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# Intercalation of poly(3,4-ethylenedioxythiophene) within halloysite nanotubes: Synthesis of composites with improved thermal and electrical properties

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## ABSTRACT

Improvements in thermal stability and electrical conductivity of poly(3,4ethylenedioxythiophene), or PEDOT, were observed by bonding it to an acidified nano-structured tubular silico-aluminate clay, Halloysite (HNT), obtaining the corresponding doped composite (PEDOT:HNT). The composites were synthesized via suspension polymerization in aqueous media using ammonium persulfate (APS) as oxidant. Changes in the hydrodynamic conditions and APS/EDOT ratio were studied. PEDOT was also doped with hydrochloric acid and poly(p-styrene sulfonic acid). PEDOT:HNT composites were characterized by Scanning Transmission Electron Microscopy with Energy-Dispersive X-ray spectroscopy (STEM-EDS), Thermogravimetric analysis (TGA), X-Ray Diffraction (XRD), Four Point Electrical Conductivity Tests and Nitrogen Adsorption Analysis in order to obtain the surface area and the pore size distribution (PSD) of bare and coated halloysite. We observed that the halloysite, which is made of multilayer nano-tubes, does not appear to work only as a template. Halloysite nanotubes interact with PEDOT as functional dopants, resulting in PEDOT:HNT composites with high thermal stability and electrical conductivity. XRD analysis revealed intercalation of PEDOT inside the halloysite nano-tubes. XRD analysis also showed that the polymer/nano-clay interaction does not merely take place at the surface or inside the lumen, but does also modify the properties at the HNT walls, restricting PEDOT mobility. STEM-EDS of a transverse observation of a single PEDOT:HNT nano-tube confirmed that carbon and sulfur (associated to PEDOT) are found inside the halloysite walls. Moreover, STEM, XRD, measured PSD and TGA tests demonstrate a strong influence of hydrodynamic synthesis variables on the amount of free and intercalated PEDOT in HNT walls and, as a consequence, on its electrical conductivity.

## 1. Introduction

Since it was discovered in the early eighties by Bayer Central Research Department, a great variety of technological solutions were proposed and implemented for poly(3,4-ethylenedioxythiophene) or PEDOT, which is one of the most common and used inherently conducting polymers (ICP) in our days [1–3]. Technology solutions comprise inks for flexible circuits, replacing indium–tin oxide (ITO) coatings over flexible or active surfaces [1,2]; organic photovoltaic cells in combination with fullerenes or other nano-carbon structures [1–3]; and active layer components in organic light emitting diodes (OLED's), electroluminescence devices (EL) [1–3] or organic field effect transistors (OFETs) [1–4].

Particular synthetic routes based on 3,4-ethylene dioxythiophene (EDOT) polymerization inside or over a specific template have been described to obtain the desired structure: PEDOT nanotubes and nanowires [5–9] capable to be used in energy

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storage devices as supercapacitors. Templates can be classified in two kinds: soft and hard templates. Soft templates, based on dispersions (self- or non-template), emulsions and microemulsion polymerizations (where micelles work as templates). For hard templates on the contrary, EDOT polymerizes over an existing nanostructured component (like ceramics), or against nanochannels (filling up previously prepared holes), or over reactive templates, where PEDOT clones the desired shape, as the polymerization process consumes the template. Despite the attractive electrical properties reported for PEDOT nanotubes and wires, processes reported to obtain them are not easy to scale up.

A convenient chemical synthetic route to large quantities of PEDOT nanotubes/fibers has remained a challenge [7]. However, the challenge must be taken for very good reasons: the use of sustainable and renewable resources.

According to some authors [10], the use of small molecular weight counter-ions results in an improvement of the electrical properties of the resulting material. But they also have observed that PEDOT dopant counter-ions not only improve electrical conductivity by a charge alteration of the π-conjugated structure of PEDOT, but also by the influence of the ion over the polymeric chain preferential growth and structural regularity while monomer is polymerizing (slackening it off or curling it up).

Heeger and co-workers [11] observed something similar in their thermogravimetric analysis (TGA) charts and conductivity measurements at different temperatures, for PEDOT films doped with $PF_6^-$, $BF_4^-$ and $CF_3SO_3^-$. The PEDOT: $BF_4^-$ system lost less mass compared with PEDOT: $PF_6^-$. But if PEDOT: $BF_4^-$ seemed to be a material with a larger thermal stability, compared with $PF_6^-$ and $CF_3SO_3^-$-doped polymers, its electrical conductivity was the lowest in the series. Although TGA profiles are different for each PEDOT:-Dopant system, these charts show that doped PEDOT is rather stable up to 150 °C. Above 150 °C, a continuous degradation takes place until major decomposition occurs in the region between 390 °C and 450 °C.

Vitoratos and co-workers [12] studied the thermal stability of a thin film of CLEVIOS PH 500, PEDOT:PSS deposited on PET. This article describes an annealing process at 120 °C from 0 to 55 min and how it influences the electrical conductivity measured at different temperatures.

