

Deposition of Laminar TiO₂-Based Nanocomposites on a Modified Quartz Crystal Gold Surface

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The deposition of hybrid organic–inorganic nanocomposites of titanium dioxide—prepared by hydrolysis of titanium tetraisopropoxide modified through exchanging one of its ligands with a butinoy-, octiloy- or phenoy-group—on a gold surface modified by a monolayer of decanethiol was studied using a Quartz Crystal Microbalance. The depositions, performed from an suspension in alcohol of the nanocomposites, consisting in titanium oxide bilayers hydrophobically functionalized, occurs by a spontaneous process ‘layer by layer.’ However the amount of deposited mass in a layer as well as the rates of deposition depend on the degree of aggregation of the nanocomposite in the suspension which is in turn determined by nature of the organic ligands.

Keywords: Titanium Dioxide Nanocomposites, Quartz Crystal Microbalance, SAM.

1. INTRODUCTION

Nanostructured materials based on semiconductor transition metal oxides like titanium dioxide displaying high surface/volume ratios are particularly attractive by their potentiality for applications in fields like catalysis and electrooptical processes.^{1–4} Although much information related to particulate and tubular nanostructures is available,^{5–9} reports on laminar materials appropriated for covering macroscopic substrates modifying their surface properties are still scarce.¹ The Quartz Crystal Microbalance has proved to be a good method for investigating the modification of surfaces by deposition of TiO₂ derivatives.^{10,11} Here we show that this method is also appropriated for studying lamellar materials. Thus, in this work, we describe the spontaneous deposition of laminar TiO₂-based nanocomposites functionalized with organic groups on a gold surface modified by a dodecanethiol self-assembled monolayer (SAM). The achieved depositions occurring by ‘layer by layer’ mechanism, together with contributing to the design and preparation of TiO₂-based films with thicknesses in the range of the nanometers, also provide information on the aggregation degree of the materials in their suspensions.

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2. EXPERIMENTAL DETAILS

2.1. Synthesis

The precursors were prepared by modification of titanium tri-isopropoxide, TTIP, by condensation reaction either with an alcohol, 3-butynol, *n*-octanol or phenol, or with palmitic acid under low humidity conditions. A 1:1 molar ratio mixture of TTIP and alcohol or the carboxylic acid was heated at 70 °C during 30 d. After that the reaction was completed, the product was hydrolyzed at the air under controlled conditions. Then the product was purified by heating at 130 °C under reduced pressure (10⁻³ mmHg) in order to remove eventual reagent excesses and the isopropyl alcohol formed during the reaction.

2.2. Equipment

Deposition studies were performed with a Quartz Crystal Microbalance (RCQM MASTEX Inc.) using Mastek 5 MHz Crystal Cr/Au Polished electrodes at 25 °C. Water Contact Angle measurements were performed in a goniometer (Pocket Goniometer Model P2 Fibro System AB) and results analyzed with the PocketGoniometer® Program version 1.7.4.0.

2.3. Cleanness QCM-Au-Electrode

Quartz crystal electrodes were cleaned by immersion (5 min) in Piranha solution rinsed in pure water (5 MΩ) and dried under nitrogen gas (AGA, 99.999%) flow.

2.4. Electrode Modification

After determining the baseline with the QC-Au electrode immersed in 45 mL of ethanol, 0.144 g of octadecanethiol (ODT, Aldrich 95% R.A.) dissolved in 5 mL of ethanol were injected to the vessel. The deposition process was monitored by recording the QC resonance frequency. After being detected the formation of a self-assembled monolayer (SAM) of ODT, the electrode labeled as QC-Au-ODT was rinsed with ethanol, water and dried under nitrogen. Thereafter the surface was tested for homogeneity and characterized by water contact angle measurements.

2.5. TiO₂-Based Nanocomposite Deposition

After stabilization of the baseline signal, with the QC-Au-ODT electrode immersed in 45 mL of ethanol, 0.001 g of the composites, suspended in 5 mL of ethanol and sonicated during 5 min, were injected to the vessel. The deposition process was monitored by recording the QC resonance frequency. Then the electrode was rinsed with ethanol and dried with nitrogen. Homogeneity and hydrophobicity of the surface were tested by water contact angle measurements.

