

Electronic supplementary information

Elaboration of nanohybrid materials by photopolymerisation of 3,4-ethylenedioxythiophene on TiO₂

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• In order to follow the PEDOT formation during the UV illumination time, the hybrid materials have been analysed by FTIR spectroscopy (figure 1). After 15 min UV lighting, characteristics bands of PEDOT are observed. Experimental bands at 1100, 1234, 1360 and 1450 cm⁻¹ are respectively assigned to: C-O-C deformation, C_α-C_α and C_β-C_β intercycle stretching modes and C=C symmetric stretching vibrations. Our results are in agreement with that published in literature [*reference: F. Tran-Van, S. Garreau, G. Louarn, G. Froyer and C. Chevrot, J. Mater. Chem. 2001, 11, 1378-1382*]. The higher is the duration of the UV illumination, the more visible is the PEDOT in FTIR spectrum.

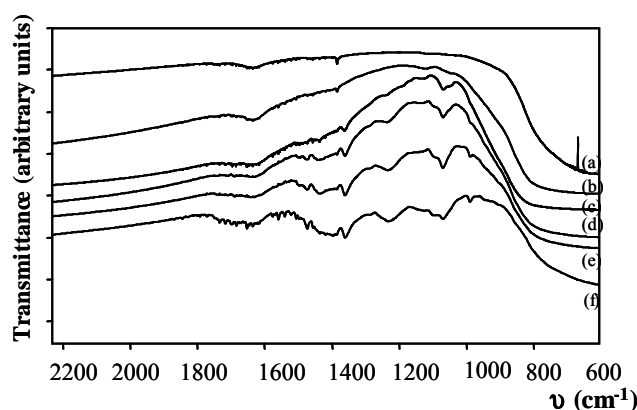


Figure 1. FTIR spectra of (a) P25, (b) composite 15 mn, (c) 30 mn, (d) 40 mn, (e) 60 mn and (f) 90 mn UV irradiation

• Terephthalic acid (TA) is known to produce fluorescence when reacting selectively with HO[•] species under many conditions. The method consists in trapping the HO[•] by TA to obtain 2-hydroxyterephthalic acid (TAOH) by aromatic hydroxylation, which resulted in an increase in the fluorescence intensity. The relative fluorescence intensity is proportional to the concentration of hydroxyl radicals. This concentration is determined indirectly, based on the increase of the fluorescence versus UV illumination time.

In order to validate the structure of the hydroxylation product, the standard 2-hydroxyterephthalic acid was synthesised adding disodium 2-bromoterephthalate (1.063g, 3.7 mmol), sodium acetate (0.66 g, 8.1 mmol) and Cu powder (0.0047 g, 0.9 mg-atom) in H₂O (17 ml). The mixture was heated at reflux for ~10 hr. Few drop of KOH (5% in water) were frequently added to maintain ca. pH = 8. During the last hour of reflux, the solution remained basic. The alkaline solution was filtered and acidified with 10% HCl until the full precipitation of 2-hydroxyterephthalic acid (TAOH) (0.431g, yield: 64.4 %). The structure was confirmed by ¹H NMR, FTIR and UV-VIS absorption spectra.

A linear evolution of the fluorescence intensity as a function of TAOH concentration is observed. Since no impurity has been detected by IR and NMR spectroscopy, fluorescence signal and TAOH concentration are reliable by a slope equal to 4.33. 10⁷ M⁻¹.

By comparison of the fluorescence intensity with that of the known concentration of TAOH, the amount of produced TAOH should be determined.

TA was dissolved in dilute NaOH solution (10⁻² M) and used for the experiments. Fluorescent probe (1 ml) was stirred with 19 ml of variable H₂O₂ concentration. The photolysis experiments were carried out using a 6 W (254

nm) UV lamp illuminating an aqueous buffered 20 ml solution of TA and semiconducting oxide (10 mg). The distance between solution and UV source was constant, 3 cm, in all experiments. The desired concentration of TA and H₂O₂ were fed into the Pyrex reactor. Then, the lamp was switched on to initiate the reaction. During irradiation, the aqueous solution was stirred and the solution was sampled after an appropriate illumination time. For TiO₂ powders, after illumination time, the sample is immediately centrifuged in order to extract and analyse the supernatant containing TAOH. TAOH (before measurements, the supernatant was then filtered, washed and dried to be sure than no H₂O₂ was present).

