Journal of Solid State Chemistry 250 (2017) 60–67

Contents lists available at ScienceDirect

Journal of Solid State Chemistry

journal homepage: www.elsevier.com/locate/jssc

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 Fisicoquímica 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 (SiO_2) or titania (TiO_2) 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 TiO_2 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 TiO_2. 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

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-TiO_2-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-TiO_2-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 deionizated water (H_2O) under vigorously stirring at 500 rpm for 30 min. In order to obtain TiO_2/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 deionizated 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-TiO_2−10-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:

$$PANI(s)+Ti(OPr)_4(l)+H_2O(g)\rightarrow PANI(s)+Ti(OH)_4(l)+4PrOH(l)+H_2O(g)\rightarrow PANI(s)+TiO_2(s)$$

The dried powders were then pressed at 50 kN/cm^2 pressure to obtain the *in situ* growth TiO_2 quantum dots, named as PANI-TiO_2-X, with X being the TiO_2/PANI weight ratio.

2.2. Characterization of PANI-TiO_2-X

PANI-TiO_2-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-TiO_2-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, confocal Raman images were obtained for a 20×20 μm^2 total area with a resolution of ~265×265 nm^2 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-TiO_2-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.

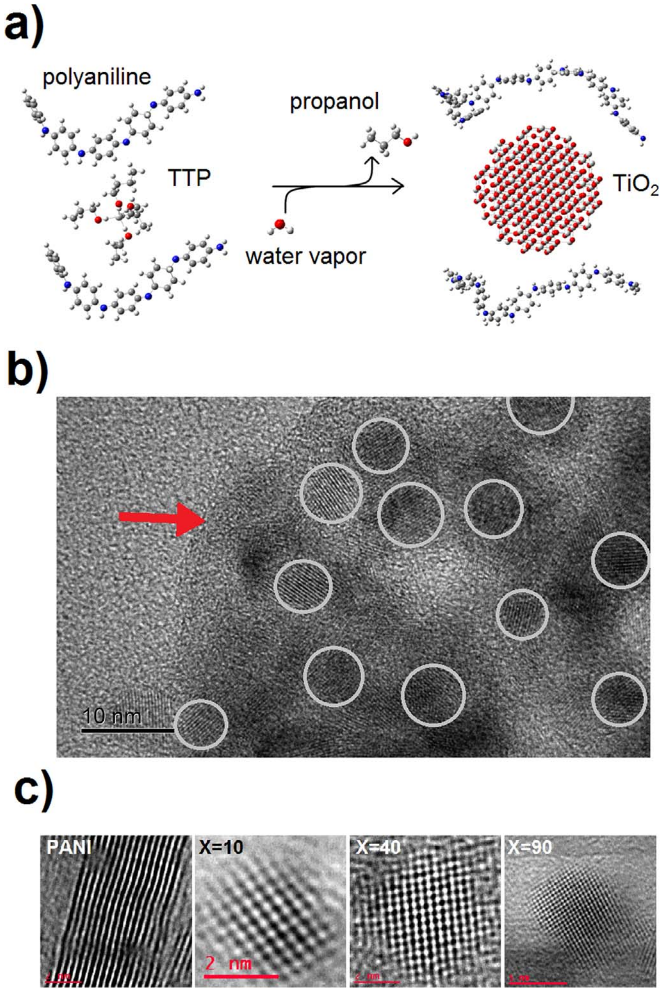

Fig. 1. (a) Scheme of the preparation route for PANI-TiO_2-X and HR-TEM images for (b) PANI-TiO_2-X in low magnification and (c) PANI and PANI-TiO_2-X with X=10, 40 and 90 in high magnification. The grey circles are a guide to the eye to show TiO_2 quantum dots and the red arrow is showing the PANI zone. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

3. Results and discussion

3.1. X-ray powder diffraction (XRD)

XRD patterns for PANI-$TiO_2$10 nanocomposites at different stages of the quantum dots growth, named as PANI-TiO_2-10-t with t=0, 1, 2, 3, 4, 5, 7 and 10 h are shown in Fig. 2a. Typical XRD profile for pure