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In situ synthesis of silver benzene-dithiolate hybrid films

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ABSTRACT

In this article, a method for in situ synthesis of silver benzene-dithiolate hybrid films is presented. Silver nanoparticles, generated on ZrO_2 films, are transformed into silver benzene 1,4-dithiolate or, partially, into silver benzene 1,2-dithiolate after sample immersion in the corresponding thiol solutions. These transformations occur at room temperature owing to the catalytic action of ZrO_2. It is also shown that TiO_2 in place of ZrO_2 is very efficient, both for the catalytic generation of silver nanoparticles and for their further transformation in benzene 1,4-dithiolate compound. This latter semiconductor has an optical bandgap of about 3 eV and the film is made of touching nanoparticles in an amorphous state. Our work has potential applications in the electronic and photovoltaic fields.

1. Introduction

Hybrid inorganic–organic frameworks are a rapidly growing new class of materials. They contain both inorganic and organic components forming an infinite and highly crystalline network connected in 1, 2 or 3 dimensions. Cheetham et al. [1] distinguish metal-organic frameworks (MOF) of dimensionality O^n made of metal atoms (M) or clusters linked by bridging organic ligands (L), and extended inorganic hybrids based on inorganic connectivity M-X-M of dimensionality I^m, where X is O or S for examples. Both M-L-M and M-X-M types of connectivity I^mO^n can coexist within the same material, offering quasi-infinite structural variations. Many hybrid frameworks contain an opened porosity and, so, have first been studied for potential applications in gas storage or separation [2]. However, due to their tremendous diversity, these functional materials are also very promising in other research fields dealing with magnetic, ferroelectric, photoluminescent, electroluminescent or non-linear optical properties [3,4,5,6].

Since a few years, electronic properties of hybrid frameworks also have aroused much interest [7]. The hope is “to combine the high conductivity and crystallinity of inorganic semiconductors with the flexibility and facile synthesis of organic semiconductors” [8]. Unfortunately, semiconductive hybrid frameworks remain rare since M-O-M units are insulating [9]. Therefore, replacing M-O by the more covalent M-S or M-Se bonds has been found as a promising way to improve conductivity [10]. The layered structure of AgSR compounds, where the ligand R is an alkyl chain, was early determined by Dance et al. [11]. More recently, Che et al. [12] have reported the synthesis, the optical and electronic characterizations of CuSRX polymers, where R is the benzene ring with different substituents X. In these materials, the charge conduction occurs within the inorganic Cu-S chains, but the substituent X has a significant influence. Whereas conductivity in organic polymers is explained by the conjugation of π bonds, conductivity is expected in chains O^1 in MOF by the possible overlap between π bonds of the bridging ligand and the d orbital of the metal. Indeed, the aromatic ring is a good choice of bridging ligand. The conductivity of the benzene 1,4-dithiol has been extensively studied [13] and this molecule has widely been used as a precursor in metal thiolate synthesis. Semiconductive properties of transition metal benzene 1,4-dithiolate polymers were early reported by Schrauzer and Prakash [14]. Vaid et al. [15] have studied the synthesis and structure of Cd and Zn thiolate MOF. The structure with chain-like O^1 polymers of $HgSC_6H_4S$ and $PbSC_6H_4S$ and their semiconductive properties were also reported [16]. This research field is the context of our present article.

Many synthesis methods of hybrid inorganic–organic frameworks have been reported [2,3], leading to bulky insoluble products. A challenge is to generate crystalline rather than amorphous structures. In this way, solvothermal methods operating up to 250 °C are very efficient. For Pb-S MOF synthesis, the use of ethylenediamine as the solvent of the precursors has been found to lead to crystallized products at temperatures around 100 °C [17]. Nevertheless, for major applications of hybrid frameworks, especially for electronic ones, the elaboration of thin films is crucial [18,19]. The growth of dense and homogeneous films with a chosen orientation is highly desirable. These constraints are imperfectly satisfied with the most widely used method of in situ

