



In situ growth of ceramic quantum dots in polyaniline host via water vapor flow diffusion as potential electrode materials for energy applications



Dominique Mombrú^a, Mariano Romero^{a,*}, Ricardo Faccio^{a,*}, Jorge Castiglioni^b, Alvaro W. Mombrú^{a,*}

^a Centro NanoMat/CryssMat/Física – DETEMA – Facultad de Química – Universidad de la República, C.P. 11800 Montevideo, Uruguay

^b Laboratorio de Físicoquímica de Superficies – DETEMA – Facultad de Química – Universidad de la República, C.P. 11800 Montevideo, Uruguay

ARTICLE INFO

Keywords:

Polyaniline
Ceramic
Nanocomposite
In situ growth

ABSTRACT

In situ preparation of polyaniline-ceramic nanocomposites has recently demonstrated that the electrical properties are highly improved with respect to the typical *ex situ* preparations. In this report, we present for the first time, to the best of our knowledge, the *in situ* growth of titanium oxide quantum dots in polyaniline host via water vapor flow diffusion as an easily adaptable route to prepare other ceramic-polymer nanocomposites. The main relevance of this method is the possibility to prepare ceramic quantum dots from alkoxide precursors using water vapor flow into any hydrophobic polymer host and to achieve good homogeneity and size-control. In addition, we perform full characterization by means of high-resolution transmission electron microscopy, X-ray powder diffraction, small angle X-ray scattering, thermogravimetric and calorimetric analyses, confocal Raman microscopy and impedance spectroscopy analyses. The presence of the polymer host and interparticle Coulomb repulsive interactions was evaluated as an influence for the formation of ~3–8 nm equally-sized quantum dots independently of the concentration. The polyaniline polaron population showed an increase for the quantum dots diluted regime and the suppression at the concentrated regime, ascribed to the formation of chemical bonds at the interface, which was confirmed by theoretical simulations. In agreement with the previous observation, the *in situ* growth of ceramic quantum dots in polyaniline host via water vapor flow diffusion could be very useful as a novel approach to prepare electrode materials for energy conversion and storage applications.

1. Introduction

In the last years, polymer-ceramic nanocomposite materials have attracted a lot of attention due to the improvement, especially for energy applications [1–7], but the preparation of these nanocomposite materials is still a challenge to step through. Recently, there has been a lot of effort in the preparation of electrode materials based in polyaniline-ceramic nanocomposites showing outstanding performance as electrode materials for supercapacitors [8], lithium batteries [9], solar cells [10] and also for electromagnetic sensing [11] devices. In addition to the high specific capacitance, high flexibility and low cost of polyaniline [12], the addition of nanoparticle fillers can be integrated in the polyaniline host matrix leading to an enhancement on the structural stability, porosity and electric conductivity [4]. Particularly, there is still a specific need in the improvement of the *in situ* preparation of polyaniline-ceramic nanocomposites, as it has been recently demonstrated that the electrical properties are strongly

improved respect to the typical *ex situ* preparations. The typical choice for the *in situ* preparation of polyaniline-ceramic nanocomposites is based in the *in situ* polymerization of polyaniline from the aniline monomer in the presence of ceramic nanoparticles [8–11]. On the other hand, polymer nanocomposites prepared by *in situ* growth of ceramic nanoparticles such as silica (SiO₂) or titania (TiO₂) via sol-gel method in aqueous medium has also been reported, revealing a great improvement on their electrical performance [6,7,13–17]. Moreover, it has been already reported that ceramic nanoparticles can be prepared via sol-gel method using vapor flow diffusion [18]. However, to the best of our knowledge, up to now there are no reports on the preparation of the *in situ* growth of ceramic quantum dots via vapor flow diffusion into a hydrophobic polymer host such as polyaniline. Although TiO₂ and polyaniline (PANI) have been previously reported as forming composite materials [19,20] these studies involve conventional ways for the hydrolysis towards the formation of TiO₂. However, the size of such ceramic particles cannot be interpreted to be in the nanoscale. In this

* Corresponding author.

E-mail addresses: mromero@fq.edu.uy (M. Romero), rfaccio@fq.edu.uy (R. Faccio), amombru@fq.edu.uy (A.W. Mombrú).

<http://dx.doi.org/10.1016/j.jssc.2017.03.016>

Received 5 February 2017; Received in revised form 6 March 2017; Accepted 19 March 2017

Available online 21 March 2017

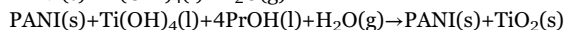
0022-4596/ © 2017 Elsevier Inc. All rights reserved.

manuscript, a more subtle procedure to achieve the hydrolysis via the use of vapor is presented, with the preparation of quantum dots, yielding to new materials with this criterion, and that could give a new insight for the interaction between the polymer and the ceramic through the different characteristics of the nanoparticles synthesized. In this report, we showed the preparation of ceramic-polymer nanocomposites based in the *in situ* growth of titanium oxide quantum dots – very relevant and related to energy applications [21,22] – in polyaniline host via water vapor flow diffusion (PANI-TiO₂-X). In addition, we report a complete characterization studying the presence of polyaniline charge carriers and interparticle interactions between charged quantum dots by means of confocal Raman microscopy and small angle X-ray scattering, respectively. The electrical properties, in correlation with the previous characterization, revealed that this preparation method is can be easily extrapolated to other sol-gel derived quantum dots into any hydrophobic polymer as potential electrode materials for energy conversion and storage applications.

2. Materials and methods

2.1. Preparation of PANI-TiO₂-X

Titanium tetrapropoxide (TTP) 98% and polyaniline doped with dodecylbenzene sulphonic acid (PANI-DBSA) with average Mw~15,000 in its emeraldine salt form 99.9% were provided by Sigma-Aldrich. PANI emeraldine salt powder (0.3g) was suspended in 20 mL of tetrahydrofuran (THF) and 1 mL of deionized water (H₂O) under vigorously stirring at 500 rpm for 30 min. In order to obtain TiO₂/PANI weight ratios of ~2%, 5%, 10%, 20%, 30%, 40%, 50%, 60%, 80%, 90% and 98%, the corresponding amount of TTP (21.3 mg, 53.4 mg, 106.8 mg, 213.5 mg, 320.3 mg, 427.0 mg, 533.8 mg, 640.6 mg, 854.1 mg, 960.9 mg, 1046.3 mg, respectively) was added dropwise to the PANI suspension and kept stirred at T=70 °C until dryness. The resulting dark green powder was grinded and exposed to deionized water vapor at T=80 °C with a vapor flow of ~1 mL/min during 10 h. The monitoring of quantum dots growth under water vapor flow was done for X=10 taking samples at t=0, 1, 2, 3, 4, 5, 7 and 10 h, named as PANI-TiO₂-10-t. All compositions were finally dried at T=80 °C under vacuum for 7 h to eliminate residual water and propanol generated from the hydrolysis process, as schematized in Fig. 1a following the reaction mechanism:



The dried powders were then pressed at 50 kN/cm² pressure to obtain the *in situ* growth TiO₂ quantum dots, named as PANI-TiO₂-X, with X being the TiO₂/PANI weight ratio.

