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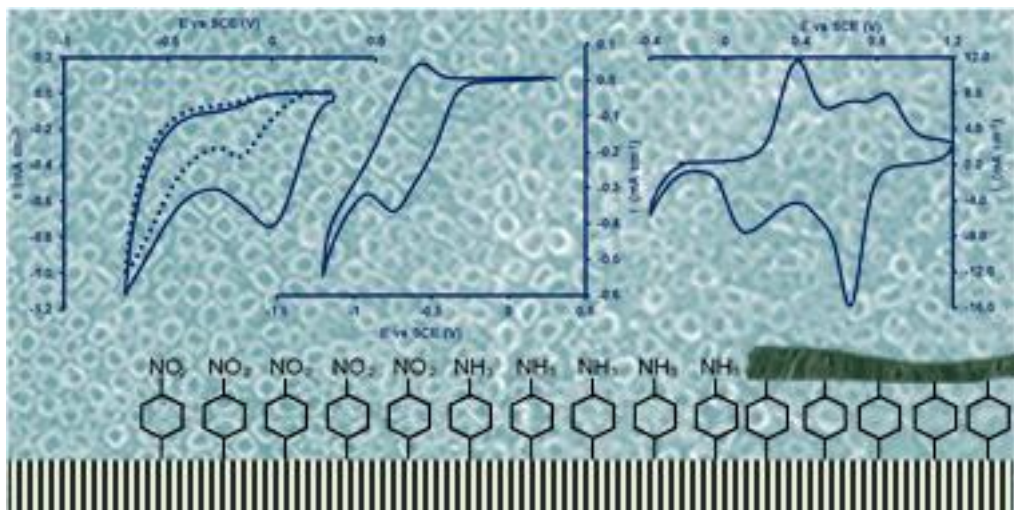
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Analysis of photocurrent and capacitance at TiO<sub>2</sub> nanotubes/polyaniline hybrid composites synthetized through electroreduction of aryldiazonium salt

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Research highlight

TiO<sub>2</sub> nanotubes/polyaniline hybrid composites were synthetized using an aminophenyl under-layer electrochemically grafted on TiO<sub>2</sub> obtaining improvements in photocurrent and capacitance.

Analysis of photocurrent and capacitance at TiO<sub>2</sub> nanotubes/polyaniline hybrid composites  
synthetized through electroreduction of aryldiazonium salt

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**Abstract:**

TiO<sub>2</sub> nanotubes/polyaniline hybrid composites were synthetized by a multi-steps electrochemical procedure as follows: 1) electrochemical oxidation of Ti foils to obtain TiO<sub>2</sub> ordered nanotubular electrodes, 2) functionalization of TiO<sub>2</sub> by electroreduction of 4-nitrobenzendiazonium salt, 3) electrochemical reduction of the nitro group to amine, 4) galvanostatic electropolymerization of aniline onto the surface of the aminophenyl-modified TiO<sub>2</sub> electrode.

Samples were also prepared by direct electropolymerization of PANI on TiO<sub>2</sub> nanostructures without the deposition of 4-nitrobenzendiazonium as under-layer. Different times of the electropolymerization step were applied. The composite materials were morphologically and electrochemically characterized by scanning electron microscopy, cyclic voltammetry and electrochemical impedance analysis. The improvement of the most relevant properties of the PANI/TiO<sub>2</sub> composites for their applications as photocatalysts and as supercapacitors was checked.

**1. Introduction**

TiO<sub>2</sub> is a n-type semiconducting material with very interesting properties for being used in many different applications. Among these properties, it should be noted its chemical stability, high photocatalytic activity, nontoxicity, low cost, availability, good mechanical flexibility and conductivity.<sup>1</sup> It has potential applications in many fields, such as lightweight battery electrodes, electromagnetic shielding devices, anticorrosion coatings and sensors.<sup>2,3</sup> In the recent years, its application in photocatalytic treatments and as supercapacitor basic material has also been

proposed.<sup>4-7</sup> However, several drawbacks can limit its use for these emerging applications. In the first place, the wide band gap energy of TiO<sub>2</sub> ( $E_g = 3.2$  eV) limits it to absorb the visible light ( $\lambda > 380$  nm). In the second place, the reported specific capacitances of TiO<sub>2</sub> are significantly smaller than those obtained from other metal oxides, such as MnO<sub>2</sub> and RuO<sub>2</sub>, generally used as supercapacitors: values of  $100 - 911 \mu\text{F}\cdot\text{cm}^{-2}$  were indicated for TiO<sub>2</sub> nanotubes arrays.<sup>4-7</sup> The relatively small specific capacitance was attributed to the poor electrochemical activity and poor electrical conductivity of TiO<sub>2</sub>.<sup>8,9</sup>

Conducting polymers, such as polyaniline, polypyrrole, polythiophene and their derivatives have been often proposed as suitable materials to enhance the performances of the electrode materials.<sup>10-12</sup> Higher conductivity, fast electrochemical switching and high specific capacitance values as well as environmental stability may be conferred to the final structure by the presence of the polymer.<sup>13</sup> A very recent work, on the use of polypyrrole, reported that its nanostructure may greatly influence the properties and overall functionality for its possible application.<sup>14</sup>

In the same way, the use of PANI as conducting polymer for electrodes and supercapacitors is very attractive because its good characteristics such as low cost, simple synthesis, high environmental stability, good electrical conductivity, good electronic and optical properties and reversible control of conductivity by charge-transfer doping and protonation.<sup>15-18</sup> Due to its delocalized conjugated structures in electron-transfer processes, PANI can be used as a photosensitizer of TiO<sub>2</sub> to remarkably improve the efficiency of photocatalytic activity under visible light.<sup>1,19</sup> The redox reversible processes associated to doping and undoping of counterions accompany charge storage in PANI giving rise to a pseudocapacitance; this contribution has to be added to a double-layer capacitance due to the separation of charges which takes place at PANI/electrolyte interface.<sup>20</sup> The theoretical specific capacitance of PANI, which is a combination of pseudocapacitance and electrical double-layer capacitance, has been estimated as  $2.0 \cdot 10^3 \text{ F g}^{-1}$ .<sup>21</sup>

However, when the electropolymerization is intended for coating of surfaces, weak adhesion between the organic layer and the substrate of different nature can occur: as it was reported in the literature, the lack of strong interfacial bonding may result in the collapse of the hybrid nanostructures.<sup>22</sup> Other authors reported that, despite the very high capacitance ( $3407 \text{ F g}^{-1}$ ) measured at ordered PANI nanorods on ITO substrate, low stability was obtained during repeated cycles, due to poor electrical connectivity between the nanorods and the smooth surface of ITO substrate.<sup>23</sup> This poor cyclability has become a major obstacle for PANI to be used in supercapacitors.

In this context, the present work considers the synthesis of hybrid TiO<sub>2</sub> electrodes and investigates on the possibility to stabilize the PANI deposition on them, by means of a preliminary surface

functionalization through the electrochemical reduction of 4-nitrobenzediazonium salt. Actually, the electrochemical reduction of diazonium derivatives is an elegant and versatile technique for surface functionalization, which was first reported in 1992 by Delamar et al.<sup>24</sup> The mechanism of attachment was described as a generation of aryl radicals and subsequent formation of covalent bonds between the surface and the aryl groups.<sup>25, 26</sup> This approach has several advantages including ease surface modification, wide potential window for subsequent electrochemistry and high stability under long term storage in air.<sup>27-29</sup> By tuning the experimental conditions, it is possible to control the surface coverage and the density of the resulting film, yielding submonolayer to multilayer films.<sup>26-30</sup> The electrodeposition of PANI using an under-layer obtained by electroreduction of aryl diazonium has been proposed in the literature to modify carbon nanotubes,<sup>31</sup> glassy carbon electrodes,<sup>32</sup> and gold:<sup>33</sup> the PANI composites obtained with this technique showed an higher chemical stability, a more uniform layer and high values of capacitance.