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thin film generation on various substrates from a solvothermal mother solution. Alternatively, the layer-by-layer growth synthesis has been demonstrated very promising to build very homogeneous and oriented films on functionalized surfaces [20]. The drawback of this method is the length of the protocol. In the special case of metal thiolate materials, films are elaborated mostly from ex situ methods. Then, pressing thiolate powder into pellets or mixing it with an organic polymer is necessary [10]. Recently, our research group has proposed the first in situ synthesis for of Ag thiolate films on ZrO_2 surfaces [21]. In this way, oriented Ag decanethiolate nanocrystals were grown in their usual lamellar structure, whereas Ag perfluorodecanethiolate grains were amorphous. An application of Ag perfluorodecanethiolate as superhydrophobic and highly transparent surfaces was further demonstrated [22]. The connectivity of such hybrids is I^2O^0, since the precursor is monothiol.

The present work is an exploratory extension of our synthesis method to dithiol bridging ligands. The formation of Ag benzene dithiolate hybrid films has been attempted, not only because this material is known for its semiconductive properties [14], but also because the benzene dithiol ligand is involved in many other metal thiolate hybrid semiconductors [10–12–15–16]. We believe that our method can be enlarged on the replacement of Ag by metals such as Pb, Zn, Cd, Cu or Mn, thus, opening many opportunities in the potential of applications in electronics of metal thiolate semiconductors, far beyond the only Ag benzene dithiolate films.

In order to gather information on the potentialities of the process, we first compare two precursors: benzene 1,4-dithiol and benzene 1,2-dithiol. In this preliminary study, the ZrO_2 surface is used, as in the original method. Nevertheless, for photovoltaic applications, ZrO_2 is not very useful. Besides, the wide bandgap semiconductive TiO_2 oxide composes the collecting electrode in Grätzel-type solar cell [23]. Recently, a promising solar cell based on iodine-doped Cu-MOF as the sensitizing layer of TiO_2 electrode has been reported [24]. These developments have prompted us to inquire into the potentialities of TiO_2 to replace ZrO_2 in our synthesis method of thiolate films. Then, we report our investigations on the efficiency of TiO_2 surfaces as a catalyst, first, for oxide initiated Ag nanoparticle generation [25] and, second, for the transformation of these nanoparticles in Ag benzene 1,4-dithiolate. The different stages of thiolate formation are followed owing to the measurements of the optical properties of the samples. The composition, the morphology and the crystallographic structure of the thiolate layers are characterized, respectively, by X-ray photoelectron spectroscopy, atomic force microscopy and X-ray diffraction.

2. Experimental

Silica substrates of dimensions $7.5 \times 2.5 \times 0.2\ cm^3$ were used. Some were coated with ZrO_2 and others with TiO_2 layers by sol-gel. The ZrO_2 sol [26] was elaborated from the mixing of an equimolar quantity of Zr n-propoxide 70% solution in propanol ($3\ cm^3$) and acetylacetone, in heptane ($1\ cm^3$) and isopropanol ($1\ cm^3$). After stirring this solution for 2 h, $25\ cm^3$ of propanol was added for obtaining the final dilution. The TiO_2 sol was elaborated from the mixing of an equimolar quantity of Ti isopropoxide ($4.5\ cm^3$) and acetylacetone, in heptane ($1.5\ cm^3$). After stirring this solution for 2 h, $18\ cm^3$ of propanol was added. For film coating, a silica substrate was dipped in the sol (ZrO_2 or TiO_2) and withdrawn at the speed of 8 cm/min. After drying at 100°C in air for 10 min, the coated substrate was annealed at 400 °C in a furnace under oxygen atmosphere for 30 min.