2.2. Characterization of PANI-TiO₂-X

PANI-TiO₂-X nanocomposites were studied by X-ray diffraction (XRD) using a Rigaku Ultima IV diffractometer working in Bragg–Brentano configuration with CuKα radiation in the 2θ =5–60° range using 2θ steps of 0.02° with a 8 s integration time per step. The size and morphology of the nanocomposites were determined by high-resolution transmission electron microscopy (HR-TEM) and energy dispersive spectroscopy (EDS) were performed using a JEOL 2100 instrument working under a 200 kV voltage. Small-angle X-ray scattering (SAXS) was performed at SAXS-1 Beamline Station as implemented in Laboratório Nacional de Luz Síncrotron (LNLS-CNPEM) working with 8 keV radiation in the q=0.1–4.0 nm⁻¹ range. Confocal Raman microscopy and Raman spectra were obtained using WITec Alpha 300-RA. Raman spectra for PANI-TiO₂-X nanocomposites were collected using an excitation wavelength of 532 nm and a laser power was adjusted at ~3 mW in order to avoid polyaniline decomposition. Additionally,

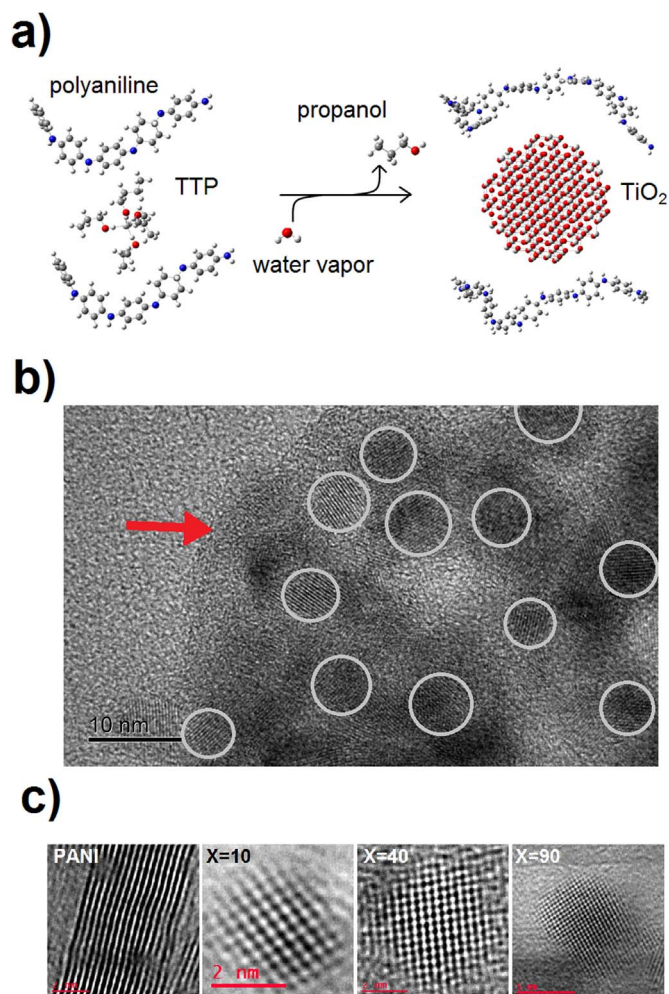


Fig. 1. (a) Scheme of the preparation route for PANI-TiO₂-X and HR-TEM images for (b) PANI-TiO₂-X in low magnification and (c) PANI and PANI-TiO₂-X with X=10, 40 and 90 in high magnification. The grey circles are a guide to the eye to show TiO₂ quantum dots and the red arrow is showing the PANI zone. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

confocal Raman images were obtained for a 20×20 μm² total area with a resolution of ~265×265 nm² per pixel by collecting the total amount of 5625 Raman spectra. For each case, a set of 20 spectra of 0.2 s integration time were averaged. Raman spectra simulation was performed using density functional theory (DFT) [23,24] using the hybrid exchange correlation potential B3LYP [25–28] for a 6–31 G(d,p)+ basis set, as implemented in Gaussian09 [29]. Thermogravimetric analysis (TGA) was performed using Shimadzu TGA-50 with a 50 mL/min air flow and a heating rate of 10°/min between 23–800 °C. Differential scanning calorimetry (DSC) was performed using Shimadzu DSC-60 differential scanning calorimeter in static air at the temperature range T=25–200 °C with a ramp rate of 5°/min. AC impedance spectroscopy analysis was performed for the PANI-TiO₂-X pellets using stainless steel electrodes. The applied AC voltage amplitude was 10 mV in the 0.01 Hz–1 MHz frequency regime at T=300 K using a Gamry Reference 3000 impedance analyzer.

3. Results and discussion

3.1. X-ray powder diffraction (XRD)

XRD patterns for PANI-TiO₂10 nanocomposites at different stages of the quantum dots growth, named as PANI-TiO₂-10-t with t=0, 1, 2, 3, 4, 5, 7 and 10 h are shown in Fig. 2a. Typical XRD profile for pure

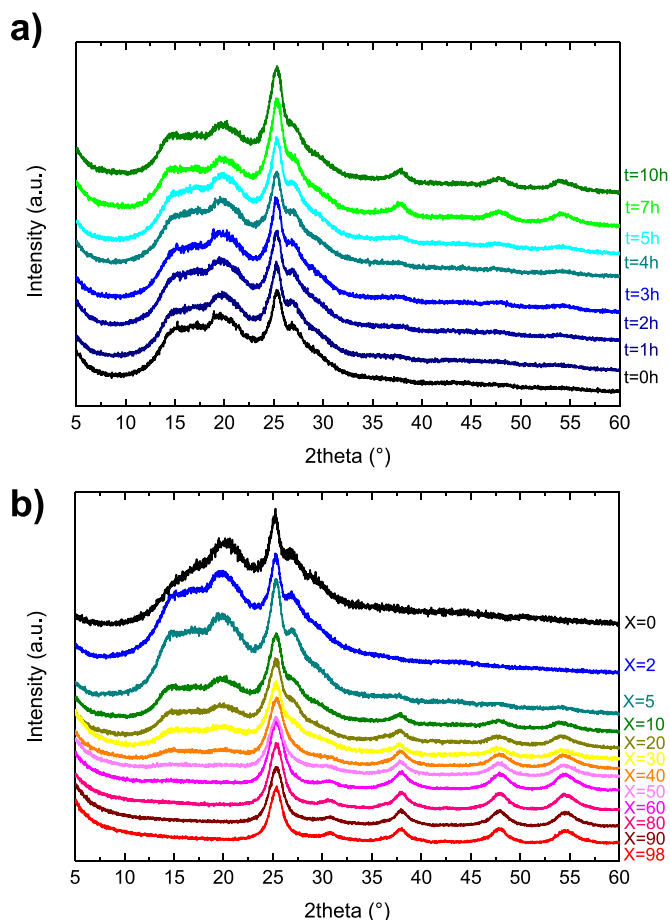


Fig. 2. XRD patterns for (a) PANI-TiO₂-10-t nanocomposite at different stages of the quantum dots growth with $t=0-10$ h and (b) PANI-TiO₂-X nanocomposites for $X=2, 5, 10, 20, 30, 40, 50, 60, 80, 90$ and 98 .

Table 1

XRD and SAXS analysis for PANI-TiO₂-X with $X=2, 5, 10, 20, 30, 40, 50, 60, 80, 90, 98$.

