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A new sensitive organic/inorganic hybrid material based on titanium oxide for the potentiometric detection of iron(III)

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ABSTRACT

The formation of a new hybrid material based on titanium dioxide as inorganic support and containing an iron organochelator (ICL670) is described. An organophosphorous coupling agent was used to graft the organic molecule on the oxide surface. The attachment of the organic substrate was well-confirmed by FTIR (DRIFT), solid-state ^{31}P and ^{13}C CPMAS NMR, thermal analysis and the integrity of the structural and morphological parameters were verified using XRD and TEM analyses. The interaction between the material and dissolved iron(III) was also investigated through potentiometric measurements and demonstrated the interest of this new non-siliceous based hybrid material. The obtained linear evolution of the open circuit potential from 10^{-2} to 10^{-6} mol L^{-1} can be used for the analytical detection of iron(III).

1. Introduction

Finding new systems to detect, discriminate and quantify important chemical species with a high sensitivity and selectivity is still an active field for many electric applications like explosive detection [1,2], food quality control [3–5], environmental measurements [6–8] and the detection of biomolecules [9–11]. An interesting and promising route to develop high performance ion sensors in liquid media is the use of sensitive hybrid materials designed with a specific ionophore covalently linked or trapped in an inorganic host. Ideally, the organic part should interact selectively with the ion to detect. The challenge is then to be able to transform this chemical interaction into a usable signal from which the concentration can be calculated. For this purpose, diverse transducing modes have been reported as a function of the measured signal. The most popular are surely based on optical or electrochemical detections. On the basis of its high sensitivity, reproducibility and the easiness of the measurements, electrochemical detection, and specifically potentiometry, is a good choice to quantify ions in solution through the formation of new materials [12]. For the formation of these materials, due to the well developed sol–gel chemistry of silicon alkoxides [13,14], most of the works are based on the modification of silica. For instance, silica-based hybrid materials have been designed for either the electrochemical or optical detection of various species such as DNA [15], phenol [16], trinitrotoluene [17], pesticides [18] or ionic species [19–21]. Furthermore, following this route, we recently reported on the modification of silica with an iron(III) chelator-based ionophore for the potentiometric detection of iron(III) [22,23]. We demonstrated that such material can lead to a reproducible potentiometric response with a linear evolution of the equilibrium voltage from 10^{-1} to 10^{-6} mol L^{-1} of Fe(III). In the present communication, we evolve from the preparation of ion sensitive materials based on silica to another inorganic matrix, namely titanium dioxide. The utilization of non-siliceous material as host is still much less developed while it could bring new properties and/or improve the sensor performances.

Due to their stabilities, non-toxicity and possibility to control the obtained morphology/structure under mild synthesis conditions [24,25], the different structural forms of titanium oxide have become largely used for very different applications such as in paints [26], for sensing [27–30], energy storage [31–33], electrochromic windows and for photoelectrochemical applications. Indeed, for example, the rutile phase is extensively used in painting [34] due to its high refractive index while anatase is rather preferred for photocatalysis [35–37] and presently largely studied as support of organic or organometallic dyes to form Dye Sensitized Solar Cell (DSSC) [38–40]. To develop class II hybrid materials based on TiO_2, an "ambidextrous" molecule that ensures the

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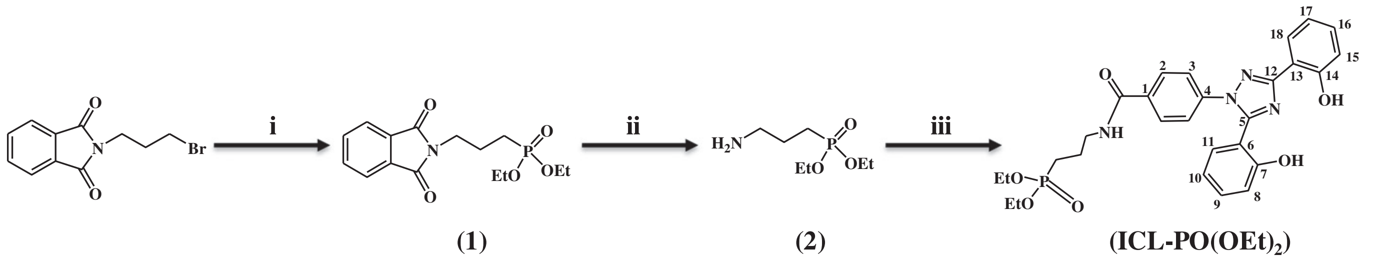

Fig. 1. Synthesis route of the organophosphorous coupling agent and its modification with ICL670. (i) $P(OEt)_3$, reflux, 18H, 98%. (ii) Aqueous hydrazine 35%, RT, 12H, 70%. (iii) ICL670, HOBt, EDCI, CH_2Cl_2.

