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# Influence of the FeO(OH) nanoparticles concentration in the in-situ synthesis of P3HT

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ABSTRACT

In general a nanocomposite material has better characteristics than each individual component, due to the effects produced by the synergies between the organic material and the nanoscale of the inorganic material. In this work new hybrid nanocomposites based on poly(3-hexylthiophene) (P3HT) and FeO(OH) nanoparticles were synthesized and characterized. FeO(OH) nanoparticles were synthesized by chemical bath. The P3HT-FeO(OH) nanocomposites were in-situ synthesized by chemical oxidation of 3HT (Sugimoto method) at different weight ratios (3HT/FeO(OH): 1/0.029, 1/0.048 and 1/0.074), using $FeCl_3$ as oxidant/catalyst. Effect of FeO(OH) nanoparticles content in P3HT on its physicochemical properties was studied. The dyads and triads configuration was determined by $^1$H NMR. In comparison with P3HT, a higher regioregularity was obtained in the composites with 3HT/FeO(OH) weight ratio of 1/0.048 and 1/0.074. The FTIR analyzes showed the presence of FeO(OH) in the P3HT and a strong interaction between P3HT and FeO(OH). Thermal stability and decomposition temperature were determined by thermogravimetry (TGA), better thermal stability and higher degradation temperature were showed by the composites. The UV–Vis and photoluminescence analyzes showed higher absorbance and higher photoluminescence intensity in P3HT-FeO(OH) nanocomposites, indicating the incorporation of FeO(OH) in the P3HT. Finally the composites were characterized by SEM and X-ray analysis. Composites showed interesting properties for optoelectronic applications.

## 1. Introduction

Nanocomposite materials have attracted a lot of attention due to their possible commercial exploitation as sensors, batteries, toners in copying machines, quantum electronic devices, smart windows, materials for electromagnetic shielding, etc. [1]. The study of conductive polymers composites has been of great interest due to the obtaining of conductive polymers with improved properties, which has increased its applicability. It is a well-known fact that nanoparticles are very small particles in the range of 10–50 nm, having more surface area or sites for reactions, high porosity and good mechanical properties [1]. Recently investigation groups have reported works related to different structures of nanoparticles that benefit the surface area, for example Li. K. et al. [2] synthesized mesoporous Pt nanospheres with tunable pore sizes. On the other hand, Liang Wang et al. [3] reported the synthesis of dendritic Pt−Pd nanocages with hollow interiors and porous dendritic shells, which were highly active catalysts in comparison with other Pt materials. This same group reported Au@Pd@Pt triple-layered core-shell structured nanoparticles, the proposed method is a significant finding for the facile creation of multilayered nanoarchitectures with designed compositions and desired functions [4]. Nanocomposites made from nanoparticles and conducting polymers possess the good properties of both components. The nanoparticles in addition to being blended are encapsulated by the conductive polymer, resulting in a significant improvement in the physical properties of the conductive polymers [5–9].

The poly(3-hexylthiophene) (P3HT) is one of the most extensively studied poly(3-alkylthiophene) (P3AT) due to its excellent electrical properties and ease processability in solution. By another hand, $Fe_3O_4$, $Fe_2O_3$, and FeO(OH) have attracted great interests due to their natural abundance, physical and chemical stability and eco-friendliness [10]. Goethite (α-FeO(OH)) has potential applications in many fields such as electrode materials, catalysts, adsorption of arsenite, and magnetic

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materials and is one of the most widespread forms of iron oxides in terrestrial soils, sediments and ore deposits, as well as a common weathering product in rocks of all types [10,11]. Further iron (hydr) oxides substantially contribute to the uptake of toxic elements in natural mineral assemblies, even when the mass fraction of iron hydroxides in these assemblies is relatively low [12].