	D (nm)	D ₁ (nm)	D ₂ (nm)	D _{eff} (nm)	P
X=2	–	7.8	2.6	–	0.9
X=5	–	8.0	3.2	–	1.6
X=10	–	7.8	2.4	–	2.1
X=20	–	8.0	2.6	–	1.9
X=30	–	7.8	3.6	4.6	2.4
X=40	–	7.6	2.8	3.8	1.8
X=50	–	8.0	2.9	5.5	1.9
X=60	4.6	6.0	3.4	5.0	2.5
X=80	4.9	7.0	3.4	5.6	2.2
X=90	4.8	6.6	3.4	6.1	2.4
X=98	5.2	6.9	3.4	6.4	2.5

Mean diameter crystallite size was obtained from XRD analysis applying the Scherrer equation $D=0.9\lambda/\beta\cos(\theta)$. Mean quantum dots diameters (D_1 and D_2) and the power law exponent (P) were extracted from SAXS analysis using the Beaucage fit. The effective diameters (D_{eff}) were extracted from the MSA fitting of the SAXS structure factor analysis.

polyaniline in its emeraldine salt conformation with two broad peaks at $2\theta\sim 15.4^\circ, 19.8^\circ$ and a sharper peak at $2\theta\sim 25.2^\circ$ is observed for $t=0$ [30]. PANI-TiO₂-10-t with $t > 5$ showed the appearance of broad peaks at $2\theta\sim 25.5^\circ, 38.0^\circ, 48.0^\circ, 54.5^\circ$ ascribed to nano-sized TiO₂ anatase polymorph [31]. The increment in the relative intensity of the peaks with increasing time is revealing the quantum dots growth. XRD patterns for PANI-TiO₂-X nanocomposites with $X=2, 5, 10, 20, 30, 40, 50, 60, 80, 90$ and 98 are shown in Fig. 2b. The increment in the relative intensity for the peaks ascribed to titanium oxide quantum dots

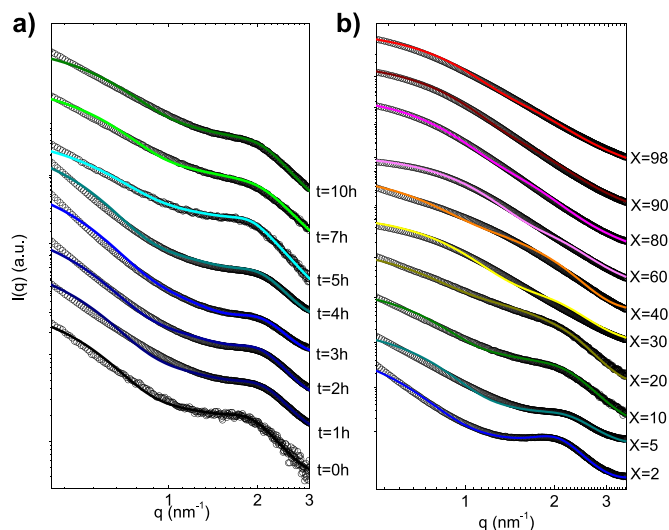


Fig. 3. SAXS curves and Beaucage fittings for (a) PANI-TiO₂-10-t nanocomposite at different stages of the quantum dots growth with $t=0-10$ h and (b) PANI-TiO₂-X nanocomposites with $X=2, 5, 10, 20, 30, 40, 50, 60, 80, 90$ and 98 .

is a mere consequence of the increment in its concentration. The mean diameter crystallite size (D) applying the Scherrer equation following $D=0.9\lambda/\beta\cos(\theta)$ [32] with CuK α wavelength (λ), the full width at half maximum (β) and the Bragg angle (θ) showed $D\sim 5$ nm for all the composition range. However, due to the coincidence with PANI peak at $2\theta\sim 25^\circ$, D values were only calculated for the concentrated regime ($X > 50$), as summarized in Table 1. This is suggesting that this preparation method lead to the formation of titanium dioxide quantum dots with almost constant crystallite size independently of their concentration in the polyaniline host matrix.

3.2. Small angle X-ray scattering (SAXS)

SAXS curves for PANI-TiO₂-10-t with $t=0, 1, 2, 3, 4, 5, 7$ and 10 h (Fig. 3a) and PANI-TiO₂-X with $X=2, 5, 10, 20, 30, 40, 50, 60, 80, 90$ and 98 (Fig. 3b) were fitted using the Beaucage unified equation for correlated spherical particles [33]. At $t=0$ a relative maximum in the curve is observed at $q\sim 2.0$ nm⁻¹ in relation with a correlation length $d\sim 3.0$ nm, probably associated to polyaniline interfibrers mean distance. This correlation length showed a slight decrease to $d\sim 2.8$ nm with increasing time ($t=0-4$ h) until its contribution to the SAXS curve became negligible and the bumps at $q < 1$ nm⁻¹ and $q\sim 1.7-1.9$ nm⁻¹ rises a consequence of the contribution of the quantum dots growth. These two bumps are associated with two populations of quantum dots mean diameters with $D_1\sim 7.8$ nm and $D_2\sim 2.4$ nm, respectively. On the other hand, the quantum dots mean diameters for all compositions showed almost no variations from $D_1\sim 8$ nm and $D_2\sim 3$ nm, as summarized in Table 1. This is suggesting that, in agreement with XRD analysis, the quantum dots mean diameter obtained using this preparation method do not drastically modify in the whole concentration regime from highly diluted (2%) to highly concentrated (98%). However, a slight increase in the Porod exponent from $P\sim 1$ to $P\sim 2.6$ with increasing X is probably ascribed to the increase in the concentration of titanium oxide quantum dots. The Porod exponent is related to the fractal dimension $D=P+1$ for $P < 3$. The increase in the fractal dimension is attributed to the increase in the quantum dots concentration. It was already observed that pure polyaniline is usually associated with a quasi-2D fractal dimension and the presence of nano-sized scatterers lead to an increase to quasi-3D fractal dimensionality [34,35]. In order to analyze the possible interactions between quantum dots for PANI-TiO₂-X nanocomposites we analyze the $S(q)$ vs. q structure factor plots, as shown in Fig. 4. The experimental structure factors $S(q)$ were extracted from the following equation: $I(q)=\phi P(q)$

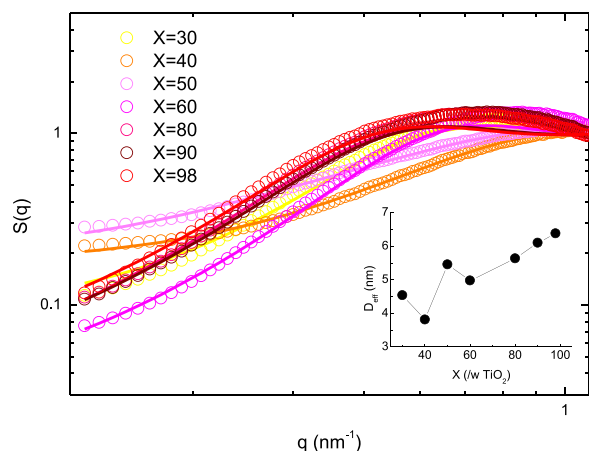


Fig. 4. Structure factor plots [$S(q)$ vs q] and screened Coulomb repulsive interaction model fitting for PANI-TiO₂-X with X=30, 40, 50, 60, 80, 90 and 98. The inset shows the effective diameter (D_{eff}) of quantum dots dependence with TiO₂ concentration (X). (For interpretation of the references to color in this figure, the reader is referred to the web version of this article.)