In the present work, the electrodeposition of PANI using aminophenyl moieties as under-layer is proposed to modify TiO<sub>2</sub> nanotubular structured electrodes obtained by electrochemical anodization of Ti foils. A first layer of nitrophenyl moieties was grafted on titania nanotubes by the electrochemical reduction of 4-nitrobenzediazonium salts; nitro-groups was then electroreduced to amino-groups. Finally, PANI was electropolymerised at modified electrodes. As a comparison, PANI was also electropolymerized on bare TiO<sub>2</sub> nanotubes. The electrodes were characterized by scanning electronic microscopies, cyclic voltammetries, electrochemical impedance spectroscopies and charge-discharge tests to evaluate their performances with particular regard to the enhancing in photocurrent and capacitance.

## 2. Experimental

### 2.1 Chemicals

Ammonium fluoride was purchased from Fluka; 4-nitrobenzediazonium tetrafluoroborate and tetrabutylammonium hexafluorophosphate (TBAPF<sub>6</sub>) were purchased from Sigma-Aldrich. Aniline was freshly distilled and stored in the dark. Alcohols and the other solvents were purchased in refined grade at Carlo Erba or Sigma Aldrich and used without further purification. The aqueous solutions were prepared with double-distilled water (18M $\Omega$  cm).

### 2.2 Apparatus

All electrochemical experiments were performed at room temperature using an AMEL Potentiostat, controlled with the Junior Assist software, coupled with an AMEL Frequency Response Analyzer, controlled with the Zassist software. Irradiation of the samples was performed by means of a 300W Xe lamp (LOT-Quantum Design Europe) equipped with suitable filters to select different wavelengths.

A conventional three-electrode cell was generally used in which the investigated samples worked as anodes; a Pt grid was used as counter electrode while saturated calomel electrode (SCE) was the reference. All the potential values given in the text refer to SCE. The exposed geometrical area of the working electrodes was  $1 \text{ cm}^2$ . A two electrode configuration was adopted for the synthesis of nanotubular structures: also in this case a grid of Pt was used as counter electrode.

### 2.3 Synthesis of the anodic materials

Titanium foils (Sigma-Aldrich®, 0.25mm thickness 99.7% metal basis) were firstly degreased by sonication in acetone, then in isopropanol and in methanol (10 min each), and finally rinsed with deionized water. The pretreated foils were then submitted to electrochemical anodization. Oxidation was performed in glycerol/water (75/25%v) solutions containing 0.14M  $\text{NH}_4\text{F}$ : a potential ramp was applied from open-circuit voltage (OCV) to a fixed potential (20V) with a scan rate of 50 mV/s; then, the applied potential was maintained at this fixed value for two hours. After oxidation, the electrodes were rinsed in deionized water and dried in a nitrogen stream. A subsequent annealing treatment was needed in order to transform the amorphous phase into crystalline structure. Thermal treatment was performed in air atmosphere for 1h at 400°C.

After anodization a functionalization of the electrode surface with 4-nitrobenzenediazonium was performed by cyclic voltammetric runs at 100 mV/s in the range of potential 0.4 to -0.7 V in Acetonitrile + 0.1 M (TBAPF<sub>6</sub>) solutions containing 2 mM of 4-nitrobenzenediazonium tetrafluoroborate. Electrochemical reduction of nitro group to amino group was performed by cyclic voltammetry in water/ethanol solutions (90/10%v) containing 0.1M of KCl; the potential was varied from the open circuit potential to -1.2 V and back to 0.2 V. Scan rate was 100 mV/s.

Finally, PANI polymerization was carried out on either bare  $\text{TiO}_2$  or phenylamine modified  $\text{TiO}_2$  electrodes. To this aim galvanostatic runs were performed at constant current density of  $20 \mu\text{A} \cdot \text{cm}^{-2}$  from aqueous solutions containing aniline (0.1M) and  $\text{HNO}_3$  (1M). Different electropolymerization steps (30, 60 and 120 minutes) were applied in order to obtain PANI films with different thickness. A minimum of 30 minutes of electropolymerization was needed to obtain measurable coverage of the polymer. According to the Faraday law, if a unit current yield is supposed, the related load of



PANI may be evaluated as 69.5 139 and 278  $\mu\text{g}/\text{cm}^2$  respectively, when 0.5 electrons/mol aniline are considered to be involved in the process.<sup>34</sup>

To simplify the discussion, thereafter NT will be used to indicate a bare nanotubular structure, while modified samples will be identified with NT/PANI<sub>x</sub>, NT/DZ/PANI<sub>x</sub>, when PANI is directly linked on nanotubes, or by means a preliminary phenylamine underlayer, respectively. The PANI load of the different samples will be indicated by the subscript number *x* which represents the time (minutes) of duration of the electropolymerization step.

#### 2.4. Characterization of the electrodes

Scanning electron microscopy (SEM) was used to study the morphology of the assembled electrodes prepared with the different approaches (NOVA 600, Nanolab dual beam). Focused ion beam (FIB) was also used to obtain very precise cross sections of samples for subsequent imaging via SEM.

In order to evaluate the performance of the samples, the trend of photocurrent with the potential was preliminarily investigated. Depending on the samples different polarization trends were obtained and the plateau of photocurrent saturation was achieved at different potential from the OCV value (data not shown). Thus, the value of 1 V above the OCV was selected to measure photocurrent in order to have a reference value at which all the samples were under saturation conditions.

Most of the measurements were done in the UV range ( $\lambda = 365$  nm); the performances were also evaluated using the lamp without filter, to better simulate the solar radiation (white light). The value of photocurrent was taken as the difference between light and dark currents. Electrochemical impedance spectroscopy (EIS) measurements were carried out in the dark, at the OCV and in a frequency range from 100 kHz down to 0.1 Hz. The complex capacitance values were derived from the impedance data evaluated at each frequency. Values of global capacitance were also derived for comparison, from typical charge/discharge tests:

$$C = i / (\Delta V / \Delta t) \quad (1)$$

According to eq 1) the capacitance was calculated from the slope  $\Delta V / \Delta t$  of the discharge curve obtained at a constant current density *i*. Typical experiments were performed in a potential range of 1.5 V with a discharge current of 0.1 mA.

### 3. Results and discussion

Figure 1 shows an example of the final raw NTs structure obtained after two hours of oxidation of Ti foils. As it can be observed, a regular structure of NTs was obtained, with average tube diameter of about 90 nm, and a mean length of about 1  $\mu$ m.

#### FIGURE 1

The NT TiO<sub>2</sub> electrodes were then processed to obtain the under-layer of phenylamine, suitable for the anchoring of PANI, with a procedure which has been indicated as a simple way to achieve a regular distribution of the subsequent layer, with a high stability.<sup>31,33</sup>

Figure 2A) shows an example of the CV obtained after two consecutive cycles of functionalization. In the first cycle, a cathodic peak is observed at about 0 V which can be related to the reduction of the diazonium group. Further cycles exhibit a displacement of the cathodic peak towards more negative potentials, as well as a decrease of the recorded current indicating the progressive blocking of the electroactive surface due to the formation of the organic film.<sup>25,26</sup>

#### FIGURE 2

A further process was performed cycling the potential from 0.2 to -1.2 V in water - ethanol solution containing 0.1M KCl to transform the NO<sub>2</sub> termination in NH<sub>2</sub> termination, to activate the aromatic ring for the subsequent electrophilic attack.

