



Contents lists available at ScienceDirect

Computational and Theoretical Chemistry

journal homepage: www.elsevier.com/locate/comptc

Palmitic acid and hexadecylamine molecules adsorbed on titania surface in hybrid composites. Effect of surfactants using density functional theory

Carlos Orellana^{a,*}, Fernando Mendizábal^{a,*}, Guillermo González^{a,b}, Sebastián Miranda-Rojas^c, Lorena Barrientos^d

^a Departamento de Química, Facultad de Ciencias, Universidad de Chile, P.O. Box 653, Las Palmeras 3425, Ñuñoa, Santiago, Chile

^b Center for the Development of Nanoscience and Nanotechnology, CEDENNA, Santiago, Chile

^c Chemical Processes and Catalysis (CPC), Departamento de Ciencias Exactas, Universidad Andrés Bello, Avenida República 275, Santiago, Chile

^d Facultad de Química, Centro de Investigación en Nanotecnología y Materiales Avanzados CIEN-UC, Pontificia Universidad Católica de Chile, Avenida Vicuña Mackenna 4860, Macul, Santiago, Chile

ARTICLE INFO

Article history:

Received 27 March 2017

Received in revised form 10 April 2017

Accepted 11 April 2017

Available online xxx

Keywords:

Titanium dioxide laminar compounds

Palmitic acid

Hexadecylamine

Dispersion term

DFT

BSSE

ABSTRACT

A complete theoretical characterization of the factors involved in the stabilization of hybrid laminar composites is reported, with the purpose of understanding the main interactions involved in the formation of these types of systems. The models were built using two different surfactants: hexadecylamine (HDA) and palmitic acid (PAC), on a cluster of titania (TiO_2) which represents its anatase crystalline phase. We explored the relevance of the titania-surfactant and surfactant-surfactant interactions, and of the protonation state of the palmitic acid in the stabilization of the hybrid laminar composites. The results were rationalized using energy decomposition analysis (EDA) and the non-covalent interaction index (NIC). The interaction energies between HDA and the TiO_2 surface without the contribution of the dispersion forces were -25 kcal/mol and -29 kcal/mol for the (100) and (101) surfaces, respectively. These results suggest the formation of a donor-acceptor bond between HDA- TiO_2 allowing its stabilization. On the other hand, the interaction energy between PAC and the TiO_2 (101) surface was about -45 kcal/mol without the dispersion term. Thus, the PAC- TiO_2 model has a higher covalent character than the HDA- TiO_2 interaction, as confirmed by the energy decomposition analyses. The results suggest new hybrid laminar composites which are better when carboxylic acid was used instead of amines. Therefore, the use of surfactants with the carboxyl functional group yielded more stable TiO_2 hybrid composites. The interaction energy between surfactant chains was about -13 kcal/mol, confirming the importance of dispersion forces in the stabilization of these types of systems. The study of systems with palmitic acid was complemented by building some anionic models to show the importance of acid protons in those systems. However, when the acidic hydrogens were removed, the interaction energy between the PAC molecules considering the dispersion correction increased to 45 kcal/mol, with a highly repulsive character. These results suggest that the acid hydrogens of the PAC surfactants play a fundamental role in terms of correctly representing the carboxylic acid- TiO_2 interface and the stabilization of the laminar hybrid composites.

© 2017 Elsevier B.V. All rights reserved.

1. Introduction

In the last decades, energy demand has been growing rapidly due to the globalization of the world's population. At present, to meet this energy demand, the most widely used energy source is

that of fossil fuels, which are highly polluting [1,2]. One of the most promising alternatives to these energy sources is solar energy, and it is estimated that the total amount of solar energy incident on the surface of the Earth in the form of photons is more than 3×10^{24} J/year (2×10^5 TW) [2].

The design of efficient photocatalysts able to transform this large amount of energy into electric and chemical energy is crucial to fulfill future energy demands [3]. In this relation, nanometer sized TiO_2 materials have been widely studied as photocatalysts,

* Corresponding authors.

E-mail addresses: carlosorellanac@ug.uchile.cl (C. Orellana), hagua@uchile.cl (F. Mendizábal).

due to their low cost, high abundance in nature, high speed of injection of electrons to an external source [4], and their photocatalytic properties when illuminated with ultraviolet light [5,6]. Among the most prominent applications that incorporate nanostructured titanium dioxide as photocatalyst are dye-sensitized solar cells (DSSCs) [2–10], water splitting [11–16], and degradation of pollutants in water [17–21]. The photocatalytic efficiency of these processes depends on the energy of the valence band (VB) and the conduction band (CB), combined with the ability of TiO₂ to generate efficient charge separation states (excitons) trying to avoid electronic recombination in this process [22,23].

Yanagida and co-workers have suggested that TiO₂ may generate more efficient charge separation states, an ability that depends on the morphology of the semiconductor. They showed that in titanium dioxide nanoparticles (TiO₂NPs) the electron recombination rate is inversely proportional to the size of the NP. Thus, the authors established that when the size of the TiO₂NPs decreases, it is highly probable that grain boundaries also increase [24]. In this respect, Thavasi and co-workers [4] have synthesized TiO₂-based composites keeping only two dimensions in the nanometer scale and one dimension in the micrometer scale (these materials are commonly called 1D nanomaterials) in order to reduce the grain boundary of these types of TiO₂NPs. They were then able to improve the photocatalytic properties of the TiO₂NPs, causing an increase of the electron transport of the semiconductor and decreasing electron recombination in the same semiconductor. However, the increased photocatalytic activity achieved was not significant enough to give a practical use to these types of TiO₂(1-D) compounds. Therefore, it is necessary to find new alternatives that can be used to achieve more efficient photocatalytic processes.