Various conductive polymer/iron oxide composites have been synthesized with different strategies and studied their properties and applications. For instance, synthesis via in-situ co-precipitation of iron oxide ($Fe_3O_4$) in the presence of the poly(4-methyl-1-phenylpenta-1,4-dien-one) semiconductor polymer was reported, according to HRTEM results, a good dispersion of $Fe_3O_4$ nanoparticles in the polymer matrix was obtained [13]. PANI-$Fe_xO_y$ composites were prepared by in situ preparation of iron oxide in presence of polyaniline by Wan et al. [14], it was determined that the structure, electrical and magnetic properties of the resulting PANI-$Fe_xO_y$ composites depend on the pH value of the reaction medium and temperature.

Another strategy has been reported on the in-situ synthesis of the polymer phase (conductive polymer) in the presence of iron oxide, different composites of iron-oxides in polypyrrole, polyaniline, PEDOT, polythiophene and poly(3-octylthiphene) have been synthesized [6–9,15,16]. For instance, Xin Li et al. synthesized PANI–β-NSA/Fe(OH) composites, the electro-magnetic properties of the core–shell micro/nanostructured composites are adjustable by changing the ratio of Fe(OH) to aniline monomer [6]. Kakarla Raghava Reddy et al. [7] synthesized nanocomposites ($Fe_3O_4$–PEDOT) by in-situ chemical oxidative polymerization of 3, 4-ethylenedioxythiophene (EDOT) in prescence of $Fe_3O_4$ nanoparticles. Zhanhu Guo et al. [15] studied the effect of iron oxide ($Fe_2O_3$) nanoparticles on the chemical polymerization of pirroles, the thermal stability of the polypyrrole (PPy) in the nanocomposites was enhanced and the electrical conductivity of the nanocomposites increased greatly upon the initial addition (20 wt%) of iron oxide nanoparticles. Aihua Chen et al., synthesized PPy–$Fe_3O_4$ composites by polymerization in-situ of pirrol and determined that the conductivity of PPy–$Fe_3O_4$ composites was much higher than that of pure PPy, and increased with the increase of $Fe_3O_4$ content in composites [9]. Tandon et al., [16] also synthesized nanocomposites of PPy-$Fe_3O_4$ using an emulsion polymerization method in aqueous solution. The resulting polymer composites possessed much higher conductivity as compared to pure PPy. The composite showed high sensitivity to humidity and gases ($O_2$, $N_2$ and $CO_2$). Hua-Ru Yin et al. [8] synthesized Polythiophene by oxidative method in prescence of γ-$Fe_2O_3$ nanoparticles modified by polyethylene glycol (PEG-400), they determined that the γ-$Fe_2O_3$ nanoparticles were encapsulated by polythiophene successfully. In relation to the in-situ synthesis of poly(3-alkylthiophenes) in presence of iron oxides to our knowledge there is only two papers: Zhiyue Han et al. [17] synthesized a conducting polymer composite, poly(3-octylthiophene)/ferric oxide (POT/$Fe_2O_3$) through the polymerization of 3OT in presence of iron oxide, the energy gap of the POT/$Fe_2O_3$ composite was decreased to 0.448 eV and a solar-to-electric energy conversion efficiency of 0.258% was attained [17]; and Csaba Janáky et al. report on the synthesis of poly(3-octylthiophene)/γ-$Fe_2O_3$ nanocomposite by oxidative method, they determined that the maghemite containing POT may combine conducting, superparamagnetic, and thermoelectric properties, and may lead to practical applications [18]. As can be seen the incorporation of different iron oxides in conjugated systems is of special interest since such nanocomposites may involve the combination of magnetic and electrical properties. Though there has been report about P3AT composites in especific P3OT with $Fe_2O_3$ and γ-$Fe_2O_3$ [17,18], up to now, the possibility of goethite/P3AT composites has never been explored. Therefore, synthesis of novel nanocomposites with iron oxide nanoparticles and conductive polymers would be of importance, and such novel materials can have interesting characteristics for several applications. Thus, this work presents the effect of the FeO(OH) nanoparticles concentration on in-situ polymerization of 3HT. P3HT-FeO(OH) nanocomposite was obtained with good physicochemical properties. Composites based in conductive polymer (P3AT) and FeO(OH) could in principle offer the advantage of production in high volume at low process cost.