As it is generally reported in the literature<sup>35,36</sup> this process occurs through an intermediate reversible step which involves the nitrous/hydroxylamine (NO/NHOH) redox couple, followed by the irreversible amination of the hydroxylamine group. According to this mechanism, data presented in Figure 2B) show the anodic peak related to the intermediate process at about -0.52 V: just a knee is observable in the direct scan of the CV, assessing the corresponding reduction, at about the same potential, due to its partial overlapping with the irreversible reduction wave, which has its maximum at around -0.8 V.

The samples functionalized were then submitted to aniline electropolymerization. The process was carried out by galvanostatic electrolysis at 20  $\mu$ A for different intervals of time. For comparison purpose, the electropolymerization was carried out also at bare NTs, with the same procedure adopted for the functionalised electrodes. The final coverage of the surface by the polymer was checked by cyclic voltammetry and SEM analyses. Figure 3 shows an example of the trend of



voltammetric runs performed in  $\text{H}_2\text{SO}_4$  0.1M at NT/DZ/PANI electrode which assesses the successful link of the polymer to the surface.

### FIGURE 3

Figures 4 shows the comparison between SEM images of NT/PANI (Figure 4A) and NT/DZ/PANI (Figure 4B) obtained after 60 minutes of electropolymerization: when bare NT electrodes are coated, PANI tends to deposit irregularly inside the tubes and on their top mouth: a partial plugging of the tubes can be also observed, which may compromise the further access of the electrolyte to the tubes. A different aspect of the final surfaces is observable for the NT/DZ/PANI samples, with a more regular distribution of the polymer. Moreover, the regular deposit does not seem to block the entrance on the NTs, while a thickening of the walls and a decrease in the diameter of the NTs is observed, indicating the polymerization mainly occurs at the NT walls.

### FIGURE 4

The photocurrents of prepared samples were evaluated in  $\text{Na}_2\text{SO}_4$  aqueous solution, under 1V of overpotential from the OCV, at which saturation current conditions were guaranteed for all the samples. Figure 5A) shows the results obtained at  $\lambda = 365$  nm for different PANI load with and without under-layer. In particular, the comparison is done in terms of ratio between the photocurrent measured at the different samples and that measured at NT bare electrode. Figure 5B) resumes data of photocurrent density obtained for NT/DZ/PANI samples irradiated with white light.

### FIGURE 5

Data shown in figure 5 indicate a positive effect only at low loading of PANI: only the performances of the PANI/30 samples overcome those of NT under UV light; the situation is slightly better under the white light, with which also the sample with 60 min load performs well. Nevertheless, in any case the performances abruptly decrease at samples highly loaded: a negative effect of PANI polymerization was observed at longer deposition times, probably due to the partial plugging of the nanotube structure previously mentioned. As highlighted by different authors<sup>37-41</sup> the combination of PANI with  $\text{TiO}_2$  can improve their performance in relation to UV light and white light because PANI is a conducting polymer and a dye with a forbidden band gap of 2.8 eV<sup>42</sup>, making it a good sensitizer of  $\text{TiO}_2$ . Based on the well-established energy band theory of

PANI/TiO<sub>2</sub> composites, the photocatalytic mechanism under visible irradiation involves the electrons in  $\pi$ -orbital of PANI which are excited to  $\pi^*$ -orbital by visible light and can readily inject into the CB of TiO<sub>2</sub> because the energy level of them matched well for the charge transfer.<sup>43</sup> Nevertheless, an excessive PANI load may occupy the active sites of TiO<sub>2</sub>; moreover, it may cause the recombination of the electrons with PANI<sup>+</sup>, which competes with the injection into the conduction band of TiO<sub>2</sub>.<sup>43</sup> The maximum of visible photoactivity implies that there is an optimal load for the interfacial electrons transfer from PANI to TiO<sub>2</sub>.

By comparing the data in Figure 5, it is worth to be noted that, PANI deposition time being the same, the gain in efficiency for NT/DZ/PANI with respect to NT samples is higher under white light, probably due to the greater absorption of PANI in the visible light. Thus, at the sample with NT/DZ/PANI<sub>30</sub>, the percentage of current increase with respect NT sample is about 100% (Figure 5B), whereas the analogous gain is only of 20% at 365 nm (Figure 5A). In absence of the under-layer the analogous comparison leads only 10% of gain (samples NT/PANI<sub>30</sub> in Figure 5A).

The presence of the under-layer also originates a lower decrease at high PANI loads: for NT/DZ/PANI<sub>120</sub> the residual activity at 365 nm is about 20% of the initial value, whereas just 6% of the initial activity was remained at NT/PANI<sub>120</sub>. This result can directly be linked to the better distribution of PANI on the surface of the TiO<sub>2</sub> nanotubes (checked by SEM analyses) when the polymerization is carried out after the functionalization of the structure with the benzen-diazonium salt.

Electrochemical impedance spectroscopy (EIS) was used to obtain information on the capacitive behavior of the samples. Cyclic voltammetry is often proposed to derive the capacitance: however, due to the large potential perturbation, the CV currents may include contributions from both localized and conduction band charge transfers, thus giving overestimated capacitance values; at the same time charge transfer kinetics could also affect the current, leading to underestimated capacitance at high potential scan rates.<sup>44</sup> As steady state technique with small potential variation, EIS has been suggested as more reliable method to have capacitance data, with minimized effect from non-capacitive Faradaic contributions.<sup>44</sup>

In this work all the EIS were performed at the OCV, superimposing a sinusoidal wave of 10 mV.

The effect of the PANI coating on TiO<sub>2</sub> is showed in Figure 6, where the trend of Nyquist plot for bare NTs is compared with those of electrodes with different PANI load (Figure 6A).

**FIGURE 6**

The general trend of the spectra always involves a first semicircle in the higher frequency range, which may be attributed to the electrode surface properties and the charge transfer resistance. A nearly vertical trend is observed in the lower frequency range which may be connected to capacitive component or/and mass transfer effects. The shape of the plots and the slope of the straight line depend on the PANI load. A gradual transition from capacitive to Warburg-like behavior was already reported in the literature for PANI based systems in the low frequency range, in aqueous and non-aqueous media and with various substrates.<sup>45</sup>

In the present case, when a high load of PANI is considered (as in the sample NT/PANI<sub>60</sub>) the presence of the new interface TiO<sub>2</sub>/PANI is well highlighted by the appearance of a second circle at the intermediate frequencies (see inset of Figure 6A).

The effect of PANI is also evident in the Bode modulus and phase angle plots (Figure 6B, C): due to the conductive character of PANI, a clear decrease in modulus is observed when PANI load increases, and a new peak appears in the phase diagram at intermediate frequency, when PANI load is enough to clearly show its contribution.

