



Highly active poly(3-hexylthiophene) nanostructures for photocatalysis under solar light

Dita Floresyona^a, Fabrice Goubard^b, Pierre-Henri Aubert^b, Isabelle Lampre^a, Jérémie Mathurin^a, Alexandre Dazzi^a, Srabanti Ghosh^{a,1}, Patricia Beaunier^c, François Brisset^d, Samy Remita^{a,e}, Laurence Ramos^f, Hynd Remita^{a,g,*}

^a Laboratoire de Chimie Physique, UMR 8000 CNRS, Université Paris-Sud, Université Paris-Saclay, 91405 Orsay, France

^b Laboratoire de Physicochimie des Polymères et des Interfaces (LPPI, EA 2528), Université de Cergy-Pontoise, 5 mail Gay Lussac, F-95031 Neuville-sur-Oise Cedex, France

^c Sorbonne Université, UPMC Univ Paris 06, CNRS, UMR 7197, Laboratoire de Réactivité de Surface, F-75005 Paris, France

^d Institut de Chimie Moléculaire et des Matériaux d'Orsay, ICMMO, UMR 8182 CNRS, Université Paris-Sud, Université Paris Saclay, Bât 410-420, Orsay F-91405, France

^e Département CASER, Ecole SITI, Conservatoire National des Arts et Métiers, CNAM, 292 rue Saint-Martin, 75141 Paris Cedex 03, France

^f Laboratoire Charles Coulomb (L2C) UMR 5221 CNRS-Université de Montpellier, 34095 Montpellier, France

^g CNRS, Laboratoire de Chimie Physique, UMR 8000, 91405 Orsay, France

ARTICLE INFO

Article history:

Received 7 December 2016

Received in revised form 6 February 2017

Accepted 21 February 2017

Available online 22 February 2017

Keywords:

Poly(3-hexylthiophene)

Conjugated polymer nanostructures

Photocatalysis

Superoxide radical

Water treatment

ABSTRACT

Conjugated polymer nanostructures have recently emerged as a new class of very active photocatalysts under solar light. Poly(3-hexylthiophene) (P3HT) is one of the commonly used conjugated polymers for photovoltaics applications. P3HT nanostructures synthesized in soft templates provided by hexagonal mesophases show high photocatalytic activity for degradation of pollutants under both UV and visible light. These photocatalysts are very stable even after repeated cycling. Addition of scavengers and mechanistic studies show that $O_2^{\bullet-}$ is the main radical responsible for degradation of phenol taken as a model pollutant. P3HT nanostructures can be easily deposited on flat supports such as quartz for photocatalytic applications avoiding a separation step by centrifugation. Most interestingly, the photocatalytic activity of these P3HT nanostructures is highly enhanced when they are supported on a solid surface opening new perspectives in photocatalytic reactors and self-cleaning surfaces.

© 2017 Elsevier B.V. All rights reserved.

1. Introduction

Titanium dioxide (TiO_2) is the most commonly used semiconductor for photocatalysis because of its low price, high stability and non-toxicity. However, TiO_2 is only active under UV light irradiation (band gap > 3.2 eV for anatase and 3.0 eV for rutile), while solar light consists of only 4% of UV light. Doping or modification of TiO_2 to enhance its photocatalytic activity under solar light is therefore a very active field of research [1–7]. Furthermore, to avoid filtration difficulties, an immobilization of the photocatalyst is necessary. For application of titania in air and water depollution, many works have focused on the deposition and immobilization of TiO_2 on different

supports such as glass beads or plates, on a non-woven glass fiber fabric, steel, or on porous materials, avoiding the separation step of the titania powder. Whatever the support, the immobilization of titania lowers in general its photoactivity because of the difficulty for the UV photons to reach a part of the solid [8]. The search for new photocatalytic materials, which are active under solar light, and mainly under visible light has therefore received a lot of attention in the last decade [9–13].

