Elaboration of nanohybrid materials by photopolymerisation of 3,4-ethylenedioxythiophene on TiO_2†

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A method for the elaboration of a heterojunction composed on *n*-type inorganic semiconducting nanoparticles, TiO_2, and a *p*-type organic semiconducting polymer poly(3,4-ethylene dioxy-thiophene) by UV illumination is described.
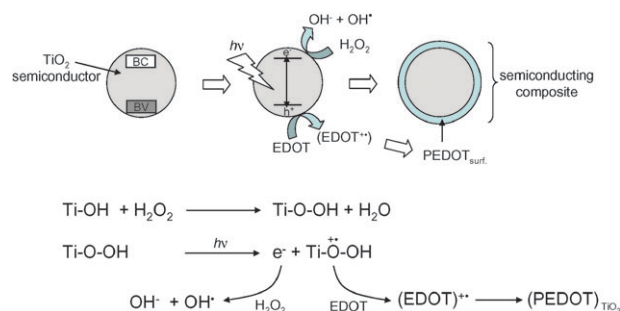
The preparation of nanocomposite particles with variable size constitutes a research area of considerable interest. Indeed, organic–inorganic nanocomposite materials have been regarded as a new class of materials, since many bulk properties can be improved compared with those of each constitutive material.[1] Conducting polymers, such as polythiophene, poly(3,4-ethylenedioxythiophene) (PEDOT), polypyrrole and polyaniline, have been intensively studied as one of the component of nanohybrids due to their remarkable electrical properties. Combined with an oxide nanoparticle core, exciting applications in photovoltaic,[2] magnetic,[3] charge storage,[4] catalysis,[5] biosensors[6] and biomedical[7] areas have motivated research in the development of original synthesis methodologies. In most cases, such nanocomposites are formed by electrochemical[8] or chemical polymerisation.[9] We would like to show that semiconducting polymeric films can also grow on inorganic semiconducting materials by photochemical polymerisation. This method is very easy and leads to extremely adhesive polymeric coatings. As far as we know, the only attempts at polymerisation on a surface by a photochemical method have been investigated with oligothiophenes and dithienothiophenes in acetonitrile solution containing an electron acceptor, such as *p*-dinitrobenzene.[10] In this paper, we describe the concept of a photofunctional interface for the elaboration of nanohybrid materials. The nanohybrid compounds are obtained by an "*in situ*" photopolymerisation of 3,4-ethylenedioxythiophene (EDOT) on TiO_2 nanoparticles, as shown in Scheme 1. The most convenient way to prepare PEDOT is to oxidize the monomer in the presence of an oxidizing agent such as Fe(III),[11] leading to a highly stable polymer in the oxidized state.[12] Foulger *et al.*[13] have recently attempted to prepare PEDOT hollow particles from silica core working as template.

In our experiment, the formation of the PEDOT layer coated on TiO_2 nanoparticles can be described by the hypothetical pathway described in Scheme 1: under UV illumination, in which the photon energy is higher than the bandgap, the creation of hole–electron pairs occurs. If charge carriers do not recombine, the pairs are dissociated at the TiO_2/solution interface: the electron may be transferred to an electrophile such as H_2O_2 or O_2. The holes, trapped at the surface by the hydrogen peroxide,[14] produce strong oxidizing species $[TiO–OH]^{+\bullet}$ that can react with the monomer to form a conducting polymer layer.

This hypothetical mechanism is supported by the following observations: under illumination in the presence of H_2O_2 without TiO_2 no PEDOT is formed within 12 h. The same result is obtained if the reaction is conducted with TiO_2 without H_2O_2.

The general procedure of composite synthesis is described as follows: titanium dioxide (P25, 80% anatase, 20% rutile, BET area, *ca.* 50 m^2 g^{-1}) was kindly supplied by Degussa. Stabilizer-free H_2O_2 was purchased from Merck. Then, pure EDOT (200 μl) was added in 1 M H_2O_2 solution. TiO_2 powder (0.5 g) was poured into the solution and the mixture was stirred under a UV beam. After polymerisation, the samples were centrifuged in deionized water several times to remove the excess of hydrogen peroxide, and then in acetonitrile to eliminate the excess of monomer on the TiO_2 surface.