## 2. Experimental

### 2.1. Materials

3-Hexylthiophene ($C_{10}H_{16}S$, 99%) and Iron Chloride ($FeCl_3$, 97%) were provided by Aldrich; Methanol ($CH_3OH$, 99.9%), Chloroform ($CHCl_3$), Acetone ($CH_3COCH_3$, 99.7%) and Hexane ($C_6H_{14}$) were provided by Fermont. 3-hexylthiophene was distilled under reduced pressure and stored in the dark prior to use.

### 2.2. Synthesis of FeO(OH)

FeO(OH) nanoparticles were synthesized using the chemical bath deposition method. In this method, two solutions were used: 0.05 M Fe$(SO_4)_2NH_4{\cdot}12H_2O$ solution as the source of $Fe^{3+}$ ions; and a urea solution (1M $CH_4N_2O$), which is decomposed into carbonate ($CO_3^{2-}$) and ammonia ($NH_4^-$) ions, where the carbonates in turn react with the water in the solution and generate hydroxyl ions ($OH^-$) and bicarbonates ions ($HCO_3^-$) [19]. The reaction temperature was brought to 70 °C, pH 2 and over a reaction time of 75 min. The precipitates obtained from FeO(OH) were recovered and washed with water and isopropanol. Finally, a thermal treatment at temperature of 150° C for 2.75 h was applied to the obtained nanoparticles.

### 2.3. Synthesis of P3HT-FeO(OH) nanocomposites

The nanocomposites synthesis was made through an in-situ polymerization reaction, 3-hexylthiophene monomer was led to chemical oxidation (Sugimoto method) in the presence of FeO(OH) nanoparticles, using $FeCl_3$ as oxidizer/catalyst, at 0 °C for 24 h in inert atmosphere. In order to investigate the effect of FeO(OH) content on the structure, morphology and optoelectronic properties, the nanocomposites were synthesized with different concentrations of FeO(OH) (3HT/FeO(OH) weight ratio: 1/0.029, 1/0.048 and 1/0.074).

The FeO(OH) nanoparticles were first dispersed by zonification in $CHCl_3$ and then added under magnetic stirring to $FeCl_3$ (6.4 mmol) in $CHCl_3$ solution. Distilled previously 3HT monomer (2.7 mmol) was dissolved in $CHCl_3$ and carefully added to the FeO(OH)/$FeCl_3$ solution, the mixture was kept under stirring for 24 h. The polymer product was precipitated in methanol, filtered and washed with methanol and hexane by centrifugation (10 min, 7000 rpm) and finally dried. For comparison, P3HT without FeO(OH) nanoparticles was synthesized following the procedure described above. Polymeric thin films were prepared on Corning glass substrates by spin-coating technique at a concentration of 20 mg/ml chlorobenzene and with a rotational speed of 2000 rpm. FeO(OH) nanoparticles were deposited on quartz substrates by drop-casting technique. Specifically for photoluminescence measurements, polymer solutions with 0.05 mg/ml concentration were prepared using toluene as solvent.

### 2.4. Characterization

Dyads and triads configuration was determined by $^1$H NMR (Varian Inova 400 instrument) using $CDCl_3$ as solvent. The dyads (HH and HT) and triads (HT-HT, HT-HH, TT-HT, and TT-HH) contents in P3HT polymer and P3HT/FeO(OH) composites were estimated from the peak areas that appeared around $\delta$ = 2.55 (HH), 2.8 (HT) ppm, 6.98 (HT-HT), 7.00 (HT-HH), 7.02 (TT-HT), and 7.05 (TT-HH) ppm in the $^1$H NMR spectrum [20]. The FTIR spectra of polymeric materials were recorded in the Perkin Elmer LR64912C FTIR-ATR spectrophotometer in the range of 4000–650 $cm^{-1}$. Thermogravimetric analysis were performed on a TGA 2050 TA instrument using a heating rate of 10 °C/