With the discovery of conductive polyacetylene in 1978, conducting polymers (CPs) have received significant interest from both scientific and engineering communities [14]. The combination between the superior electronic properties of semiconductors (such as high conductivity, mechanical and thermal stability) and the advantages of organic materials (low cost and easy processing) render CPs promising materials for a variety of optoelectronic applications such as solar cells, light emitting diode, field-effect transistors, etc [15–20]. Among conductive conjugated polymers, poly(alkylthiophenes) have emerged as one of the most popular class. Poly(3-hexylthiophene) (P3HT) is an organic semiconduc-

* Corresponding author at: Laboratoire de Chimie Physique, UMR 8000 CNRS, Université Paris-Sud, Université Paris-Saclay, 91405 Orsay, France.

E-mail address: hynd.remita@u-psud.fr (H. Remita).

¹ Present address: Department of Chemical, Biological and Macromolecular Sciences, S. N. Bose National Centre for Basic Sciences, Block JD, Sector III, Salt Lake, Kolkata 700 098, India

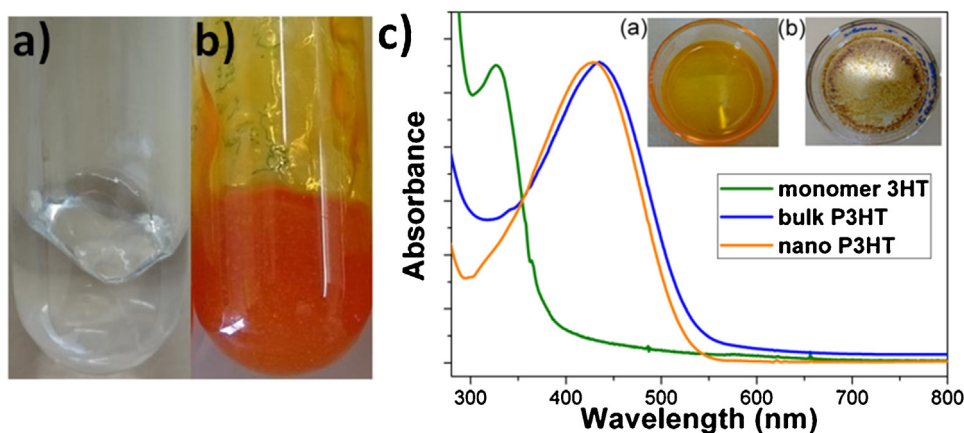


Fig. 1. Pictures of hexagonal mesophases doped with (a) 3HT monomer and (b) P3HT polymer; (c) Normalized UV-vis spectra of the 3HT monomer, nano P3HT, and bulk P3HT in chloroform, Inset: Pictures of nano P3HT extracted in ethanol (a) and after drying (b).

tor that has been mainly used for the fabrication of transistors, photovoltaic cells, strain sensors, and light emitting devices. P3HT appears to be the most commonly used CP in organic photovoltaics because of its desirable electronic properties [21]. The incorporation of P3HT into other semiconductors such as TiO_2 or Bi_2MoO_6 leads to the improvement of the photocatalytic activity [22,23].

Recently, we have shown that conjugated polymers (in particular Polydiphenylbutadiyne) (PDPB) and Poly(3,4-ethylenedioxythiophene (PEDOT)) emerge as a new class of photocatalysts very active under visible light [24,25]. Oil-swollen surfactant stabilized hexagonal mesophases have been used as a versatile template to synthesize several metal and polymer nanomaterials, either in the aqueous phase or in the oil phase [26–33]. In this context, we have shown that the nanostructuring of PDPB and PEDOT polymers, thanks to their synthesis in a soft template formed by hexagonal mesophases, leads to an enhancement of their photocatalytic activity. [24,25]

Here, we show for the first time that nanostructures of P3HT are also highly efficient for the degradation of pollutants under UV and visible light. These photocatalysts, which are very stable with cycling, can furthermore be easily deposited on a flat solid support (quartz or glass) for photocatalytic application. Interestingly, we measure a much faster kinetics for the degradation of pollutant once P3HT nanostructures are deposited on a solid surface.