In order to better understand these results, the impedance data may be analyzed in terms of complex capacitance.<sup>46</sup> Starting from the real and imaginary impedance values, we can express as:

$$C(\omega) = C'(\omega) - jC''(\omega) \quad (2)$$

$$C'(\omega) = \frac{-Z''(\omega)}{\omega |Z(\omega)|^2} \quad (3)$$

$$C''(\omega) = \frac{Z'(\omega)}{\omega |Z(\omega)|^2} \quad (4)$$

Where  $Z'(\omega)$  and  $Z''(\omega)$  are the real and imaginary parts of the complex impedance  $Z(\omega)$ , respectively, and  $\omega$  is the angular frequency  $\omega = 2\pi f$ . At low frequency,  $C'(\omega)$  corresponds to the capacitance of the electrode material and  $C''(\omega)$  corresponds to the dissipation of energy by irreversible processes that lead to a hysteresis.<sup>47</sup>

Data in terms of Bode modulus plot are resumed in Figure 7: the inset reports the trend of the relative Nyquist  $C''$  vs  $C'$ .

FIGURE 7

Data in Figure 7 illustrate the gain in capacitance obtained due to the PANI load, with values of  $C$ , evaluated at 0.1Hz, ranging from 813  $\mu\text{F}/\text{cm}^2$  for NT to 14  $\text{mF}/\text{cm}^2$  measured at NT/PANI<sub>120</sub>.

The effect of the underlayer is illustrated in Table 1, which reports the comparison in terms of ratio between  $C$  of the different samples and  $C$  of the related bare NT, with and without the under-layer.

Table 1

The high effect of PANI results in values of capacitance up to 15-fold the values of the bare NT. The presence of the under-layer increases this effect especially for sample with 60 min of PANI load; the effect of the under-layer is less evident at 120 min of PANI loading, probably because its effect of plugging of pores, previously mentioned.

Capacitance was also measured by the charge/discharge tests in order to make a comparison: values of 800  $\mu\text{F}/\text{cm}^2$ , 1.8 $\text{mF}/\text{cm}^2$ , and 12  $\text{mF}/\text{cm}^2$  were respectively obtained at NT, NT/DZ/PANI<sub>30</sub> NT/DZ/PANI<sub>120</sub> which resulted in a good agreement with those obtained from EIS.

As the comparison with the literature is concerned, the capacitance value measured for NT is in good agreement with the data reported for titania NTs<sup>4-7</sup>. However, if TiO<sub>2</sub>/PANI are considered, the comparison is not so straightforward. Resistance and capacitance of PANI depend on the thickness of the film and on the preparation procedures; moreover, the values of capacity depend on the techniques used for their measure.<sup>44</sup>

Also of particular concern is the trend of  $C''$  vs  $f$  plot (Figure 8), because it allows to directly compare the resonant frequency ( $f_0$ ) for the different samples. As it is generally obtained for semiconductor materials, the trend of the imaginary capacitance with the frequency passes through a maximum at a value  $f_0$ , which virtually separates the range of the capacitive ( $f < f_0$ ) and resistive ( $f > f_0$ ) behavior of the sample. Moreover, from the resonant frequency, the value of the relaxation time constant ( $\tau_0$ ) can be calculated as:

$$\tau_0 = \frac{1}{2\pi f_0} \quad (5)$$

This parameter is another important figure of merit which determines the charge/discharge time of the condenser. Low time constants (of the order of ms) are preferred for electrochemical supercapacitors to ensure fast charge–discharge characteristics.<sup>45</sup>

FIGURE 8

Data in Figure 8 indicate that PANI layer over the sample surface makes the capacitive behavior active at lower frequency, and samples with higher load have slower charge/discharge process.

### FIGURE 9

In Figure 9 the  $C''$  vs  $f$  trends for different samples are compared, in particular, two extreme cases are represented. From one hand, we observe the trend related to a conducting Pt electrode, which is reported in the same figure as a comparison: a regular increasing trend without any peak is presented by this sample, as we expected due to its completely resistive behavior. On the opposite side, we observe the behavior of NTs bare electrode (see inset) which shows a capacitive behavior for frequency lower than 310 Hz ( $f < f_0$ ); the abrupt increase on  $C''$ , which is measured at very low frequency, may be due to a faradic capacitance contribution, related to possible charge transfer at the electrode/solution interface.

The trends obtained with the other modified samples differ in terms of displacement of  $f_0$  and/or faradic response contribution. The main effect of the PANI is an increase in conductivity of the surface, and after 60 min the semiconductor character of the titania NT is about completely masked and the trend is very similar to that of Pt.

When the interlayer is interposed in between, the capacitive behavior is maintained: the resonance frequency is shifted to lower values with respect to that of NT bare sample, and the faradic capacitance contribute becomes to be evident at  $f$  lower than 10 Hz. However, the shifting to the right of the curve related to the sample NT/DZ/PANI<sub>120</sub> lets us to conclude that also in this case, the prevailing conductive character of the polymer will prevail at high PANI loads.

### Conclusions

From the results presented in this work, the following conclusions can be drawn:

- The morphology of PANI deposit onto the TiO<sub>2</sub> NT electrodes is highly improved by the under-layer of phenylamine, with a more regular distribution of the polymer. Moreover, the PANI deposit does not plug the entrance on the NTs because the polymerization mainly occurs at the NTs walls.
- The photocurrent responses indicated that the electropolymerization process should not be too much prolonged. After 30 min, the photocurrent obtained is higher than working with bare NTs, but it worsens applying higher duration polymerization process. This negative effect has been attributed to the plug of the nanotubes.

- When light without any filter is applied, the highest photocurrent values were obtained in the samples with underlayer. This result is due to the greater absorption of PANI in the all spectrum of the visible/UV light.
- The presence of the PANI layer results in characteristic shapes in the Nyquist and Bode diagrams, related to the gain in the capacity. The hybrid composites have a capacitance 15-fold the value of bare NTs, with the highest values obtained working with the samples NT/DZ/PANI.
- Although the deposition of PANI produces an increase in the conductivity of the TiO<sub>2</sub>, so masking its semiconductor characteristics, with the use of underlayer the capacitive behavior prevails, even at high PANI loads.

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*Tables*

PANI load min	NT/PANI $C_{NT/PANI} / C_{NT}$	NT/DZ/PANI $C_{NT/DZ/PANI} / C_{NT}$
30	2.6	3.1
60	7.5	12.9
120	15.7	16.5

Table 1 - *Ratio between Capacitance of the modified electrode with respect to the capacity of bare NT. Blue bars refer to NT/PANI samples, while red bars refer to NT/DZ/PANI samples*

## Figure captions

*Fig.1: SEM (A) and FIB (B) images of TiO<sub>2</sub> nanotubes synthesized in glycerol solutions*

*Fig.2: Functionalization process of NT surface. First step (A): two consecutive CV runs performed in acetonitrile solution containing 2mM nitro-benzendiazonium salt; second step (B): CV performed in water - ethanol solution containing 0.1M KCl*

*Fig.3: Trend of CV performed in 0.1M H<sub>2</sub>SO<sub>4</sub> at NT/DZ/PANI electrode.*

*Fig.4: SEM images of the surface of NT/PANI<sub>60</sub> (A) and NT/DZ/PANI<sub>60</sub> (B) samples.*

*Fig.5. Effect of PANI load on photocurrent measured at 365nm, in 0.1M Na<sub>2</sub>SO<sub>4</sub> at 1V of overpotential. A) The percentage between the photocurrent measured at the different samples to that measured at NT bare electrode. B) photocurrent density measured at samples irradiated with white light*

*Fig. 6 – Effect of the PANI load on the impedance measured for different NT/PANI samples A): Nyquist plots; B) Phase and Modulus (C) Bode diagrams.*

