P. Katre, A.J. Chandwadkar, P. Karandikar, Aniline as a stabilizer for metal nanoparticles, *Mater. Lett.* 57 (2003) 3889-3894.
- [12] J. G. Wang, K. G. Neoh, E. T. Kang, Preparation of nanosized metallic particles in polyaniline, *J. Colloid Interface Sci.* 239 (2001) 78-86.
- [13] A. Drelinkiewicz, M. Hasik, M. Choczynski, Preparation and properties of polyaniline containing palladium, *Mater. Res. Bull.* 33(5) (1998) 739-762.
- [14] A. Drelinkiewicz, M. Hasik, S. Quillard, C. Paluszkiewicz, Infrared and Raman studies of palladium-nitrogen-containing polymers interactions, *J. Mol. Struct.* 511-512 (1999) 205-215.
- [15] M. Hasik, A. Drelinkiewicz, E. Wenda, C. Paluszkiewicz, S. Quillard, FTIR spectroscopic investigations of polyaniline derivatives-palladium systems, *J. Mol. Struct.* 596 (2001) 89-99.
- [16] W. Dhaoui, M. Hasik, D. Djurado, A. Bernasik, A. Pron, Redox behaviour of polyaniline-palladium catalytic system in the presence of formic acid, *Synth. Met.* 160 (2010) 2546-2551.
- [17] O.P. Dimitriev, Doping of polyaniline by transition-metal salts, *Macromolecules* 37 (2004) 3388-3395.
- [18] O.P. Dimitriev, Interaction of polyaniline and transition metal salts: formation of macromolecular complexes, *Polym. Bull.* 50 (2003) 83-90.
- [19] M. Hasik, E. Wenda, A. Bernasik, K. Kowalski, J.W. Sobczak, E. Sobczak, E. Bielanska, Poly(*o*-toluidine) as the matrix for incorporation of palladium species from PdCl₂ aqueous solutions, *Polymer* 44(2003) 7809-7819.

- [20] D. Nicolas-Debarnot, M. Pascu, C. Vasile, F. P-Epaillard, Influence of the polymer pre-treatment before its electroless metallization, *Surf. Coat. Tech.* 200 (2006) 4257-4265.
- [21] H. Kebiche, D. Debarnot, A. Merzouki, F. Poncin-Epaillard, N. Haddaoui, Relationship between ammonia sensing properties of polyaniline nanostructures and their deposition and synthesis methods, *Anal. Chim. Acta* 737 (2012) 64-71.
- [22] L. Rasmusen, Chr.K. Jorgensen, Palladium (II) complexes: spectra and formation constants of ammonia and ethylènediamine complexes, *Acta Chem. Scand.* 22 (1968) 2313-2323.
- [23] F. Bozon-Verduras, A. Omar, J. Escard, and B. Pontvianne, Chemical state and reactivity of supported palladium: I. Characterization by XPS and UV-visible spectroscopy, *J. Catal.* 53 (1978) 126-134.
- [24] G.R. Tauszik, A. Marzi, and R. Covini, Electronic reflectance spectra of palladium-on-alumina catalysts, *React. Kinet. Catal. Lett.* 7 (1977) 7-14.
- [25] A.V. Gaikwad, G. Rothenberg, In-situ UV-visible study of Pd nanocluster formation in solution, *Phys. Chem. Chem. Phys.* 8 (2006) 3669-3675.
- [26] S. Golczak, A. Kanciurzevska, M. Fahlman, K. Langer, J.J. Langer, Comparative XPS surface study of polyaniline thin films, *Solid State Ionics* 179 (2008) 2234-2239.
- [27] B. Sreedhar, M. Sairam, D.K. Chattopadhyay, P.P. Mitra, D.V. Mohan Rao, Thermal and XPS studies on polyaniline salts prepared by inverted emulsion polymerization, *J. Appl. Polym. Sci.* 101 (2006) 499-508.
- [28] P. Xu, X. Han, B. Zhang, Y. Du, H.L. Wang, Multifunctional polymer-metal nanocomposites via direct chemical reduction by conjugated polymers. *Chem. Soc. Rev.* 43 (2014) 1349-1360.

- [29] Y. Xia, J.M. Wiesinger, A.G. MacDiarmid, Camphorsulfonic acid fully doped polyaniline emeraldine salt: conformations in different solvents studied by an ultraviolet/visible/near-infrared spectroscopic method, *Chem. Mater.* 7 (1995) 443-445.
- [30] X. Li, X. Li, G. Wang, Fibrillar polyaniline/diatomite composite synthesized by one-step in situ polymerisation method, *Appl. Surf. Sci.* 249 (2005) 266-270.
- [31] P.L.B. Araujo, E.S. Araujo, R.F.S. Santos, A.P.L. Pacheco, Synthesis and morphological characterization of PMMA/Polyaniline nanofiber composites, *Microelectr. J.* 36 (2005) 1055-1057.
- [32] S.E. Moulton, P.C. Innis, L.A.P. Kane-Maguire, O. Ngamna, G.G. Wallace, Polymerisation and characterisation of conducting polyaniline nanoparticle dispersions, *Curr. Appl. Phys.* 4 (2004) 402-406.
- [33] J.F. Moulder, W.F. Stickle, P.E. Sobot, K.D. Bomben, *Handbook of X-ray Photoelectron Spectroscopy*, Physical Electronics Inc., New York (1995).
- [34] J.G. Wang, K.G. Neoh, E.T. Kang, Polyaniline-palladium composite coatings for metallization of polyethylene substrate, *Appl. Surf. Sci.* 218 (2003) 231-244.
- [35] W.J. Dressick, C.S. Dulcey, J.H. Georger, G.S. Calabrese, J.M. Calvert, Covalent binding of Pd catalysts to ligating self-assembled monolayer films for selective electroless metal deposition, *J. Electrochem. Soc.* 141 (1994) 210-220.
- [36] A.Q. Zhang, C.Q. Cui, J.Y. Lee, and F.C. Loh, *J. Electrochem. Soc.* 142 (1995) 1098.
- [37] M. Higuchi, D. Imoda, and T. Hirao, Redox Behavior of Polyaniline-Transition Metal Complexes in Solution, *Macromolecules* 29(1996) 8277-8279.
- [38] I. Kulszewicz-Bajer, A. Pron, J. Abramowicz, C. Jeandey, J-L Oddou, J.W. Sobczak, Lewis acid doped polyaniline: preparation and spectroscopic characterization, *Chem. Mater.* 11 (1999) 552-556.

- [39] A. Mansour, F. Poncin-Epaillard, D. Debarnot, Affinity and distribution of silver nanoparticles within plasma polymer matrices, *J. Mater. Sci.* 54 (2019) 12972-12987.
- [40] D. Chaudhuri, A. Kumar, I. Rudra, D. D. Sarma, Synthesis and spectroscopic characterization of highly conducting BF_3 -doped polyaniline, *Adv. Mater.* 13 (2001) 1548-1551.