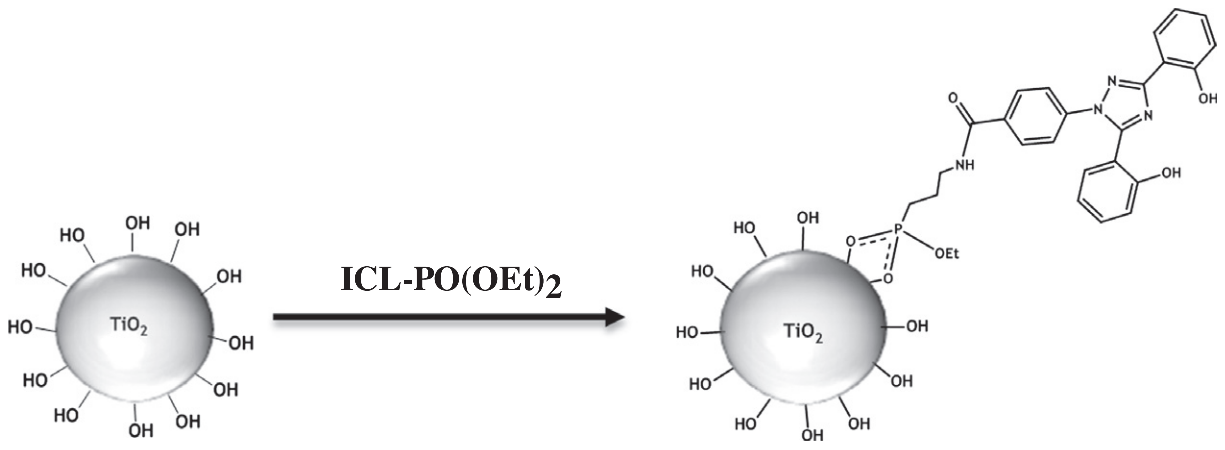

Fig. 2. Representation of the ICL-PO(OEt)$_2$ anchoring onto the anatase titanium dioxide nanoparticles.

surface grafting of an organic (functional) fragment is needed. For example, in DSSC, a carboxylic function is classically used for the dye immobilization and leads to good conversion yields. However, many other entities are available to perform such anchoring, namely catechol [41], hydroxamate [42], ketonic derivative [43] or phosphonate coupling agents [44–46]. Among them, organophosphoric acid and phosphonate derivatives have been preferentially used and remain the best anchoring pathway to produce stable and well-defined (generally as a monolayer) TiO_2 based hybrid material [47] in a way similar to the formation of silica based hybrid materials [48]. We present here, the synthesis and the characterization of a new hybrid material based on titanium oxide including an iron chelator (ICL670) for the potentiometric detection of iron(III) ions in aqueous solution. The iron chelator was anchored onto the surface of titanium oxide via an organophosphorous coupling agent previously modified with ICL 670 (Fig. 1).

This organophosphorous chelator (ICL-PO(OEt)$_2$) was introduced on anatase nanoparticles first prepared by titanium isopropoxide hydrolysis [31,49]. This step was performed at room temperature without hydrolysis of the diethyl ester phosphonate in a binary solvent system following the procedure described by Guerrero et al. [50] (Fig. 2).

2. Experimental

2.1. Reagents and chemicals

All the solvents were purchased from Fisher Scientific and Acros and were used without purification. Triethylphosphite, *N*-(3-bromopropyl)phthalimide, aqueous hydrazine 35% and *N*-(3-dimethylaminopropyl)-*N*′-ethylcarbodiimide (EDCI) were purchased from Aldrich and used as received. The tridentate iron(III) chelator ICL670 was synthesized in two steps according to the procedure reported by Steinhauser et al. [51].

2.2. Instrumentation

Textural and microtextural characterizations of the titanium nanoparticles were performed by means of transmission electron microscopy (TEM) with a Philips TECNAI 200F20 microscope. X-ray powder diffraction patterns were obtained at room temperature, using a Philips PW1729 diffractometer with Cu Kα ($\lambda = 1.5418$ Å) radiation. FTIR spectra in diffuse reflectance (DRIFT) mode were recorded at room temperature with a Nicolet AVATAR 370 DTGS spectrometer from Thermo Electron Corporation. The spectra were acquired at room temperature over a range of 4000–400 cm^{-1} with a resolution of 2 cm^{-1}. ^{1}H, ^{13}C and ^{31}P liquid NMR spectra were recorded on a Bruker 300 spectrometer. The chemical shifts are reported in parts per million (ppm) and the signals are quoted as s (singlet), bs (broad singlet), d (doublet), bd (broad doublet), dd (doublet of doublet), dt (doublet of triplet), t (triplet), bt (broad triplet), q (quartet), bq (broad quartet), m (multiplet). *J* values are given in Hertz. Signal assignment was made using HMBC, HSQC, COSY, and NOESY experiments when necessary. Mass spectra and high resolution mass spectra (electrospray in positive mode – ESI$^+$) were recorded on a Waters Q-TOF Ultima apparatus.

The ^{13}C CPMAS NMR spectra were carried out on a Bruker AVANCE 300 spectrometer with an executive frequency of 7.04 T. ^{13}C chemical shifts were referenced to external adamantine (used as a secondary reference), the high frequency peak being set to 38.5 ppm. The ^{31}P CPMAS NMR spectra were recorded on a Bruker AVANCE 500 spectrometer with an executive frequency of 11.4 T. The experiments were performed with a 4 mm probe, a magic an-