3. RESULTS AND DISCUSSION

The well known affinity of gold for species containing sulfur in low oxidation states, which in case of thiols reaches about 40 kcal mol⁻¹, is often used for the functionalization of gold surfaces. In the particular case of long-chain alkyl thiols, in addition to the mercaptan-gold interactions, inductive interactions among the hydrocarbon chains generates an additional stability factor, thus leading to the formation of a very stable, dense and highly organized arrangement of thiols molecules on the gold surface. In Figure 1(A) is illustrated the variation of the quartz crystal resonance frequency produced by the spontaneous deposition of octadecanethiol (ODT) on a 5-MHz QCM-Cr/Au electrode. As it was observed, after a relatively short time the equilibrium is achieved, agreeing the amount of deposited mass with the formation of an alkylthiol SAM. According to the nature of Au-alkylthiol interactions already commented, the surfactants molecules are expected to be bonded to the gold surface through the mercaptan group with the hydrocarbon chains oriented perpendicularly to the electrode plane. The modified surface is therefore highly hydrophobic. The water contact angle measurements reported in the same figure

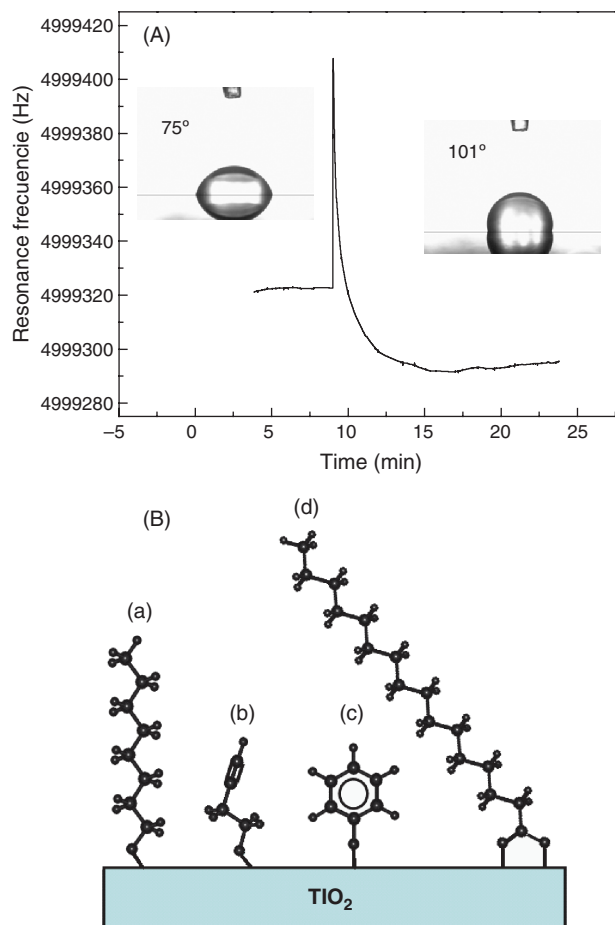


Fig. 1. (A) QC Resonance frequency shift as function of time for the deposition of ODT on a QC-Au Electrode. Insert: Water contact angle before and after the deposition of ODT. (B) Molecular structures of the organic components in the nanocomposites (a) TiOC8, (b) BTO, (c) TiOPh, (d) TiAcP.

agrees with that description. Then this modified electrode is used for the deposition of a series of hybrid TiO₂-based organic-inorganic nanocomposites.

The hybrid TiO₂-based composites used in the deposition experiments were in general prepared by the hydrolysis of titanium tetraisopropoxide (TTIP) modified by the substitution of one of its isopropoxy ligands by either an alkoxy or a carboxy group like those shown schematically in Figure 1(B). Here we specifically describe the deposition of nanocomposites arising from the hydrolysis of precursors prepared by reaction of TTIP with 3-butanol, BTO; phenol, TiOPh; 1-octanol, TiOC8; and palmitic acid, TiAcP, respectively.

In Figure 2(A) is illustrated the variation of the quartz crystal resonance frequency produced by spontaneous deposition of the nanocomposite TiOC8 on the electrode modified with a SAM of DDT. The shape of the curve shows the process occurs stepwise, where every step having approximately the same height corresponds to the formation of one layer on the electrode; so the electrode