2. Experimental section

2.1. Materials

3-hexylthiophene (3HT) as monomer, iron (III) chloride as oxidative agent, cetyltrimethylammonium bromide (CTAB) ($\geq 98\%$) as surfactant, sodium chloride (NaCl), toluene ($>99\%$), *n*-pentanol ($\geq 99\%$) and phenol ($\text{C}_6\text{H}_5\text{OH}$) were purchased from Sigma-Aldrich. Rhodamine B (RB) was purchased from Fluka. Titania (P25, surface area = $50 \text{ m}^2 \text{ g}^{-1}$, 80% Anatase, 20% Rutile and a small amount of amorphous TiO_2) was obtained from Evonik for comparative photodegradation. All compounds were used as received. Ultrapure water (Millipore System, $18.2 \text{ M}\Omega \text{ cm}$) and ethanol ($\geq 99\%$ for HPLC, purchased from Sigma-Aldrich) were used as solvents. All experiments were performed at room temperature.

2.2. Photocatalysts preparation

Poly(3-hexylthiophene) (P3HT) nanostructures (hereafter called nano P3HT) were synthesized inside the oil phase of hexagonal mesophases. The hexagonal mesophases were pre-

pared following the previously published method with some modifications. This system consists of surfactant and co-surfactant-stabilized oil (toluene) tubes regularly arranged on a triangular lattice in water. To prepare the hexagonal mesophases, 1.03 g of CTAB was first dissolved in 2 mL of sodium chloride 0.1 M and then, vortexed for a few minutes. The mixture was then let in an oven at 50°C for 1 h to form a transparent and viscous micellar solution. Then, 1 mL of toluene containing $54 \mu\text{L}$ of the 3HT monomer was added to the micellar solution under vortex. Subsequently, 2 mL of toluene containing 96 mg of FeCl_3 was added, and the mixture was vortexed for a few minutes. This led to an opaque unstable emulsion. The cosurfactant ($20 \mu\text{L}$ of *n*-pentanol) was added dropwise and strongly vortexed until an orange, translucent and birefringent gel (a hexagonal mesophase) was formed. The polymerization of 3-hexylthiophene was induced by oxidation with FeCl_3 . To avoid the bulk polymerization, the monomer and oxidizing agent were never put together, but instead were dissolved in toluene separately and then added to the mixture during mesophase formation.

Bulk P3HT was synthesized in toluene without any surfactant. The ratio between monomer and oxidizing agent (FeCl_3) was the same as that used for the synthesis of nano P3HT in mesophases.

After polymerization, the materials were extracted by adding ethanol and water, followed by centrifugation and washed several times to remove the excess of surfactant and oxidant. The polymer was then extracted with ethanol and dried for one night at 40°C .

The photocatalytic activity of nano and bulk P3HT was compared to that of plasmonic titania and PDPB nanowires. Plasmonic titania (TiO_2 modified with Ag nanoparticles) consist in small silver nanoparticles synthesized on TiO_2 (P25) by radiolysis. The synthesis is described in details in reference 6. PDPB nanowires were synthesized using swollen hexagonal mesophases as soft template following the previously published method [24].

2.3. Material characterization

The mesophases before and after polymerization were analyzed using Small Angle X-Ray Scattering (SAXS). The mesophases were inserted in a glass capillaries of 1.5 mm diameter and high brightness low power X-Ray tube, coupled with an aspheric multilayer optic (GeniX 3D from Xenocs) was employed, which delivered an ultralow divergent beam (0.5 mrad). Scatterless slits were used to give a clean 0.87 mm diameter X-Ray spot with an estimated flux around 35 mph s^{-1} at the sample position. A transmission configuration was used. The scattered intensity was collected on a two dimensional Schneider 2D image plate detector prototype, at

Download English Version:

<https://daneshyari.com/en/article/6454124>

Download Persian Version:

<https://daneshyari.com/article/6454124>

[Daneshyari.com](https://daneshyari.com)