Optik 160 (2018) 218–226

Contents lists available at ScienceDirect

Optik

journal homepage: www.elsevier.de/ijleo

Original research article

Optical and dielectric properties for the determination of gap states of the polymer semiconductor: Application to photodegradation of organic pollutants

C. Belabed [a,*], B. Bellal [b], A. Tab [b], K. Dib [b], M. Trari [b]

[a] Laboratory of Materials Physic, Faculty of Physic, U.S.T.H.B., BP 32 El-Alia, 16111, Algiers, Algeria
[b] Laboratory of Storage and Valorization of Renewable Energies, Faculty of Chemistry, U.S.T.H.B., BP 32 El-Alia, 16111, Algiers, Algeria

ARTICLE INFO

Article history:
Received 5 January 2018
Accepted 27 January 2018

Keywords:
Polymer conductor
Optical dispersion parameters
Dielectric properties
Optical constants
Photodegradation

ABSTRACT

The conductor polymer emeraldine polyaniline (PANI) prepared by chemical route at −7 °C, is thermally stable up to 300 °C. The optical and electrical properties were studied by the diffuse reflectance spectra R(λ) in the range (300–2500 nm) to calculate the refractive index n (λ), optical conductivity (σ_{opt}), extinction coefficient (k), dissipation factor (tan δ) and relaxation time (τ). The forbidden band (E_g = 1.8 eV), was evaluated and confirmed by different methods. As application, the results show that the adsorption kinetic follows a pseudo first order for Orange II and the second order for Quinoline Yellow. The PANI thus prepared and studied has been used in the field of the environment. A systematic study of adsorption and photodegradation of Orange II and Quinoline yellow was carried out giving a depollution rate >90% in a time of 90 min.

1. Introduction

The growing demand of energy and increasing costs for the remediation of the water pollution [1,2], make the exploitation of the solar energy highly desirable [3,4]. The solar power, considered as eco-friendly energy [5–7], is attractive because of its abundance, consistency and can be exploited thermally [8], electrically [9] and chemically [10]. The last case includes the photocatalysis [11] which is an ecological alternative that is widely used through the dyes degradation metals reduction [12] and hydrogen production [13–15]. Indeed, the dyes even at low concentrations [16,17], decreases the transparency of water, thus affecting the photosynthesis and in this way aquatic life. An ideal treatment leads to the mineralization of organic molecules with no toxic compound [18]. In this respect, the advanced oxidation process (AOP) is an attractive strategy for the environmental protection [19]. It has been used for the degradation a variety of dyes drugs and pesticides. AOP occurs the radicals O_2° and OH°, which attack the organic matter and the oxygen plays a key role in the oxidation processes. It is well established now that the reactive radicals OH° are responsible of the photodegradation of many organic molecules [20].

The wide band gap semiconductor (SC) oxides like $BaTiO_3$ [21], SnO_2 [22] and TiO_2 [23] currently used in the photoelectrochemical (PEC) conversion, are chemically stable but their gap (E_g) exceeding 3 eV, makes them unattractive for the solar energy conversion which contains ~5% of UV light [24,25]. Accordingly, intense research was oriented to organic semiconductors (SCs) [26,27] and the conducting polymers have attracted a great interest from both scientific and industrial points of views [15]. Such materials not only work in a similar way to inorganic SCs but have other advantages like

* Corresponding author.
E-mail address: cbelabed@usthb.dz (C. Belabed).

https://doi.org/10.1016/j.ijleo.2018.01.109

environmental safety, easy synthesis and light weight. The use of polymers as photoelectrodes is attractive and polyaniline (PANI) is promising for the solar conversion [28]. The potential of the conduction band (CB) makes PANI interesting for the water treatment. Moreover, PANI is relatively low cost and has an optical gap (Eg) of ~1.8 eV allowing the capture of a large part of sunlight. It has demonstrated its efficiency in the hydrogen production [13]. The present work is devoted to the optical properties of PANI prepared by chemical route and its application, for discoloration of the synthetic solutions of Quinoline Yellow (QY) and Orange II (OII) by adsorption/photocatalysis on PANI has been invetsigated. The main objective is to evaluate the adsorption capacity of the PANI and its photocatalytic activity for the two dyes, OII and QY. A kinetic study for two photocatalytic adsorption phenomena will also be discussed; the results are satisfactory and the work will be published in near future.

2. Exprimental

2.1. Preparation of PANI

The emeraldine Polyaniline PANI was synthetized by chemical route and all chemicals were purchased from Sigma-Aldrich, Double distilled water was used for the preparation aniline (1 M) was dissolved in HCl solution. The two solutions were mixed at (−7 °C) under agitation. $(NH_4)_2S_2O_8$ was added drop wise to the initial solution and the reaction was achieved under magnetic agitation during 4 h. The green precipitate was filtered, thoroughly washed with distilled water and ethanol and dried at ambient temperature during 48 h.

2.2. Materials

The thermal analysis (TG) data were recorded with a thermo analyzer (Perkin Elmer STA 6000) at a heating rate of 10 °C mn^{-1}. The UV–vis diffuse reflectance spectra were plotted with a Carry 5000 UV vis NIR spectrophotometer. The powder was cold compacted into pellets under 9 kbar leading to good mechanical properties.

2.3. Photocatalysis of dyes

The photocatalytic tests of PANI were done in an open double walled Pyrex reactor (200 mL capacity) connecting to a thermostated bath and the temperature maintained at 25 ± 1 °C. The photocatalysis was realized at neutral pH (~7), the solid/liquid ratio was fixed at 0.1 g L^{-1}. The powder was maintained in the dark under magnetic agitation until reaching the adsorption equilibrium; no particles settling was observed in the reactor. The system was irradiated by visible light (LED, 10.5 mW cm^{-2}) and the aliquots were withdrawn at regular times and centrifuged for the analysis. The residual concentration of OII and QY was determined with a UV–vis spectrophotometer (Analytic Jena-Specord 200 plus, λ_{max} = 484.5 and λ_{max} = 413 nm resp.).

3. Results and discussion

3.1. Thermogravimetric analysis

The TG analysis is used for studying the thermal decomposition of conducting polymers. For this purpose, the TG was studied to get preliminary insights on the thermal stability of PANI which constitutes one of the key factors for the industrial applications. Fig. 1 shows both the TG and ATD curves, the first stage is attributed to the loss of water through the formation of intra- and inter-molecular bonds. The second stage starts at 300 °C and ends at 620 °C, accounting for a weight loss of

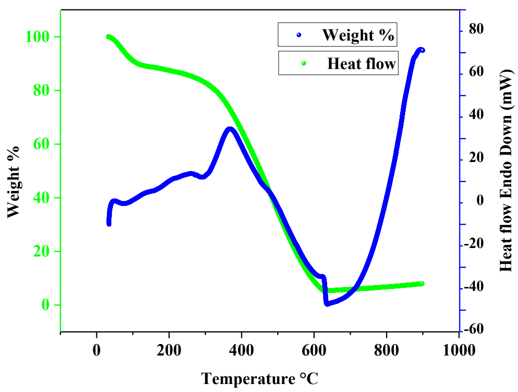

Fig. 1. TDA/TG plots along with derivative curve of PANI.