In order to follow the PEDOT formation during the photopolymerisation, the hybrid materials have been analysed by FTIR spectroscopy. After 15 min, characteristics bands of PEDOT are observed. The higher the duration of the UV illumination, the more visible is the PEDOT in the FTIR spectrum. The formation of a thin layer of PEDOT has also been studied by XPS analysis looking at the signal of sulfur

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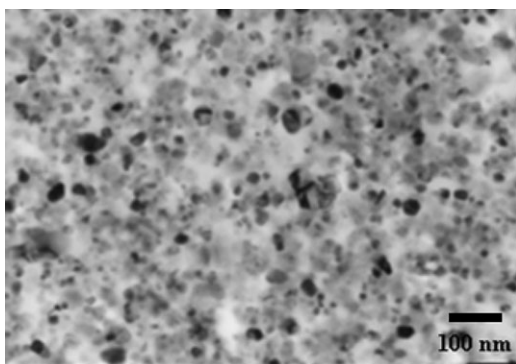

Scheme 1 Hypothetical synthetic route to the elaboration of the nanocomposite TiO_2/PEDOT.

Fig. 1 TEM picture of the TiO₂/PEDOT composite.

and carbon atoms. It was also possible to follow the PEDOT coverage using terephthalic acid as a fluorescent probe which is specific to HO• radicals: the rate of formation of HO• decreases upon the covering of PEDOT at the surface of TiO₂. (Details of FTIR, XPS and chemiluminescence experiments are furnished in the ESI.)†

Before and after the polymerisation, the specific area of the materials was determined by BET: no change was detected (surface area equal to *ca.* 53 m² g⁻¹ after synthesis of nanocomposites). The TEM image (Fig. 1) of TiO₂/PEDOT composite reveals homogeneous particle shape without aggregation, and narrow size distribution (particle diameter around 20–30 nm). These results indicate that only a thin layer of PEDOT has grown at the surface. XRD measurements of the composite reveal crystallinity and a proportion of rutile and anatase phases identical to that of P25. No crystallisation of PEDOT has been observed.

Cyclic voltammetry (CV) was performed for several composites obtained after 15, 30, 45, 60 and 90 minutes of photopolymerisation, as shown in Fig. 2 (curves a–e). The powders were mechanically pressed at the surface of the working platinum electrode and dipped into the electrolyte solution. Details of the experiments are given in the ESI.† The
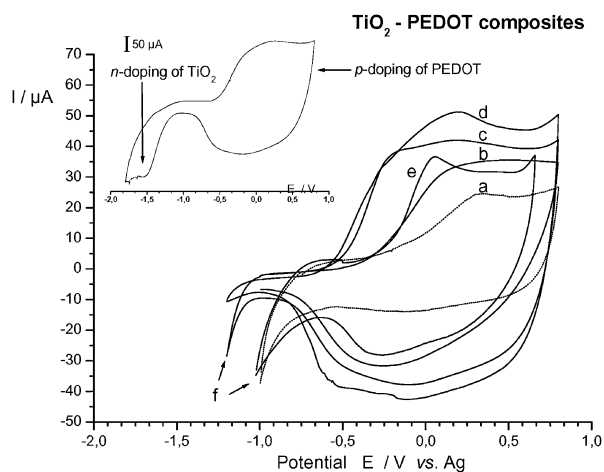
CV shape is very similar to that of a PEDOT electrochemically synthesised,[12] indicating clearly the presence of PEDOT on the TiO₂ nanoparticles: at the early stage of photopolymerisation (curve a), it is clear that E_{onset} is 300 mV higher than in the other conditions, suggesting that only small oligomers are produced. Then, increasing the photopolymerisation time, a characteristic *p*-doping process of the PEDOT occurs with an onset potential and peak potential at −0.65 V and 0.10 V, respectively (see curves c and d). It is useful to note that the electrochemical oxidation of PEDOT is getting poorer for composites prepared with longer exposure times (*i.e.* 90 minutes, *cf.* curve e). This trend indicates possible side-reactions of the PEDOT backbone with hydroxyl radicals. Crispin *et al.* also reported that the photo-oxidation of PEDOT can lead to the formation of sulfone groups, SO₂, resulting in a disruption of π-conjugation in the backbone, hence diminishing the electronic properties of the PEDOT.[15] Nevertheless, we noticed neither chemical- nor photo-degradation of the hybrid materials after one month.