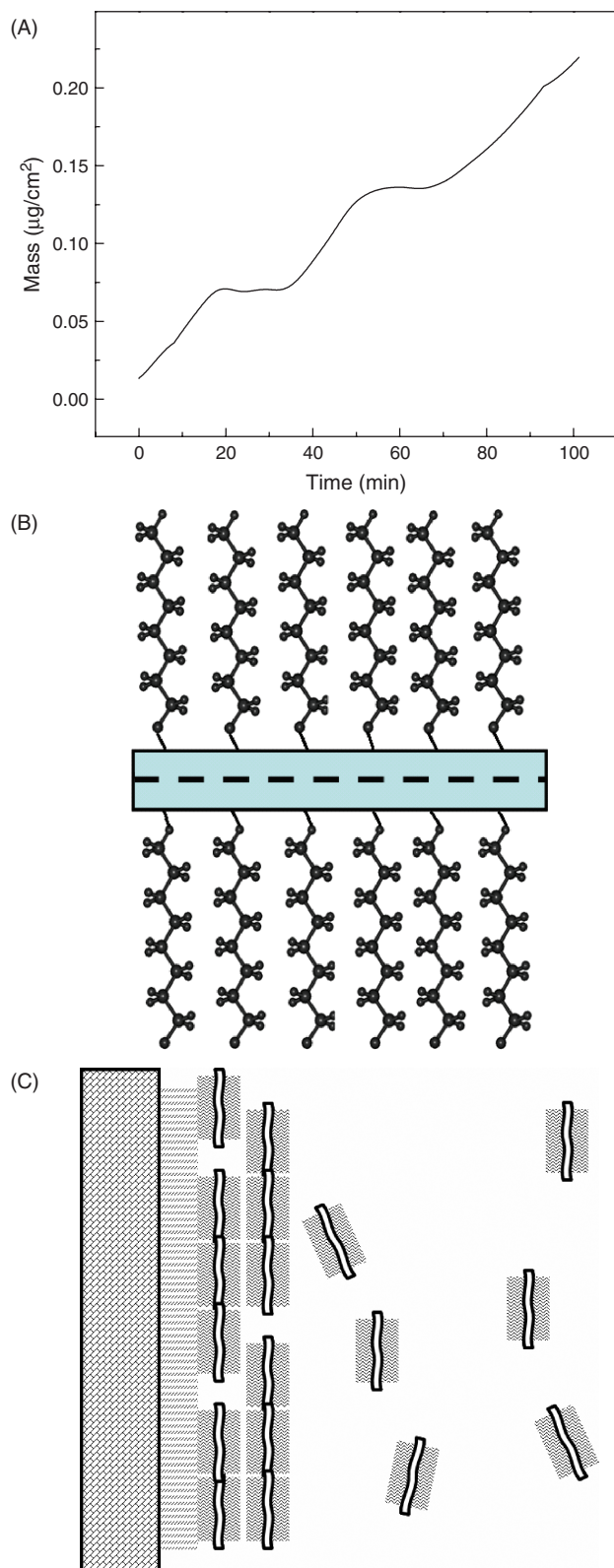


Fig. 2. (A) Deposition of TiOC8 composite on a QC-Au-ODT electrode. (B) Functionalized hybrid titanium oxide bilayer. (C) Schematic representation of the deposition of nanocomposites on QC-Au-ODT modified electrode.

appears being covered layer by layer by nanocomposite fragments as shown schematically in Figure 2(B). Considering the molecular weight of the TiOC8, the observed mass difference between two steps results to be similar to the mass necessary to cover the electrode with a layer constituted by two molecular units of the nanocomposite. To understand these results it is convenient to analyze the nature of the suspension used in these depositions taking in account the synthesis of the nanocomposites and the mechanisms involved in their formation. Since substituents in the TTIP derivatives used as precursors contain linear hydrocarbon chains, the species to be hydrolyzed are amphiphilic molecules able to undergo intermolecular hydrophobic interactions, thus leading to laminar supramolecular aggregates. Such a molecular arrangement would avoid the hydrolysis of the corresponding Ti-OR bonds or, at least, reduce considerably its rate. Thus, the rapid Ti-isopropoxide bond hydrolysis propagation is mainly limited to in-plane condensation reactions. Meanwhile in the perpendicular direction, only the condensations between two neighboring layers should be possible. Thus the formation of functionalized titanium oxide bilayers like that illustrated in Figure 2(C) would be expected. That agrees with results described in Figure 2(A), where the composition of each deposited layer is equivalent to the condensation of two TiOC8 molecular units. Contact angle measurements on films formed by deposition of the composites either on polyethylene surfaces or on the modified gold electrode (see below) agree with such a description showing that there are only slight differences with the observed on the ODT-surface (Fig. 1(A)), namely of about 10° for BTO and TiOPh and of 1° or 2° for TiOC8 and TiAcP. Thus, the surface of the nanocomposites always results to be hydrophobic.

Results obtained for studied nanocomposites are summarizing in Figure 3(A). The curves observed in this figure show that both the deposition rates and the number of layers appear to depend on the nature of the organic component in the nanocomposite. Although the deposition rate seems to be related with the length of the organic molecules in the composite, a better understanding of this behavior is reached considering the number and the composition of layers detected in these experiments. Thus, in the case of the BTO showing the highest deposition rate as well for the TiAcP with the lowest deposition rate, only one step may be identified. However in the former the composition of layer corresponds approximately to 30 molecular units of BTO, while in the latter the deposited layer contains two TiAcP molecular units. That may be interpreted as a consequence of the degree of agglomeration of the particles in the respective suspensions. In the case of the TiAcP like in that of the TiOC8 discussed above the particles in the suspension are formed by discrete functionalized titanium oxide bilayers while in the BTO suspension there are agglomerates constituted