The generation of the silver nanoparticles on the 2 opposite faces of a sol-gel coated substrate was achieved according to the following procedure [20]. An ethanolic solution with 5 mM $AgNO_3$ was prepared. The substrate was soaked in a bottle of this solution, and the whole was placed in an electric oven pre-heated at the temperature of 32 °C for the chosen duration. This duration was, respectively, 15 and 5 h for the ZrO_2 and TiO_2-coated silica substrates. For rinsing, the substrates covered with silver nanoparticles were transferred (without drying) from the elaboration solution successively into 4 bottles containing pure ethanol for the first one, mixing ethanol-heptane (2/3–1/3 volumic) for the second one, mixing ethanol-heptane (1/3–2/3 volumic) for the third one and pure heptane for the fourth one. Finally, the samples were dried under the laboratory hood. For thiolate formation, the silver-coated samples were immersed in a bottle containing benzene 1,4-(or 1,2) dithiol (2 mM) in dichloromethane for two days, then, rinsed in pure dichloromethane and finally dried.

For optical characterization, the transmittance and reflectance of the sample was determined with an incident angle of 4° using a Lambda900 spectrophotometer from Perkin-Elmer. The film composition was measured by X-ray photoelectron spectroscopy (XPS). The XPS measurements were carried out in a Vacuum Science Workshop chamber (base pressure less than 10^{-9} Pa) equipped with a monochromatic X-ray source Al K_α (1486.6 eV). The angle between the X-ray source and the photoelectron detector is set at the magic angle (54.7°). The acceptance angle of the hemispherical analyser is around 3°. The core levels were recorded at normal emission. Since the samples are insulators, we have used a flood gun for charge compensation in order to reduce charging phenomena. Besides, the grounding was at the sample surface via metallic clamps. The surface morphology was revealed by atomic force microscopy (AFM). An Asylum instrument was used in tapping mode with a scan rate of 1 Hz. For structural characterization, X-ray diffraction was performed in the θ-2θ geometry using a Rigaku diffractometer equipped with a rotating anode operating at 9kW. The beam was monochromatized with a two reflection Ge(220)x2 crystal which selects the Cu-Kα1 radiation at the wavelength of 0.15406 nm. The 2θ values were varied in the range 0.01 to 70°.

3. Results and discussion

3.1. ZrO_2 surface

The evolution of the optical properties of the sample is depicted in Fig. 1A–C. The bandgap of ZrO_2 is responsible for the large absorptance value in spectrum (s) of the ZrO_2-coated silica substrate for $\lambda < 230$ nm. The two extrema around $\lambda = 245$ and 390 nm on the transmittance and reflectance spectra (s) are due to the Fabry-Perot resonance of the ZrO_2 layer. The refractive indices of silica (see Fig. 2, curve 1) and ZrO_2 (curve 2a), fitted according to Cauchy's laws, are in good agreement with the literature [27]. The fitted thickness of the ZrO_2 layer is 53 nm. After immersion of the sample in the silver nitrate solution for 15 h, the generation of silver nanoparticles on ZrO_2 is revealed by a rather wide plasmon absorption inducing increase of absorptance and decrease of transmittance around the resonance wavelength $\lambda = 456$ nm in spectra (1) in Fig. 1A and C. Because of the silver nanoparticles on ZrO_2 present on the back side of the substrate, the effect of the plasmon band on the reflectance is a minimum in spectrum (1) in Fig. 1B, around $\lambda = 456$ nm.

After immersion of the sample in the benzene 1,4-dithiol solution for 2 days, the absorptance spectrum (2) clearly shows the vanishing of the plasmon band, indicating that the silver nanoparticles on ZrO_2 have disappeared. Besides, the sample presents a new and intense light absorption for $\lambda < 500$ nm. For $\lambda > 500$ nm, the transmittance and reflectance spectra (2) become, respectively, lower and higher than the transmittance and reflectance spectra (s) of ZrO_2 on silica. These optical evolutions clearly indicate that a new top film has formed on ZrO_2. With the use of decanethiol in similar experimental conditions, a top film made of lamellar silver decanethiolate was recently proved by X-ray diffraction [21]. Hence, in the present experiments, the top film is expected to be silver benzene 1,4-dithiolate. Nevertheless, the X-ray analysis has not exhibited any Bragg peak suitable for convincing characterization. So, XPS analysis has been undertaken.

The XPS spectra of Ag 3d, S 2p, C 1s, Zr 3d and O 1s core levels are plotted in Fig. 3. As these spectra are collected with a flood gun, the binding energies have been calibrated owing to a reference. According