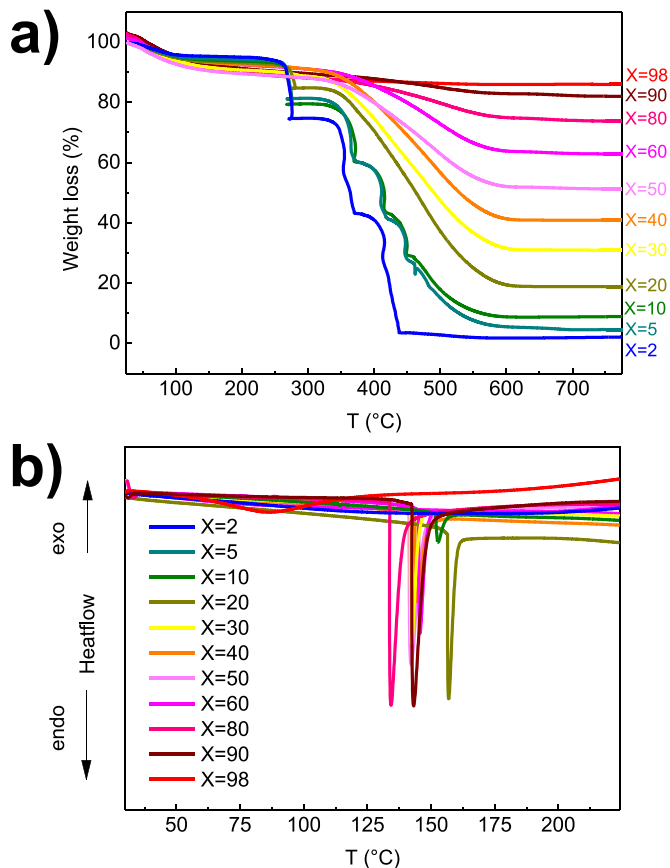


Fig. 5. (a) TGA and (b) DSC analyses for PANI-TiO₂-X nanocomposites with X=0, 2, 5, 10, 20, 30, 40, 50, 60, 80, 90 and 98. (For interpretation of the references to color in this figure, the reader is referred to the web version of this article.)

Table 2

TGA and DSC analyses for PANI-TiO₂-X with X=2, 5, 10, 20, 30, 40, 50, 60, 80, 90 and 98.

X	2	5	10	20	30	40	50	60	80	90	98
X_{real} (%w)	2	5	9.5	20.1	33.6	43.6	56.3	66.4	79.8	88.1	94
T_f (°C)	–	–	153	157	142	145	146	142	134	143	–

The real weight fraction of titanium oxide quantum dots (X_{real}) was extracted from TGA analysis and the fusion temperature (T_f) was extracted from DSC analysis.

$S(q)$ where ϕ is the volume fraction, using X=10 as the reference for poorly interacting quantum dots assuming that $I(q)_{X=10}=P(q)$. In all cases analyzed ($X > 30$), $S(q)$ decreases from the non-interacting unity value at the low- q region ($q < 1 \text{ nm}^{-1}$) suggesting the presence of screened Coulomb repulsive interactions between neighbor quantum dots. It is important to remark, that for highly concentrated quantum dots, other short-range interactions could also be present, such as capillary forces between quantum dots [36]. However, for simplicity, we neglect that contribution and fit $S(q)$ experimental data using only the screened Coulomb repulsive interaction implemented by the mean spherical approximation (MSA) [37]. The effective diameter (D_{eff}) extracted from the MSA analysis showed a slight increase with increasing X, as shown in Fig. 4-inset, suggesting the increment in the Coulomb repulsive interactions as a consequence of the increasing concentration of TiO₂ quantum dots. In addition to the physical impediment due to the presence of polymer chains, in analogy with the blocking agent effect in the preparation of mesoporous anatase [38], these Coulomb repulsion interactions could be also responsible of the equally-sized quantum dots independently of the concentration. The repulsion forces between the growing quantum dots are probably interrupting the growing process avoiding its coalescence, even in the concentrated regime.

3.3. High resolution transmission electron microscopy (HR-TEM)

HR-TEM image in low magnification for PANI-TiO₂-X with X=90 is shown in Fig. 1b, showing the presence of quantum dots embedded in the polymer matrix. In addition, HR-TEM images for three selected nanocomposites in the diluted (X=10), medium (X=40) and concentrated (X=90) regime are shown in Fig. 1c. For all samples we observed TiO₂ quantum dots with low aspect ratio, sized between 3 and 8 nm diameter, in agreement with XRD and SAXS analyses. The Fourier transform pattern showed an inter-planar spacing $\sim 3.5 \text{ \AA}$, ascribed to anatase (101) plane, in accordance with the peak at $2\theta=25.5^\circ$ observed in XRD diagrams. We also observed for X=10, that the polyaniline zone showed local structural order as shown in Fig. 1c, with an associated inter-planar spacing $\sim 3.5 \text{ \AA}$, ascribed to polyaniline (110) plane in its emeraldine salt form, associated to the peak at $2\theta=25.5^\circ$ observed in XRD diagrams. Additionally, EDS analysis showed the presence of Ti, O and C, N, S, O elements for the quantum dots and polyaniline zones, respectively.

3.4. Thermogravimetric analysis (TGA)

TGA analyses for PANI-TiO₂-X nanocomposites with X=2, 5, 10, 20, 30, 40, 50, 60, 80, 90 and 98 are showed in Fig. 5a. From the total weight loss in the 25–700 °C range we obtain the real quantum dots weight fraction for all nanocomposites (X_{real}), as summarized in Table 2. In all cases, the real quantum dots weight fraction (X_{real}) is very similar for the theoretical weight fraction (X) assuming total reaction of titanium propoxide to form titanium oxide quantum dots. In the higher concentration regime (X=30–98) a small weight loss is observed below $\sim 100^\circ \text{C}$, probably related to the loss of humidity and a broad weight loss at $T=300\text{--}550^\circ \text{C}$ associated to the total decomposition of polyaniline. In addition to the total decomposition of polyaniline, X=20 showed a previous decomposition step associated with an associated weight loss at $\sim 250^\circ \text{C}$, that could be attributed to the degradation of DBSA. X=2, 5 and 10 showed additional previous decomposition steps associated to weight losses starting around 270°C and 370°C , probably due to evaporation and degradation of pure DBSA and destruction of the interaction between the polymer chain and the dopant [39]. In all cases, above 450°C the weight loss could be related to the chemical structure decomposition of the backbone of PANI polymer.