TiO₂/PEDOT composites nanoparticles are attractive materials in the design of photovoltaic cells with the possibility of forming a large *p/n* heterojunction. Here, while the core–shell structure of the composite is not convenient for such applications, it is interesting to note that the *n*-doping of TiO₂ can occur in spite of the presence of an undoped layer: the electrons are injected in TiO₂ through the PEDOT layer (see inset of Fig. 2). This result suggests that the morphology of as prepared PEDOT makes the diffusion of the counter-ions easy during *n*- or *p*-doping processes. It is notable to look at the onset potential of the *n*-doping of TiO₂: this potential shifts ∼300 mV more negative (see Fig. 2f), suggesting that the TiO₂ nanoparticle is getting covered by the PEDOT.

Charge carriers production in the semiconductor has been evaluated from microwave absorption experiments using the time resolved microwave conductivity method (TRMC).[16] This method is based on the measurement of the relative variation of the microwave power ($\Delta P(t)/P$) before and after reflection by the powder sample. This change, linked to microwave absorption, is caused by a variation of the conductivity $\Delta\sigma(t)$ of the sample induced by a laser pulse. For small perturbations of conductivity, a linear relationship between $\Delta P(t)/P$ and $\Delta\sigma(t)$ has been established. The conductivity change is related to the sum of the concentration and mobility of charge carriers which are present (electrons and holes). The TRMC signal can be characterised by two parameters: the maximum value of the current at the end of the pulse and the current decay. Fig. 3 shows the TRMC transients obtained on excitation at 355 nm of a TiO₂ powder, PEDOT polymer and the composite TiO₂/PEDOT. The TiO₂ signal is attributed to the formation of mobile charge carriers in the surface by direct bandgap excitation.

Several studies show that mobile charge carriers are mainly electrons in TiO₂, due to its high mobility in TiO₂ surface.[17] Meanwhile, the TRMC signal of PEDOT corresponds to hole transport (hole mobility is higher than electron mobility). Charge carriers injection, characterised by I_{max}, is higher in the composite than the sum of the TRMC signals of PEDOT and TiO₂, more indicative of a surface polymerization than a blend formation. On the other hand, a fast decay process is
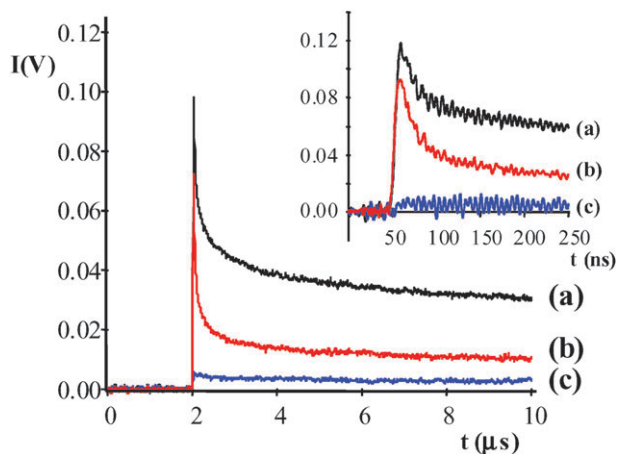

Fig. 2 CVs of TiO₂/PEDOT composites recorded during the photopolymerisation after (a) 15 minutes, (b) 30 minutes, (c) 45 minutes, (d) 60 minutes, and (e) 90 minutes. (f) Beginning of *n*-doping of TiO₂. Inset: CV of TiO₂/PEDOT composite during *p*- and *n*-electrochemical doping (same conditions as previously).

Fig. 3 TRMC signals induced by 355 nm light pulse of (a) a TiO$_2$ (P25)/PEDOT composite synthesised under 15 mn of UV illumination, (b) TiO$_2$ (P25) powder and (c) PEDOT powder. Inset: same TRMC experiments, signals are recorded at smaller time scale (0–250 ns).

observed, which reveals an increase of electron–hole recombination rate. These results could mean that a strong interaction between PEDOT and TiO$_2$ occurs, and suggest that this behavior is due to the absence of connectivity for electron transport. Then, the increase of I_{max} in TRMC is due to the electron transfer from PEDOT to TiO$_2$ as the result of the presence of PEDOT at TiO$_2$ interface. In order to increase the life-time of charge carriers, we are testing the use of a thin bilayer film in which a network of nanostructured TiO$_2$ would be re-covered by PEDOT film. This work is in progress in our group.

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