Fluorescence spectra of TAOH were measured on a JASCO FP-6200 fluorescence spectrophotometer. A 1 ml standard quartz cell of 1 cm path length was used. UV–VIS absorption spectra were recorded using a UV–VIS absorption spectrophotometer (JASCO V-570).

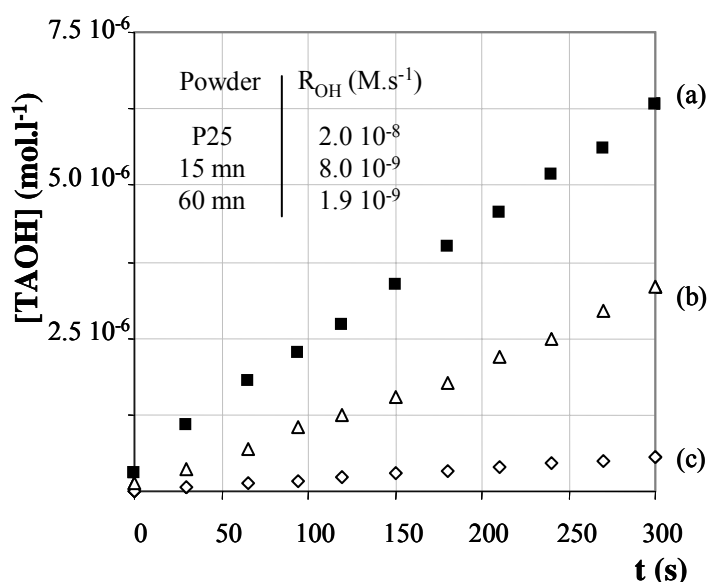


Figure 2. Formation of TAOH against irradiation time for (a) P25, (b) composite 15 min and (c) 60 min UV irradiation. Insert: rate of HO• formation for these different powders.

We investigated the ability of P25 and different variety of composite to produce HO• by means of this terephthalic acid-fluorescence probe method. Figure 2 presents the linear relationship between TAOH and the duration of UV irradiation. From the slope, the rate of formation ($R_{HO\bullet}$) was calculated (insert).

$R_{HO\bullet}$ decreases upon the formation of the composite: this behaviour is characteristic of the progressive covering of the TiO₂ during the illumination.

- Electrochemical apparatus: experiments were carried out in a three-electrode cell with a platinum disk as working electrode (diameter 1mm). Cyclic voltamperometry was performed at 50mV/s in acetonitrile containing 0.1M tetrabutylammonium hexafluorophosphate (TBAPF₆) as supporting electrolyte. The experiments were carried out under inert atmosphere. The potentials are measured relatively to a silver wire pseudo-reference electrode. In these conditions, the redox potential of the ferrocene/ferricinium couple is measured at 206 mV.

- XPS signals were recorded using a VG Scientific ESCALAB 250 system equipped with a micro-focused, monochromatic Al K α X-ray source (1486.6 eV) and a magnetic lens which increases the electron acceptance angle and hence the sensitivity. An X-ray beam of 650 μ m size was used at a power of 20mA x 15 kV. The spectra were acquired in the constant analyser energy mode, with pass energy of 150 and 40 eV for the survey and the narrow regions, respectively. Charge compensation was achieved with an electron flood gun operated under argon; at a partial pressure of 2×10^{-8} mbar in the analysis chamber. No implanted argon was detected at the surface of the materials in these conditions. With the combination of both electron and argon guns, the surface charge was neutral and perfectly uniform.