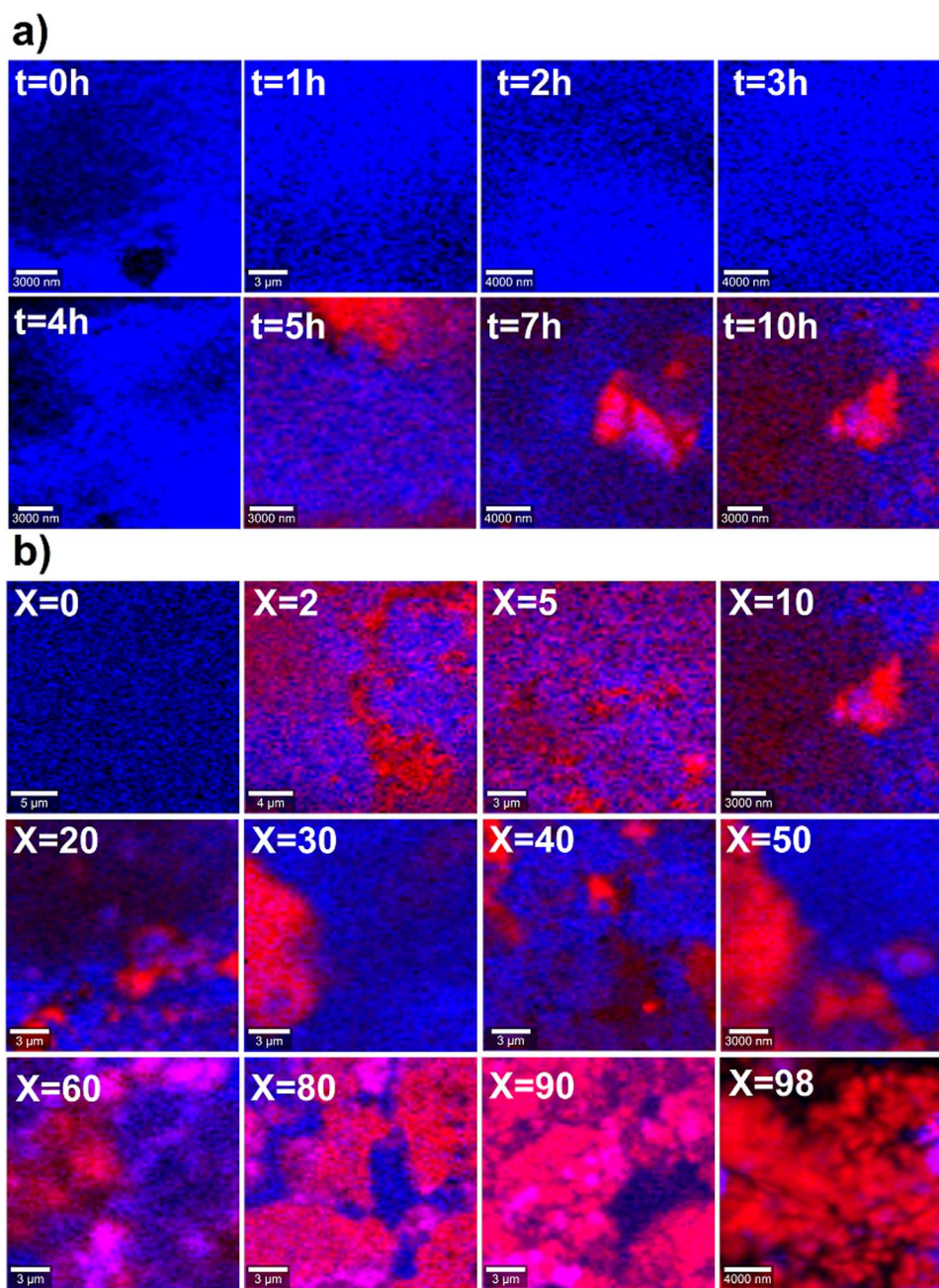


Fig. 6. Confocal Raman images for PANI-rich (blue), TiO₂-rich (red) and PANI-TiO₂-interphase (purple) zones for (a) PANI-TiO₂-10-t nanocomposite at different stages of the quantum dots growth with t=0–10 h and (b) PANI-TiO₂-X nanocomposites with X=0, 2, 5, 10, 20, 30, 40, 50, 60, 70, 80, 90 and 98. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

3.5. Differential scanning calorimetry (DSC)

DSC analyses for PANI-TiO₂-X are shown in Fig. 5b. X=0 and 5 compositions showed no evidence of glass transition or fusion processes in the 20–250 °C temperature range. However, X=10 to 90 composition range showed a sharp endothermic peak at T=145–160 °C associated with the melting process, suggesting an increase in the degree of order of polymer fibers, as already observed previously for other polyaniline-quantum dots nanocomposites [35]. The composite with higher quantum dots concentration (X=98) showed no fusion peak or at least it could not be detected, probably due to the low amounts of polyaniline fibers ($X_{\text{real}} \sim 6\%$ w/w). It is important to remark that the temperature range where the fusion process takes place showed no weight loss in TGA analyses corroborating that the peak is associated to a process without any weight loss, such as a fusion process.

3.6. Confocal Raman spectroscopy

Confocal Raman images for PANI-TiO₂-10-t nanocomposites at different stages of the quantum dots growth with t=0, 1, 2, 3, 4, 5, 7 and 10 hs are shown in Fig. 6a and PANI-TiO₂-X with X=0, 2, 5, 10, 20, 30, 40, 50, 60, 80, 90 and 98 are shown in Fig. 6b. Confocal Raman images with a resolution of $\sim 265 \times 265 \text{ nm}^2$ per pixel were obtained by collecting the total amount of 5625 Raman spectra to generate the $20 \times 20 \mu\text{m}^2$ total area images shown in Fig. 6a and b. In order to generate the red and blue contrast in the images, one can choose to filter each Raman spectra by components based in the relative intensity of selected Raman peaks. Confocal Raman images were obtained by filtering the TiO₂ E_g mode at $\sim 153 \text{ cm}^{-1}$ and PANI $\delta(\text{C-H})$ bending mode at $\sim 1170 \text{ cm}^{-1}$, in order to obtain TiO₂-rich (red) and PANI-rich (blue) zones, respectively. Confocal Raman spectra for PANI-TiO₂-10-t

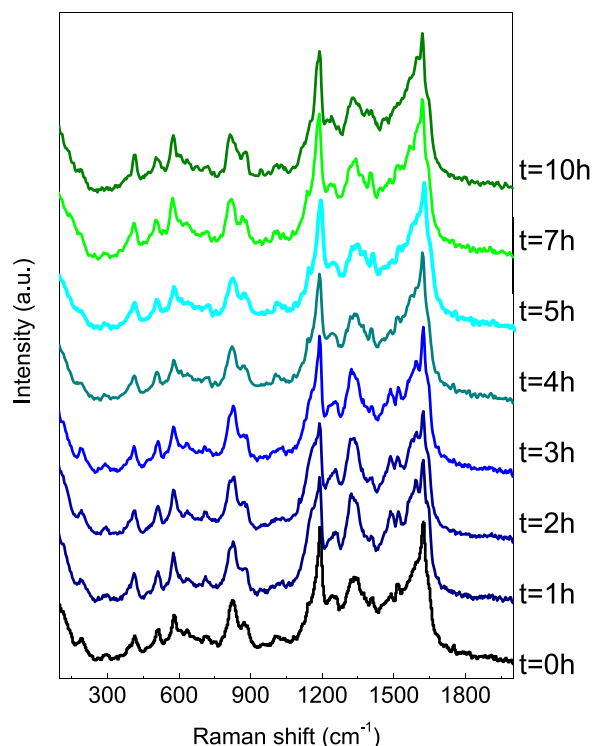


Fig. 7. Confocal Raman spectra at PANI-TiO₂-10-t nanocomposite at different stages of the quantum dots growth with t=0–10 h.