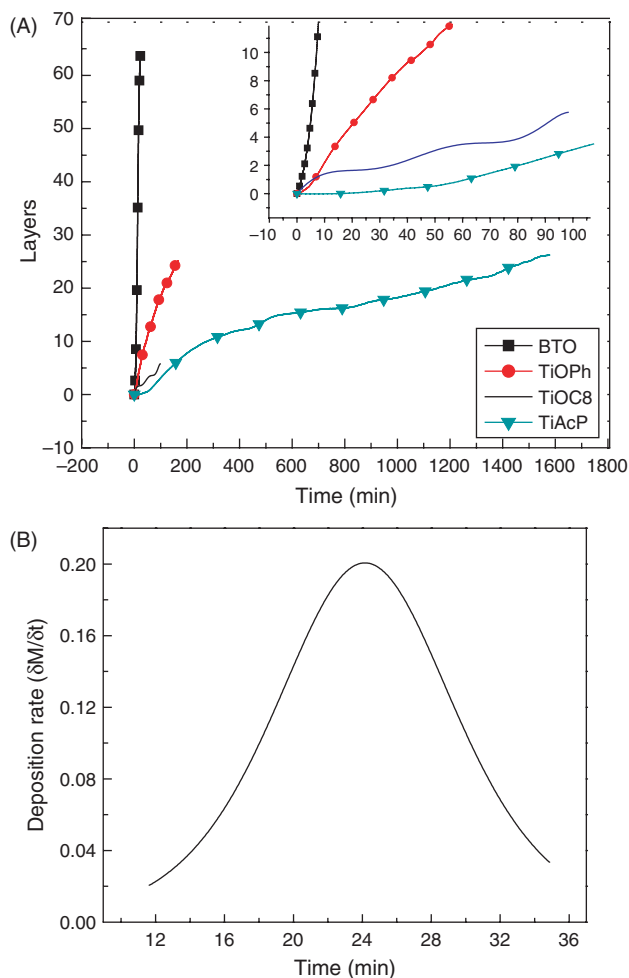


Fig. 3. (A) Deposition of hybrids TiO₂-based organic-inorganic nanocomposites on the QC-Au-ODT electrode: BTO (■), TiOPh (●), TiOC8 (▲) and TiAcP (▼). (B) Variation of the deposition rate during the formation of a layer of BTO.

by about 30 functionalized titanium oxide bilayers. The different trends to bilayers agglomeration probably arise from the differences in dielectric effects produced by the organic surface of the nanocomposite which are expected to be much higher for long chain hydrocarbons than for organic constituents in the other derivatives.

Finally it also interesting to comment the kinetic of the process observed in each step of the curve, i.e., for the deposition of one layer which always shows a sigmoid behavior. As observed in Figure 3(B) illustrating the variation of the deposition rate with the time for the formation of one layer of BTO aggregates on the electrode. During the initial stadium, the deposition rate is slow, in spite of the high availability of free sites on the surface. However the rate rapidly increases with increasing degree of occupation, probably due to cooperative effects associated to phenomena like the molecular recognition and self assembling with the particles previously deposited on the surface. The maximal rate is reached when an

occupation degree is about 50%. Thereafter the rate begins to decrease probably dominated by the diminution of the free sites available on the surface and eventual rearrangement processes necessary for reducing the total surface energy.

4. CONCLUSIONS

The modification of the titanium tetraisopropoxide by replacing one of the isopropyl groups by other one with a linear hydrocarbon chain leads to the formation of laminar bilayered organic-inorganic nanocomposites with hydrophobic surfaces. Depending on the nature of the surface these species may undergo further aggregation. The suspensions of these products may be spontaneously deposited on hydrophobic substrates like a gold surface covered by an alkylthiol SAM in a layer by layer process. The amount of mass deposited on as well as deposition rates depend essentially on the degree of aggregation of the nanocomposites in the suspension. The characteristics of the deposition process may be followed observing the quartz crystal resonance frequency changes in a quartz crystal microbalance which allows determining the amount of deposited materials as well as the kinetics of the deposition of each monolayer.

Although all the composites show a spontaneous multilayer deposition processes, they differ in both, amount of deposited material and their kinetics behaviors. The number of the layers deposited at infinite time correlates with the interlayer distances defined by the molecular length of the organic radicals. However this relationship is non-linear so other factors like the nature of the functional groups appear to be also involved. Particularly interesting results the kinetics observed in the case of the nanocomposite with a long alkyl chain where two behaviors may be distinguished, a rapid process associated to the assembling of the hydrocarbon chains and another much slower corresponding to the rearrangement of units on surface.

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