Zheng and co-workers [13,14] described the synthesis of PEDOT: p-toluene sulfonic acid salt nanoparticles, by a reversed micelle polymerization method. The experimental design varied the synthesis conditions and dopant compositions. The observed thermal stability allowed to conclude that PEDOT nanoparticles, made by a reverse micelle method, present a higher thermal stability and electrical conductivity than particles synthesized by conventional methods [14]. Moreover, they related this behavior to different causes: the dopant employed and its concentration with respect to the amount of PEDOT in the dispersion media.

It seems that the thermal stability of PEDOT composites improves with those changes without losing electrical conductivity by taking into account considerations such as the chosen dopant, having small PEDOT particle sizes, the PEDOT/dopant ratio and the absence of volatile components in the composite. Almost all considerations are easy to achieve, except for the dopant selection. PEDOT:Dopants for blending purposes to obtain polymer composites or other related applications, have many dopant options available.

A practical solution is to combine PEDOT with nano-structured templates, which work not only as supporting material, but also as dopant and template at the same time [6,9,15–24]. Other conducting polymers different from PEDOT use a variety of materials as templates such as: carbon nanotubes or fullerenes [6,15], sepiolites, nano-rod varieties of silico aluminates [25], attapulgites, sulfured cubic nano-silico aluminates [17,21]. Also halloysite, a nano-tubular silico aluminate was used with poly(pyrrole), poly(aniline) and 2,5-bis(2-benzoxazolyl) thiophene [16,18,20,22–24].

Halloysite is a nano-tubular silico-aluminate clay, with similarities in crystallographic and chemical structure to kaolin. It is about 500–2000 nm length, 50–100 nm diameter with a mean thickness of 20 nm in the wall of the tube, (Fig. 1a) [26–31]. Accordingly to some authors, halloysite's lumen occupies around 20% of the nanotube volume. This lumen can be chemically or biologically loaded with active substances for controlled released processes [31]. Although halloysite has been described and studied since 1826 by Omalius d'Halloy, it was until the mid 50ś of the last century, when researchers studied its nanometric nature and structure, (Fig. 1b) [28]. Moreover, how researchers conceive the halloysite wall structure, in accordance to crystallographic evidence, has changed during the decades. The idea from a solid wall, based on the combination of silicon and aluminum oxides [28], lead to the concept a series of curled layered porous walls, made of successive dehydrated “blanks” of aluminum oxide (inner part of the wall) and silicon oxide, with molecules of water intercalated nearby the exterior surface of the tube [29–31], (Fig. 1c). Lvov and co-workers describe halloysite nanotubes with this ideal chemical formula, $Al_2Si_2O_5(OH)_4 \times nH_2O$. They emphasize that recently mined halloysite contains two water molecules ($n = 2$), but after thermally treated or dried, halloysite nanotubes dehydrates, loosing water in an irreversible process, leading to halloysite products called 7 Å indicating its interlayer spacing.

The evolution of the model is relevant to understand that halloysite walls have pores, and such pores can be filled with molecules (with similar size as EDOT molecules).

The intercalation of chemical compounds inside halloysite walls (microporous) has been reported before for small inorganic species [31,32] and for monomers that diffuse inside pores and “in situ” polymerize to yield an inherently conducting polymer, like polyaniline [18]. In both cases, the authors follow the progress of their respective intercalation by observing spectroscopic results, mainly x-ray diffraction spectroscopy (XRD). Luca and co-workers for example [18], worked with copper catalysts dispersed in water to polymerize aniline. They showed that, prior to aniline exposure, the basal reflection gives a signal at 8.0 Å, attributed to the combined diffraction from the interlayer region (at 7.2 Å), the separation between the inner collapsed tube walls (~5 Å), and the separation between adjacent particles (~5 Å). But after the polymerization of aniline, the relative intensity of the shoulder assigned to the 7.1 Å interlayer was observed to increase slightly, attributed to the aniline-copper intercalation followed by the subsequent polymerization [18]. However, several authors, based on other techniques, do not support the idea of intercalation. Moreover, some inherently conductive polymers give reflections in XRD between 6 Å and 8 Å as it has been reported for PEDOT synthesized without any nano-clay [7,13,14].

Halloysite nanotubes surface is generally repented as silicon oxide having aluminum oxide beneath the silicon structure [31]. The importance of this conception is related to which chemical species are possible to attach outside the nanotube. In the case of halloysite composites, there are no reports on the material deposited in the exterior of the nanotubes. There has been no discussion on the benefits or consequences, in the composite properties, due to the intercalation of materials inside halloysite walls. Further characterization techniques, besides the spectroscopic ones, are required to support the idea of intercalation.

In this article, we describe how we dispersed EDOT and ammonium persulfate in water, inside halloysite walls, for consequently having the same components outside to polymerize EDOT to produce PEDOT under different hydrodynamic conditions. To