nanocomposites at different stages of the quantum dots growth with t=0, 1, 2, 3, 4, 5, 7 and 10 hs are shown in Fig. 7. Raman spectra for TiO₂-rich showed four typical peaks at ~153, ~415, ~515 and ~630 cm⁻¹, ascribed to E_g, B_{1g}, A_{1g} and E_g anatase polymorph modes, respectively [40]. On the other hand, Raman spectra for pure PANI showed peaks at ~576 cm⁻¹ ascribed to C-N-C-H out-of-plane deformation mode, ~830 cm⁻¹ ascribed to C-H wagging mode, ~1170 and 1250 cm⁻¹ ascribed to C-H bending modes of the aromatic ring, at ~1334 cm⁻¹ to the polaron C-N+• stretching mode, at ~1415 and 1486 cm⁻¹ to C-N and C=N stretching modes, and at ~1590 and 1620 cm⁻¹ ascribed to C-C and C=C stretching mode of the aromatic ring. No evidence of TiO₂ quantum dots formation was observed for t < 4 h. However, the peak ascribed to the polaron C-N+• stretching mode showed a relevant increase in its relative intensity with increasing time for the t < 4 h range, while a suppression in its relative intensity was observed for t > 4 h. The suppression in the polyaniline polaron population together with the appearance of titanium oxide quantum dots observed for t > 4 h could be suggesting the presence of charge interactions at the interphase. Confocal Raman spectra for PANI-TiO₂-X with X=0, 2, 5, 10, 20, 30, 40, 50, 60, 80, 90 and 98 are shown in Fig. 8. The peak ascribed to the polaron C-N+• stretching mode showed an increase in its relative intensity with TiO₂ additions, for X=2 and 5 at the TiO₂-rich zones and at the PANI-TiO₂-interphase zones for X=10, 20 and 30, as shown in Fig. 8. The presence of low amounts of TiO₂ quantum dots is somehow interacting with the charge carriers of polyaniline leading to an increase of the polaron population, as already observed previously for similar nanocomposites [34,35]. On the other hand, the peak ascribed to the polaron C-N+• stretching mode showed a decrease in its relative intensity at the PANI-TiO₂-interphase and PANI-rich zones for X=40, 50, 60, 80, 90 and 98. Moreover, at the higher concentration regime (X=90 and 98), confocal Raman spectra showed an increment in the relative intensity of a peak at ~1500 cm⁻¹, which was especially observed at the PANI-TiO₂-interphase zones. The additional zone in the confocal Raman images and spectra (purple in Figs. 6a and b and 8, respectively) corresponding to PANI-TiO₂-interphase zones was filtered using the ~1500 cm⁻¹ peak. In order to

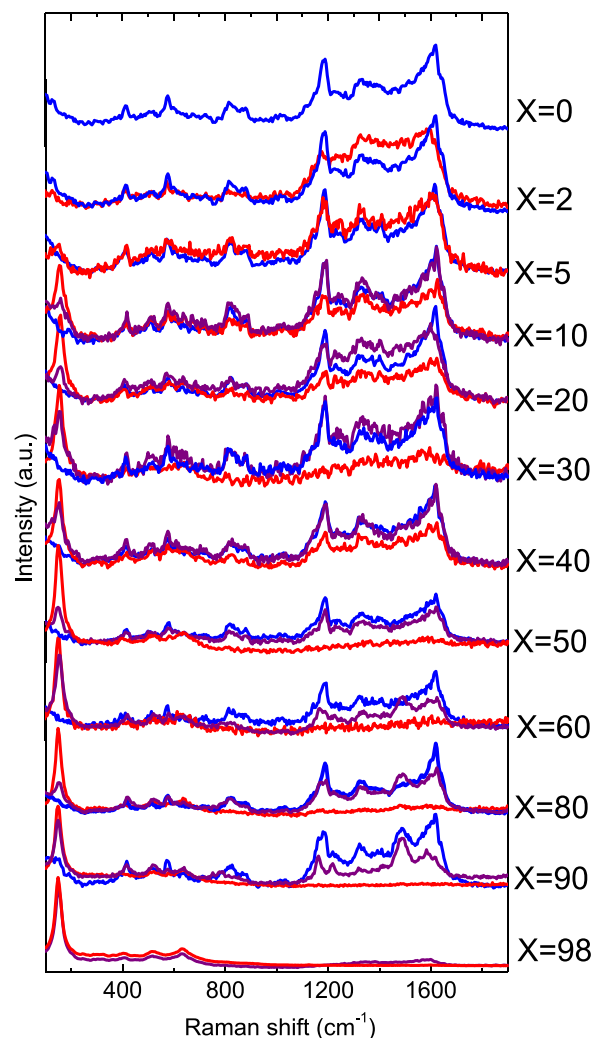


Fig. 8. Confocal Raman spectra at selected ~266×266 nm² area marked in Fig. 6 for PANI-rich (blue), TiO₂-rich (red) and PANI-TiO₂-interphase (purple) zones for PANI-TiO₂-X nanocomposites.

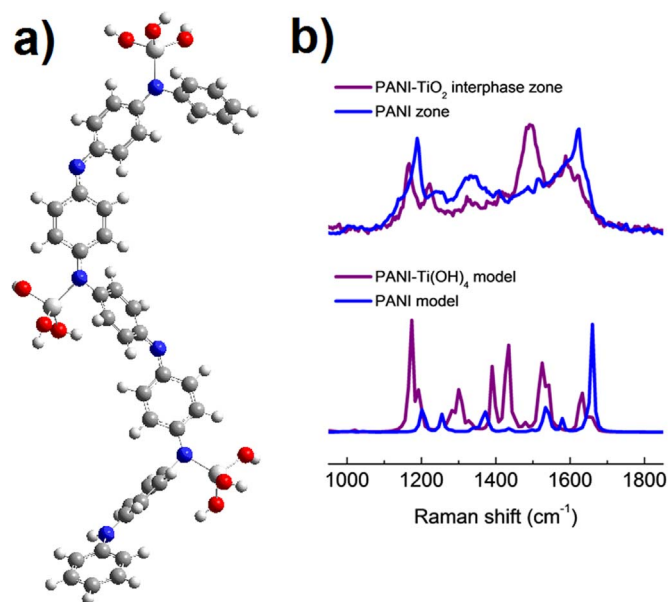


Fig. 9. (a) PANI-Ti(OH)₄ model after DFT optimization and (b) experimental (X=90) and theoretical Raman spectra calculated for PANI and PANI-Ti(OH)₄ model.

Table 3

Experimental Raman frequencies for PANI-TiO₂-90 at PANI-TiO₂-interphase zone and theoretical Raman simulation for PANI-Ti(OH)₄ model.

Experimental	Theoretical	Assignment
1166 cm ⁻¹ (s)	1171 cm ⁻¹ (s)	δ (C–H)
1220 cm ⁻¹ (m)	1190 cm ⁻¹ (m)	δ (C–H)
1322 cm ⁻¹ (m)	1303 cm ⁻¹ (m)	ν (C–N ⁺)
1378 cm ⁻¹ (w)	1392 cm ⁻¹ (s)	ν (C–N)
1419 cm ⁻¹ (w)	1431 cm ⁻¹ (s)	ν (C–N)
1490 cm ⁻¹ (s)	1521 cm ⁻¹ (s)	ν (C–N)
1589 cm ⁻¹ (s)	1628 cm ⁻¹ (m)	ν (C–C)

Raman intensities are symbolized as follows: s (strong), medium (m), weak (w). Assignments are symbolized as follows: bending (δ), stretching (ν).