*Fig.7: Trend of capacitance modulus vs frequency measured at NT samples modified with different PANI loads. Inset: Nyquist plot.*

*Fig. 8: Trend of imaginary capacitance vs frequency measured at NT samples modified with different PANI loads*

*Fig.9: Comparison between imaginary capacitance trends for samples differently modified with and without interlayer. Inset: zoomed data in the low range of C'': for reason of clarity data related to NT/PANI are not reported in this zoomed view. Red curve related to Pt behavior is reported as a comparison.*

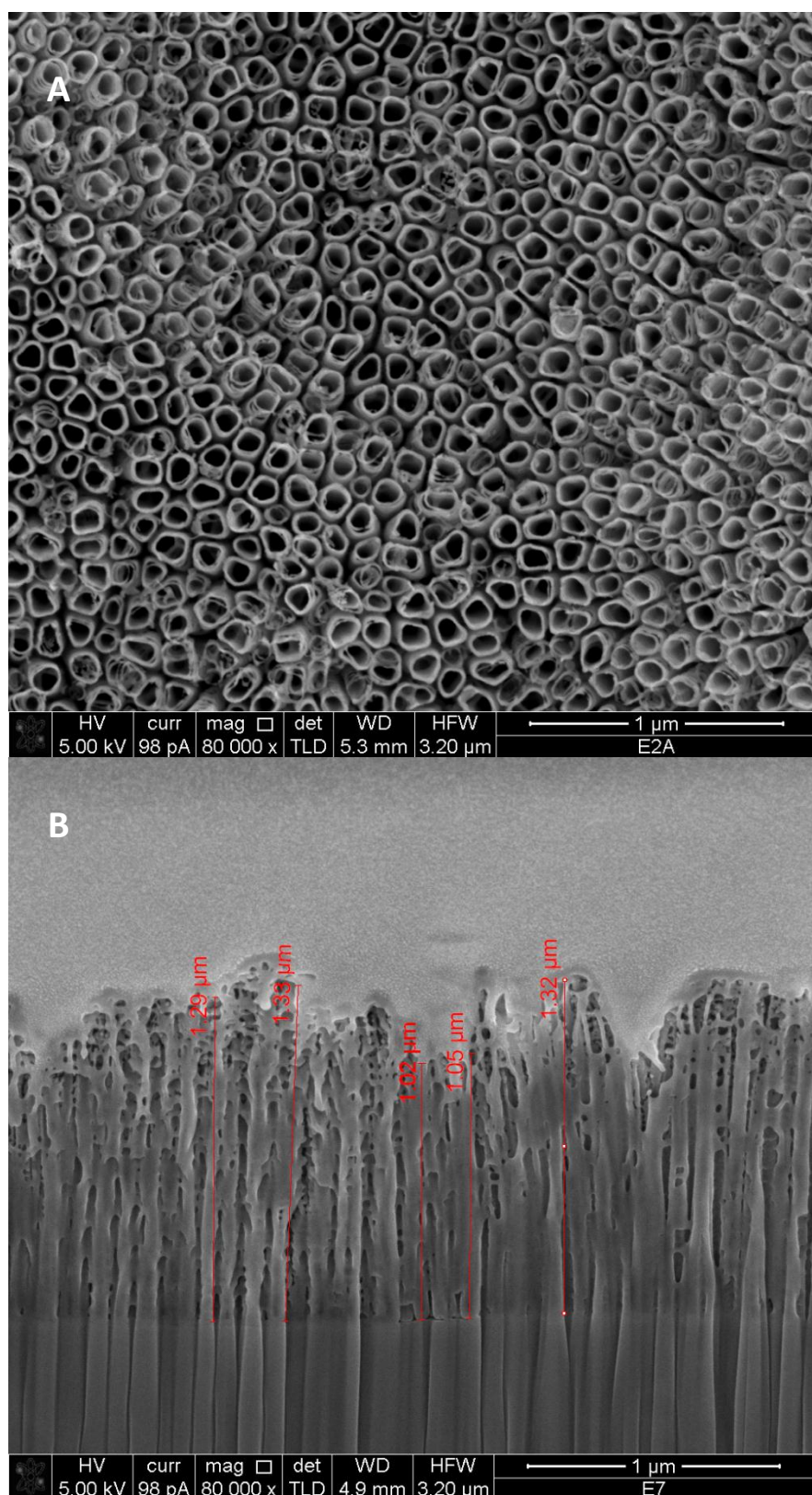


Fig. 1 SEM (A) and FIB (B) images of  $\text{TiO}_2$  nanotubes synthesized in glycerol solutions

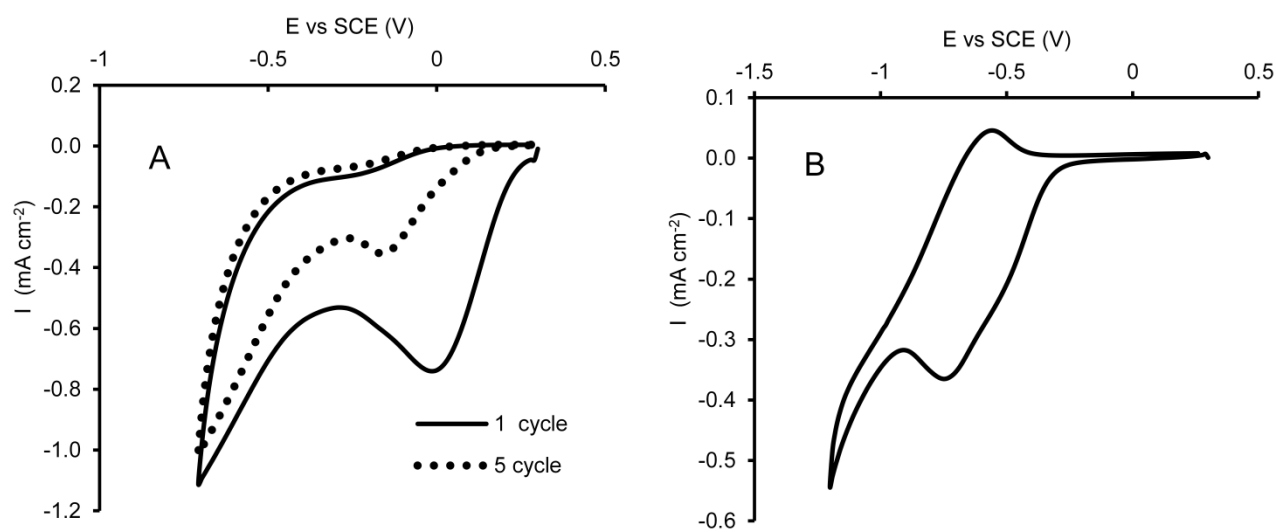


Fig. 2 – Functionalization process of NT surface. First step (A): two consecutive CV runs performed in acetonitrile solution containing 2mM nitro-benzendiazonium salt; second step (B): CV performed in water - ethanol solution containing 0.1M KCl



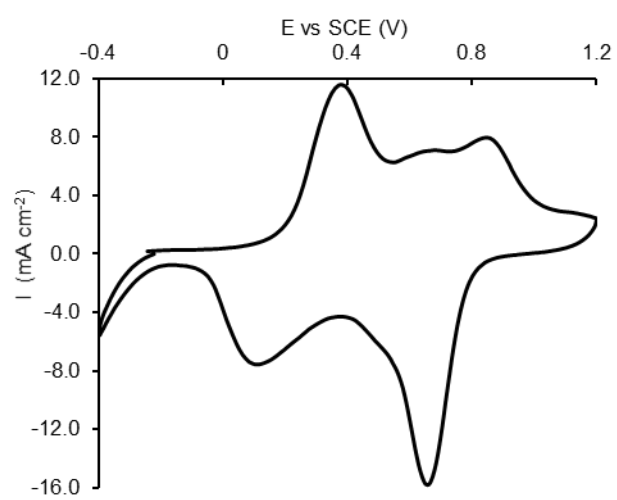


Fig. 3 Trend of CV performed in 0.1M  $H_2SO_4$  at NT/DZ/PANI electrode.