Figure 3 shows high resolution C_{1s} spectra of PEDOT bulk powder and TiO₂-PEDOT (60). In the PEDOT bulk powder (see Figure 3a) the main peak is fitted with five components due to α -position of EDOT unit C-S bond (285.3 eV), β -position of the EDOT unit C=C-O (286.3 eV) and carbon atom of the ethylene bridge C-O-C, and (287 eV). The latter feature is due to a partial oxidation of PEDOT. In addition, there is a low-intensity feature at 289.8 eV due to a π - π^* “shape-up” satellite which is characteristic of the aromatic of

thiophene ring.

For the nanohybrid at 60 mn (see Figure 3b), there are again five main components. The lowest binding energy feature is assigned to C-S (285.2 eV), followed by a peak at 286 eV (C=C-O), and an intense peak at 287.0 eV (C-O-C). Again, these peaks are accompanied by a weak feature attributed to a $\pi-\pi^*$ “shape-up” signal due to thiophene ring at 289.9 eV.

Clearly, the line shape of the C_{1s} spectrum of the nanohybrid prepared during 60 minutes under UV illumination more closely resembles that of PEDOT bulk powder which confirm the presence of the polymer conducting on the surface of TiO_2 powder.

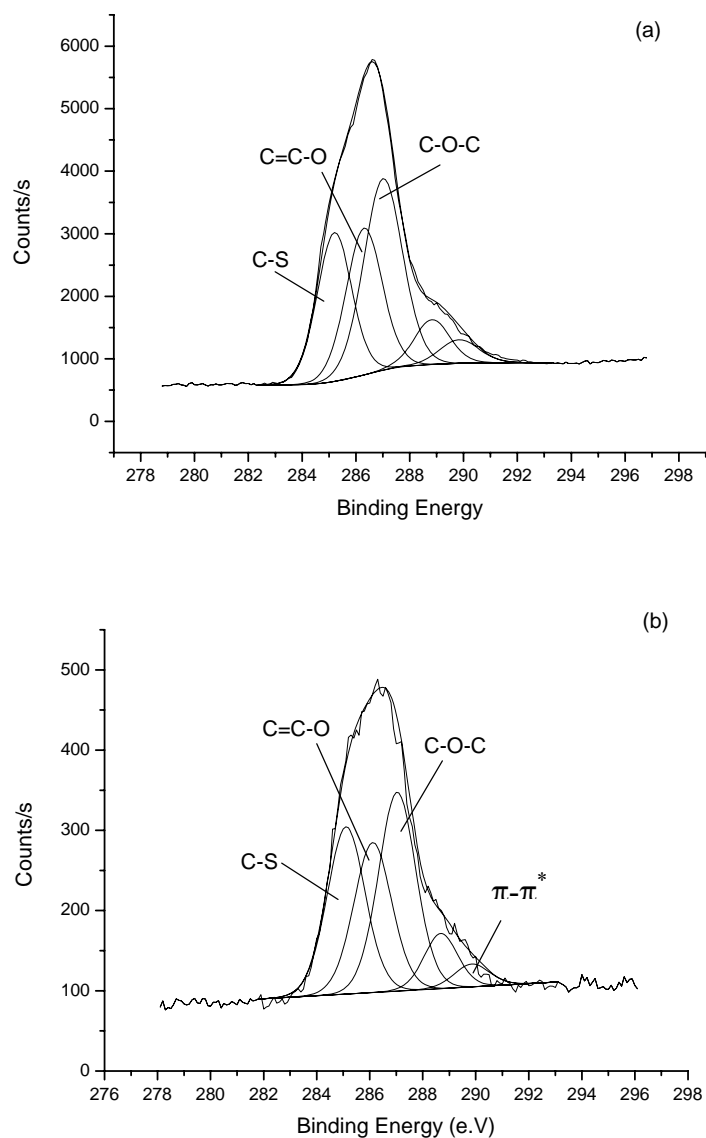


Figure 3. High resolution C_{1s} structure of (a) PEDOT , (b) TiO_2 -PEDOT (60)