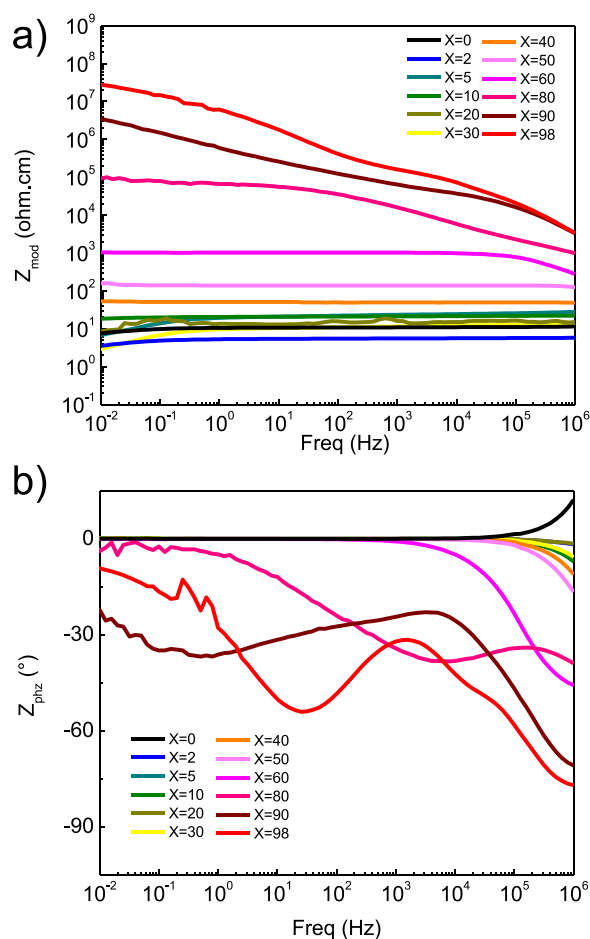


Fig. 10. Impedance modulus (a) and phase (b) versus frequency plots for PANI-X nanocomposite.

explain the appearance of this peak, we performed DFT calculations in order to obtain PANI and PANI-Ti(OH)₄ optimization and theoretical Raman spectra. The PANI-Ti(OH)₄ model shown in Fig. 9a was used to evaluate the effect of possible chemical functionalization between PANI and titanium oxide quantum dots. Theoretical Raman spectra for PANI and PANI-Ti(OH)₄ and comparison with experimental data are shown in Fig. 9b and the vibrational modes assignments are summarized in Table 3. Both the frequencies and relative intensity related to theoretical simulation are in good agreement with those observed experimentally at the PANI-TiO₂-interphase zones. Based in this simulation, we can assume that for higher concentration of titanium oxide quantum dots, there is a well-defined chemical interaction between PANI and TiO₂, which is also consistent with the suppression in the polaron population.

3.7. Impedance spectroscopy

The impedance modulus versus frequency plots for PANI-TiO₂-X with X=0, 2, 5, 10, 20, 30, 40, 50, 60, 80, 90 and 98 are shown in Fig. 10a. The presence of low amounts of TiO₂ quantum dots (X=2–30) lead to a decrease in the impedance modulus showing the highest AC conductivity values for X=30, as already reported [41]. This is in agreement with the increase in the polaron population for X < 30 respect to pure PANI observed from the Raman analyses. The increase in the conductivity, observed for these low concentrations of TiO₂ quantum dots, is a crucial aspect for improving the performance of these materials as potential electrodes for supercapacitor applications. However, X > 50 showed a notorious increase in the impedance modulus respect to pure PANI also in relation to the suppression in the polaron population observed from the Raman analyses. The phase (φ) versus frequency plots are shown in Fig. 10b. X < 50 showed a dominant resistive behavior, ascribed to the zero values of the phase (φ) for almost the whole frequency regime (f=10⁻²–10⁵ Hz). On the other hand, an increasing capacitive behavior is observed for X > 50 in agreement with the decrease in the charge carrier mobility for PANI-TiO₂-X composites with higher TiO₂ quantum dots concentration. However, in spite of the lower conductivity observed at the higher concentrated regime of TiO₂ quantum dots, the enormous interface area and the chemical functionalization of polyaniline chains could be very promising as electrode materials for lithium-ion batteries.

4. Conclusions

In this report, we present for the first time, the *in situ* growth of titanium oxide quantum dots in polyaniline host via water vapor flow diffusion as an easily adaptable route to prepare other ceramic-polymer nanocomposites. High resolution transmission electron microscopy revealed the presence of ~3–8 nm quantum dots in the whole concentration regime and small angle X-ray scattering showed the presence of interparticle Coulomb repulsive interactions which can be partially interrupting the growing process to form equally-sized quantum dots, independently of the concentration. Confocal Raman spectroscopy showed an increase in the polyaniline polaron population for the quantum dots diluted regime and a suppression at the concentrated regime ascribed to the formation of chemical bonds at the interface confirmed by theoretical simulations. The enhancement and suppression of the polaron population was directly related to the lowering and enhancement in the impedance for diluted and concentrated regime, respectively. In agreement with the previous observation, the *in situ* growth of ceramic quantum dots in polyaniline host via water vapor flow diffusion could be very useful as a novel approach to prepare electrode materials for energy conversion and storage applications.

Acknowledgments

The authors wish to thank the Uruguayan CSIC, ANII and PEDECIBA funding institutions. We would also like to thank financial support of EQC-X-2012-1-14 and LNLS-CNPEN-20160292 research projects, as well as technical support of the LNLS-CNPEN SAXS-1 station members. In addition, we would like to thank technical support of Alvaro Olivera and the collaboration of Laura Fornaro at GDMEA-CURE high-resolution transmission electron microscopy laboratory.

References

- [1] K. Vallé, P. Belleville, F. Pereira, C. Sanchez, Hierarchically structured transparent hybrid membranes by *in situ* growth of mesostructured organosilica in host polymer, *Nat. Mater.* 5 (2006) 107–111.
- [2] C. Peng, S. Zhang, D. Jewell, G.Z. Chen, Carbon nanotube and conducting polymer composites for supercapacitors, *Prog. Nat. Sci.* 18 (2008) 777–788.
- [3] M. Zhi, C. Xiang, J. Li, M. Li, N. Wu, Nanostructured carbon-metal oxide composite