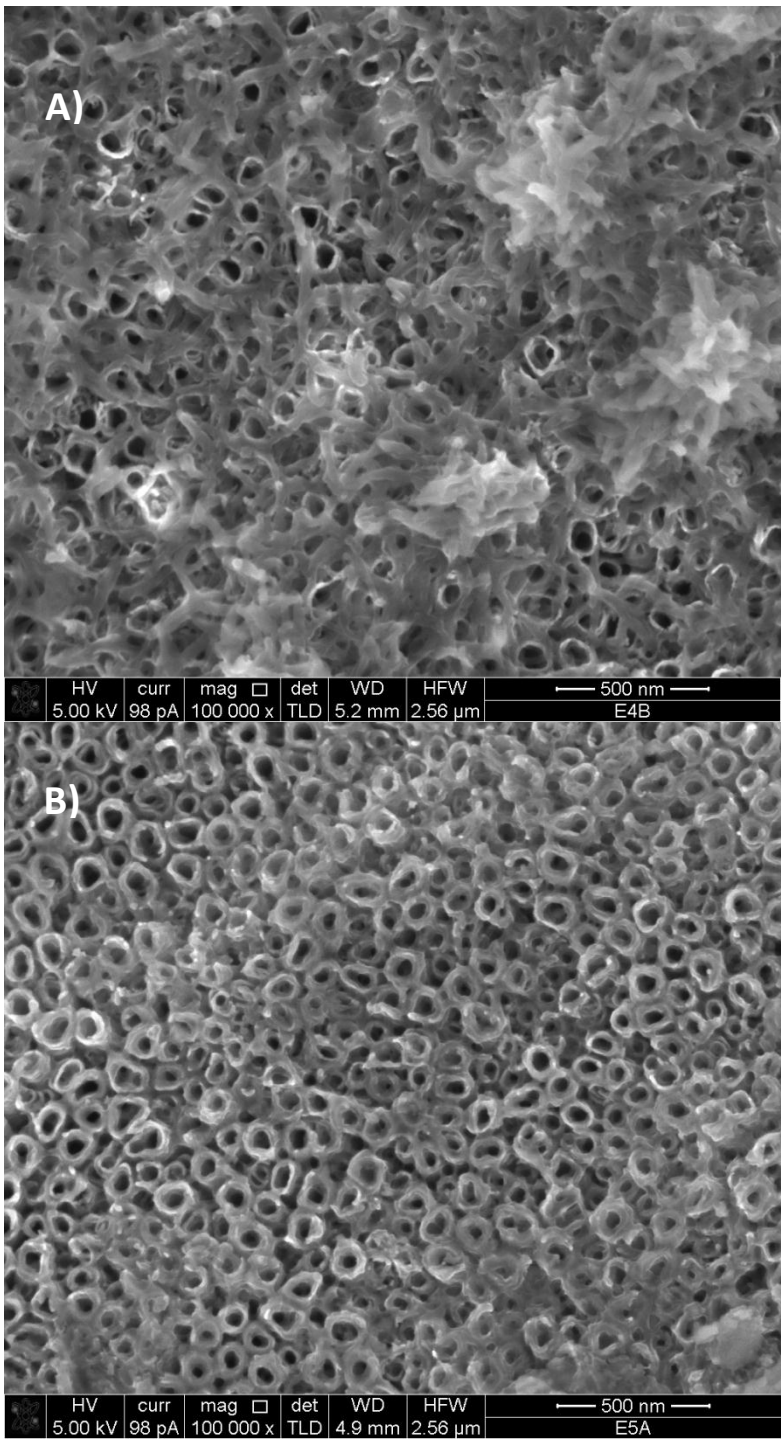


Fig. 4: SEM images of the surface of NT/PANI<sub>60</sub> (A) and NT/DZ/PANI<sub>60</sub> (B) samples.

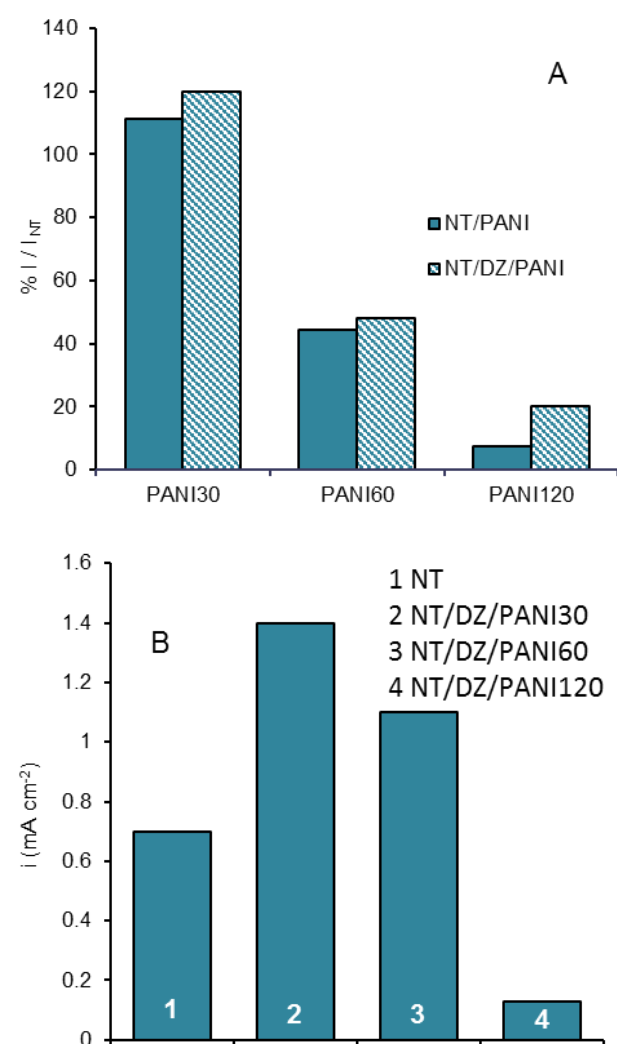


Fig. 5. Effect of PANI load on photocurrent measured at 365nm, in 0.1M  $\text{Na}_2\text{SO}_4$  at 1V of overpotential. A) The percentage between the photocurrent measured at the different samples to that measured at NT bare electrode. B) photocurrent density measured at samples irradiated with white light

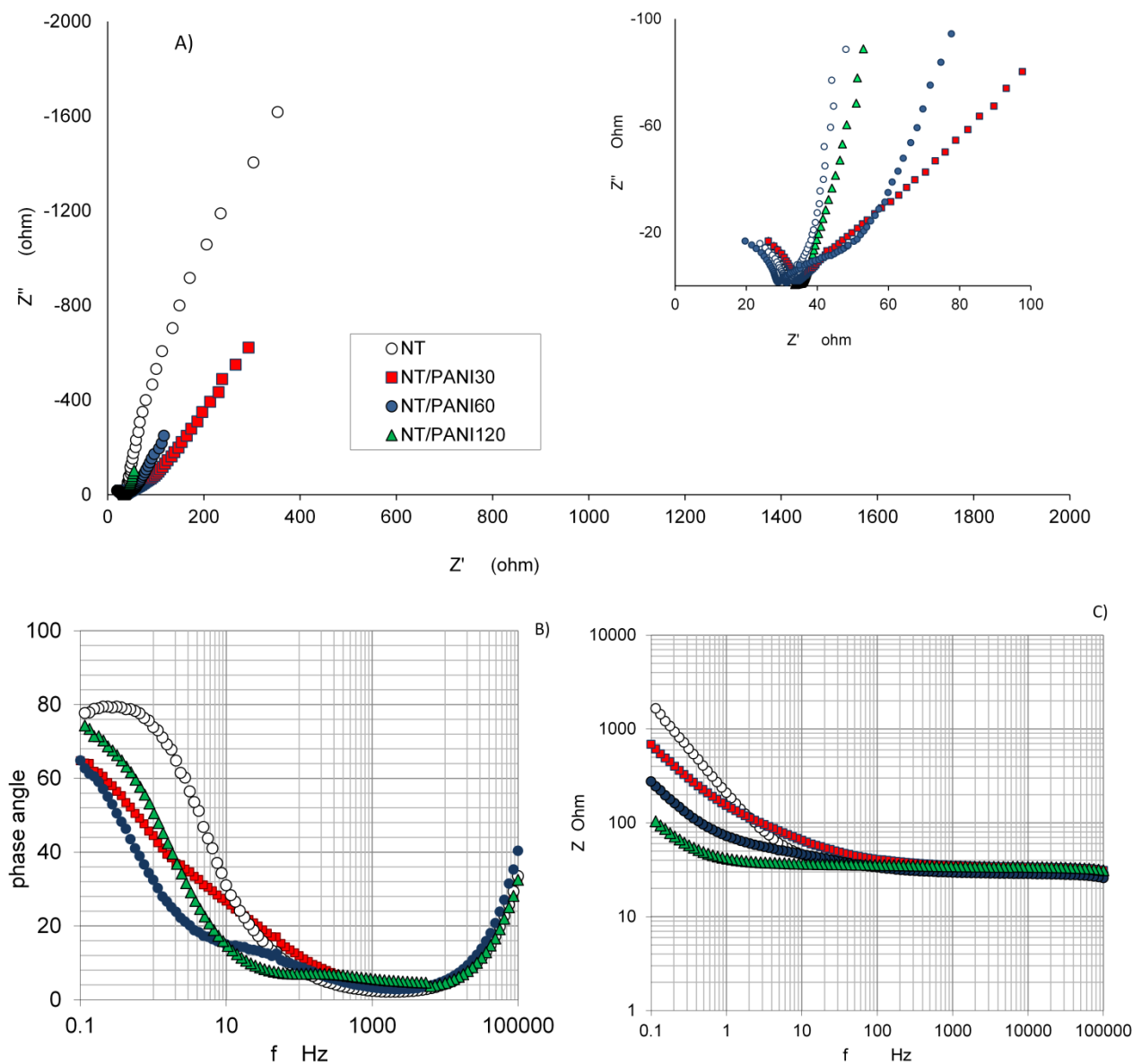


Fig. 6 – Effect of the PANI load on the impedance measured for different NT/PANI samples A): Nyquist plots; B) Phase and Modulus (C) Bode diagrams.

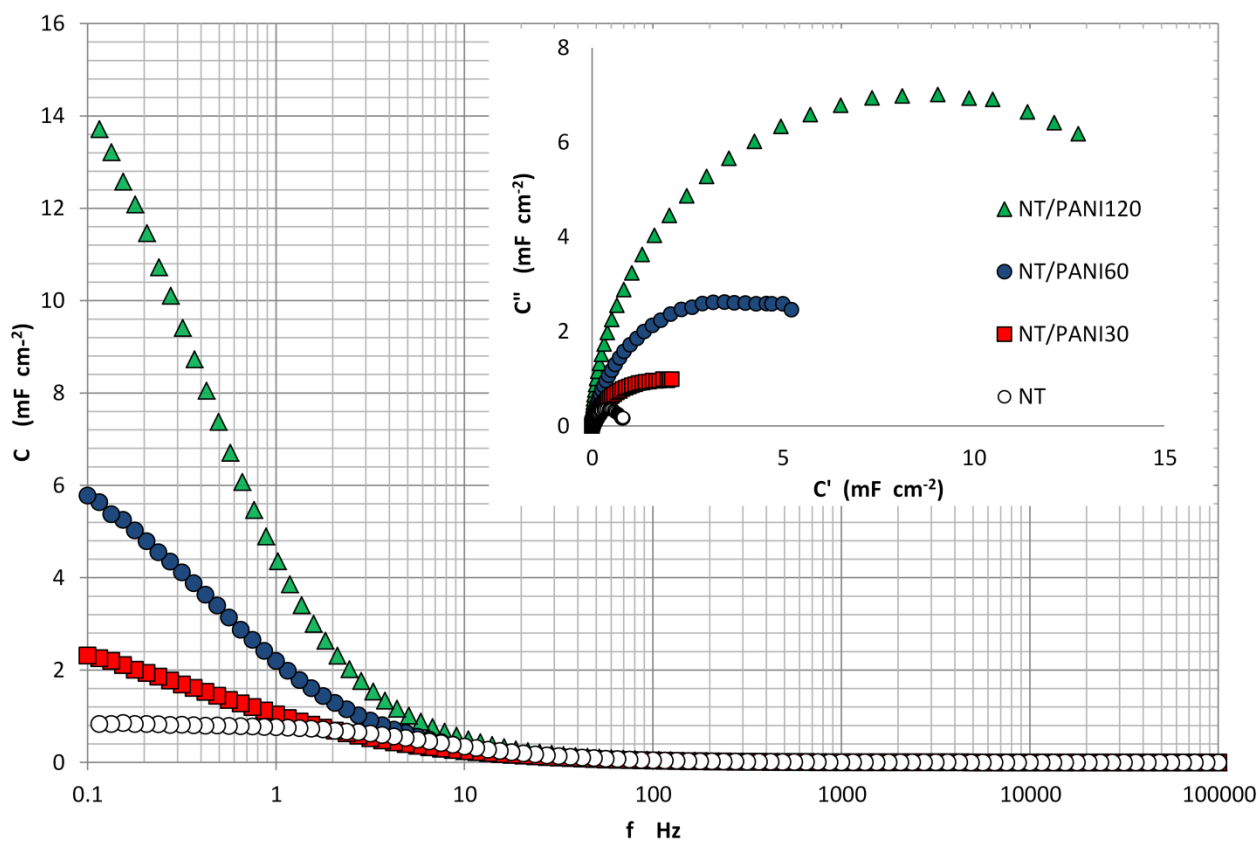


Fig. 7 - Trend of capacitance modulus vs frequency measured at NT samples modified with different PANI loads. Inset: Nyquist plot.