- electrodes for supercapacitors: a review, *Nanoscale* 5 (2013) 72–88.
- [4] L. Yang, S. Wang, J. Mao, J. Deng, Q. Gao, Y. Tang, O.G. Schmidt, Hierarchical MoS_2 /Polyaniline nanowires with excellent electrochemical performance for lithium-ion batteries, *Adv. Mater.* 25 (2013) 1180–1184.
 - [5] Z. Tu, Y. Kambe, Y. Lu, L.A. Archer, Nanoporous polymer-ceramic composite electrolytes for lithium metal batteries, *Adv. Energy Mater.* 4 (2014) 1300654.
 - [6] D. Lin, W. Liu, Y. Liu, H.R. Lee, P.C. Hsu, K. Liu, Y. Cui, High ionic conductivity of composite solid polymer electrolyte via in situ synthesis of monodispersed SiO_2 nanospheres in poly(ethylene oxide), *Nano Lett.* 16 (2016) 459–465.
 - [7] W.K. Shin, J. Cho, A.G. Kannan, Y.S. Lee, D.W. Kim, Cross-linked composite gel polymer electrolyte using mesoporous methacrylate-functionalized SiO_2 nanoparticles for lithium-ion polymer batteries, *Sci. Rep.* 6 (2016) 26332.
 - [8] K. Xie, J. Li, Y. Lai, Z. Zhang, Y. Liu, G. Zhang, H. Huang, Polyaniline nanowire array encapsulated in titania nanotubes as a superior electrode for supercapacitors, *Nanoscale* 3 (2011) 2202–2207.
 - [9] C. Lai, G.R. Li, Y.Y. Dou, X.P. Gao, Mesoporous polyaniline or polypyrrole/anatase TiO_2 nanocomposite as anode materials for lithium-ion batteries, *Electrochim. Acta* 55 (2010) 4567–4572.
 - [10] S. Peng, J. Liang, S.G. Mhaisalkara, S. Ramakrishna, In situ synthesis of platinum/polyaniline composite counter electrodes for flexible dye-sensitized solar cells, *J. Mater. Chem.* 22 (2012) 5308.
 - [11] H. Gu, J. Guo, X. Zhang, Q. He, Y. Huang, H.A. Colorado, N. Haldolaarachchige, H. Xin, D.P. Young, S. Wei, Z. Guo, Giant magnetoresistive phosphoric acid doped polyaniline–silica nanocomposites, *J. Phys. Chem. C* 117 (2013) 6426–6436.
 - [12] K. Wang, J. Huang, Z. Wei, Conducting polyaniline nanowire arrays for high performance supercapacitors, *J. Phys. Chem. C* 114 (2010) 8062–8067.
 - [13] D.C. Schnitzler, M.S. Meruvia, I.A. Hümmelgen, A.J.G. Zarbin, Preparation and characterization of novel hybrid materials formed from $(\text{Ti}, \text{Sn})\text{O}_2$ nanoparticles and polyaniline, *Chem. Mater.* 15 (2003) 4658–4665.
 - [14] S. Jain, H. Goossens, M. Van Duin, P. Lemstra, Effect of in situ prepared silica nano-particles on non-isothermal crystallization of polypropylene, *Polymer* 46 (2005) 8805–8818.
 - [15] E.A. Olivetti, J.H. Kim, D.R. Sadoway, A. Asatekin, A.M. Mayes, Sol-gel synthesis of vanadium oxide within a block copolymer matrix, *Chem. Mater.* 18 (2006) 2828–2833.
 - [16] L. Zhang, L. Chen, Q.H. Wan, Preparation of uniform magnetic microspheres through hydrothermal reduction of iron hydroxide nanoparticles embedded in a polymeric matrix, *Chem. Mater.* 20 (2008) 3345–3353.
 - [17] S. Obuchovsky, H. Frankenstein, J. Vinokur, A.K. Hailey, Y.L. Loo, G.L. Frey, Mechanism of metal oxide deposition from atomic layer deposition inside nonreactive polymer matrices: effects of polymer crystallinity and temperature, *Chem. Mater.* 28 (2016) 2668–2676.
 - [18] F.A. Rabuffetti, J.S. Lee, R.L. Brutchey, Vapor diffusion sol-gel synthesis of fluorescent perovskite oxide nanocrystals, *Adv. Mater.* 24 (2012) 1434–1438.
 - [19] X. Li, H. Zhang, G. Wang, Z. Jiang, A novel electrode material based on a highly homogeneous polyaniline/titanium oxide hybrid for high-rate electrochemical capacitors, *J. Mater. Chem.* 20 (2010) 10598–10601.
 - [20] N. Parveen, M.O. Ansari, M.H. Cho, Route to high surface area, mesoporosity of polyaniline-titanium dioxide nanocomposites via one pot synthesis for energy storage applications, *Ind. Eng. Chem. Res.* 55 (2016) 116–124.
 - [21] G. Liu, X. Gao, H. Wang, A.Y. Kim, Z. Zhao, J.K. Lee, D. Zou, A novel photoanode with high flexibility for fiber-shaped dye sensitized solar cells, *J. Mater. Chem. A* 4 (2016) 5925–5931.
 - [22] M. Shang, H. Hu, G. Lu, Y. Bi, Synergistic effects of SrTiO_3 nanocubes and Ti^{3+} dual-doping for highly improved photoelectrochemical performance of TiO_2 nanotube arrays under visible light, *J. Mater. Chem. A* 4 (2016) 5849–5853.
 - [23] W. Kohn, L.J. Sham, Self-consistent equations including exchange and correlation effects, *Phys. Rev. A* 140 (1965) 1133.
 - [24] P. Hohenberg, W. Kohn, Inhomogeneous electron gas, *Phys. Rev. B* 136 (1964) 864.
 - [25] R.G. Parr, W. Yang, Density-Functional Theory of Atoms and Molecules, Oxford University Press, 1989.
 - [26] A.D. Becke, A new mixing of Hartree-Fock and local density-functional theories, *J. Chem. Phys.* 98 (1993) 5648.
 - [27] J.P. Perdew, J.A. Chevary, S.H. Vosko, K.A. Jackson, M.R. Pederson, D.J. Singh, C. Fiolhais, Atoms, molecules, solids, and surfaces: applications of the generalized gradient approximation for exchange and correlation, *Phys. Rev. B* 46 (1992) 6671.
 - [28] P.J. Hay, W.R. Wadt, Ab initio effective core potentials for molecular calculations, *J. Chem. Phys.* 82 (1985) 270–283.
 - [29] M.J. Frisch, et al., Gaussian, Inc., Wallingford CT, 2009.
 - [30] J.P. Pouget, M.E. Jozefowicz, A.J. Epstein, X. Tang, A.G. MacDiarmid, X-ray structure of polyaniline, *Macromolecules* 24 (1991) 779–789.
 - [31] R. Mo, Z. Lei, K. Sun, D. Rooney, Facile synthesis of anatase TiO_2 quantum-dot/graphene nanosheet composites with enhanced electrochemical performance for lithium-ion batteries, *Adv. Mater.* 26 (2014) 2084–2088.
 - [32] A. Patterson, The Scherrer formula for I-ray particle size determination, *Phys. Rev.* 56 (1939) 978–982.
 - [33] G. Beaucage, Approximations leading to a unified exponential/power-law approach to small-angle scattering, *J. Appl. Crystallogr.* 28 (1995) 717–728.
 - [34] M. Romero, R. Faccio, H. Pardo, M.A. Tumelero, B. Montenegro, C.C. Plá Cid, A.A. Pasa, A.W. Mombrú, The effect of manganite nanoparticle addition on the low field magnetoresistance of polyaniline, *J. Mater. Chem. C* 3 (2015) 12040.
 - [35] D. Mombrú, M. Romero, R. Faccio, A.W. Mombrú, Tuning electrical transport mechanism of polyaniline–graphene oxide quantum dots nanocomposites for potential electronic device applications, *J. Phys. Chem. C* 120 (2016) 25117–25123.
 - [36] J. Bahadur, D. Sen, S. Mazumder, G. Santoro, S. Yu, S.V. Roth, Y.B. Melnichenko, Colloidal nanoparticle interaction transition during solvent evaporation investigated by in-situ small-angle X-ray scattering, *Langmuir* 31 (2015) 4612–4618.
 - [37] J.P. Hansen, J.B. Hayter, A rescaled MSA structure factor for dilute charged colloidal dispersions, *Mol. Phys.* 46 (1982) 651–656.
 - [38] I.L. Violi, M.C. Perez, M.C. Fuertes, G.J.A.A. Soler-Illia, Highly ordered, accessible and nanocrystalline mesoporous TiO_2 thin films on transparent conductive substrates, *ACS Appl. Mater. Interfaces* 4 (2012) 4320–4330.
 - [39] T. Chen, C. Dong, X. Li, J. Gao, Thermal degradation mechanism of dodecylbenzene sulfonic acid- hydrochloric acid co-doped polyaniline, *Polym. Degrad. Stab.* 94 (2009) 1788–1794.
 - [40] F. Tian, Y. Zhang, J. Zhang, C. Pan, Raman spectroscopy: a new approach to measure the percentage of anatase TiO_2 exposed (001) facets, *J. Phys. Chem. C* 116 (2012) 7515–7519.
 - [41] S. Manjunath, K.R. Anilkumar, M. Revanasiddappa, M.V.N. Ambika Prasad, Frequency-dependent conductivity and dielectric permittivity of polyaniline/ TiO_2 composites, *Ferroelectr. Lett.* 35 (2008) 36–46.