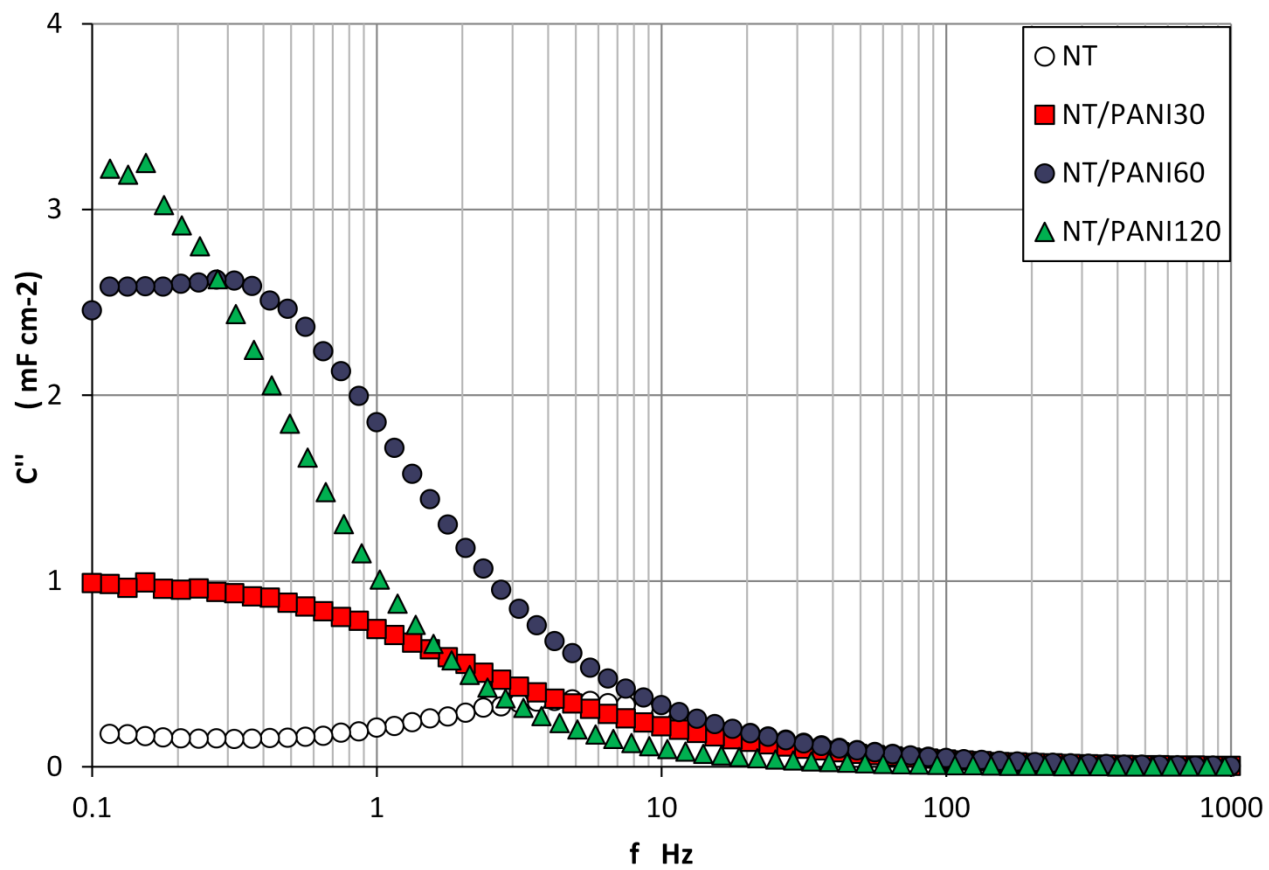


Fig. 8 - Trend of imaginary capacitance vs frequency measured at NT samples modified with different PANI loads



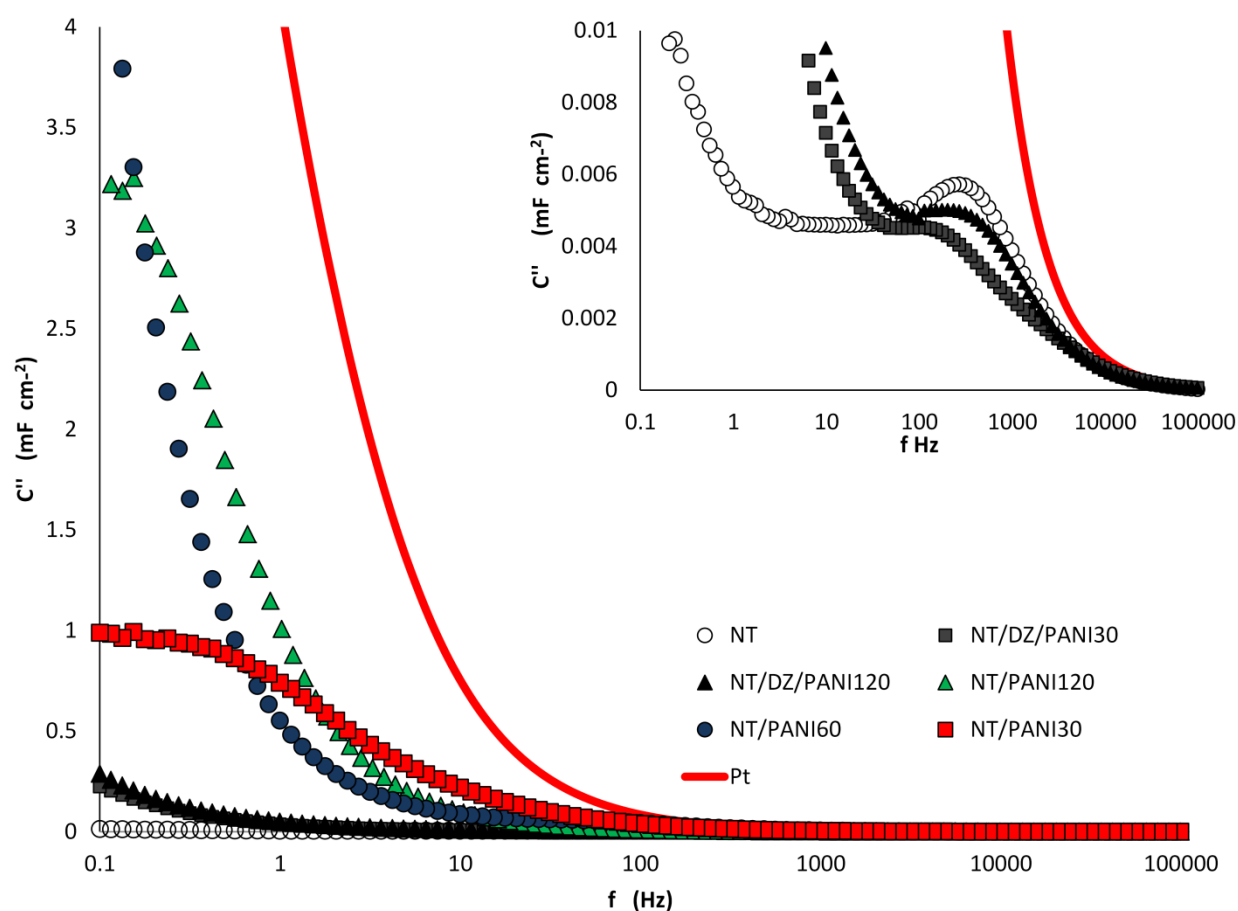


Fig. 9 – Comparison between imaginary capacitance trends for samples differently modified with and without interlayer. Inset: zoomed data in the low range of  $C''$ : for reason of clarity data related to NT/PANI are not reported in this zoomed view. Red curve related to Pt behavior is reported as a comparison.