Following this research line, González's group have synthesized a hybrid organic-inorganic composite based on TiO₂ a few atoms thick as the inorganic part, keeping two dimensions in the microcrystalline size (2D nanomaterial) [25–27]. They used a linear surfactant of the R-X type, where R corresponds to a long aliphatic chain and X is a functional group capable of anchoring the surfactant to the TiO₂ surface. The functional group acts as a structural anchor in the formation of these types of compounds through the sol-gel method. They were able to synthesize these types of compounds using TiO₂ [25] and zinc oxide (ZnO) [26] as the inorganic semiconductor. In both cases, the resulting systems displayed improved photocatalytic activity compared to unmodified nanostructured semiconductors.

These hybrid composites have a laminar architecture that may be determined by interactions between the metal cation of the semiconductor and the functional group of the surfactant, and supramolecular interactions between the organic components. Furthermore, to our knowledge, there are no other studies about these types of composites. Furthermore, there is no information about the atomic arrangement of the inorganic semiconductor in these systems. These arguments have been taken into account, and the present work was focused on the study of the magnitude of the interaction energies involved in the formation processes of these hybrid composites arranged in a lamellar phase. Models involving the [H₄Ti₁₆O₃₄] cluster (symbolized as TiO₂) representing the (100) and (101) faces of the anatase crystal phase were studied. These two models were chosen because the (101) phase is thermodynamically the most stable [28], and the (100) plane has been obtained when the semiconductor is synthesized using some Lewis base in the sol-gel synthesis method [29]. In both cases, this semiconductor is interacting with the surfactants hexadecylamine (HDA) or palmitic acid (PAC) (see Fig. 1), which allowed the effect of the functional group from the surfactant on the stability of the complexes to be assessed.

These models are symbolized as TiO₂^(m)[X]_n, where m stands for the representative plane of the anatase system used in the respec-

tive models (m = a when TiO₂ is oriented in the (100) plane, or b when it is oriented in the (101) plane). Also, in both cases X is the surfactant used (HDA or PAC) and n = 1 or 2 is the number of surfactant molecules contained in the model that is being studied. The main goal of this work is to describe the nature of the interaction that occurs in experimentally characterized hybrid composites based on titanium dioxide and palmitic acid [27] or hexadecylamine. To this end we present a series of models which are able to provide a detailed picture of the interaction between the carboxylic acid and the amino group with the TiO₂ surface. We have also involved interactions with the three-body approximation.

2. Models and computational details

The anatase (100) and (101) surfaces were modeled using a closed-shell cluster of formula [H₄Ti₁₆O₃₄] (TiO₂ cluster), which was built from a crystallographic model obtained from the Inorganic Crystal Structure Database (ICSD) [30]. Four hydrogen atoms have been added to saturate the frontier orbitals of oxygens in the cluster vertex. The H₄Ti₁₆O₃₄ cluster was constructed to represent a cluster of sixteen TiO₂ units. It has been reported in the literature that the (TiO₂)₁₆ cluster type is the minimum size to obtain significant results due to its stability [31], which means that these models can give results with chemical meaning equivalent to periodic models and large clusters [32–35]. The surfactants, HDA or PAC (one or two molecules), were deposited on the surface of the cluster. Then, the geometry of every model was optimized by keeping fixed the geometry of the TiO₂ cluster during the optimizations, in order to maintain the atomic ordering of the TiO₂ which is present in the nanometric scale, avoiding the deformation of the model due to the size effect of the cluster. To model the interaction between PAC and TiO₂, models have been built that incorporate the hydrogen atom of the carboxylic acid, and others without it. The purpose of this is to understand the interaction that occurs between the Pac-type surfactants and the TiO₂ surface either when the acid hydrogen of PAC is in the model or when it is not present in the model. We have not incorporated the solvent effect because the models represent a part of a system which is in the solid state.

All calculations were carried out with the TURBOMOLE program (version 6.6) [36]. The optimization of the geometry of all the models presented in this study was carried out within the scope of density functional theory (DFT) at the PBE [37,38] and TPSS [39] levels as exchange-correlation density functionals. The choice of these functionals is due to the fact that several studies have used these types of functionals to structurally describe compounds based on TiO₂ [40–43]. Furthermore, our research group has shown that there is no substantial difference in determining structural parameters and surface-substrate interaction energies when using GGA functionals and hybrid functionalities such as B3-LYP [44,45], which is recommended for the description of TiO₂ properties [22]. In all the calculations the identity approach of resolution applied to Coulomb integrals of the systems (RI-J) [46,47] was used in order to increase the computational efficiency of the calculations. The Grimme dispersion correction (D3 correction level) [48,49] was used to describe dispersion forces involved in the interactions. This is of great importance to describe interactions between low polarity molecules such as the surfactant molecules studied here [49,50].

The titanium [51], carbon, oxygen, and nitrogen [52] atoms were treated with the Stuttgart pseudopotentials, using the Stuttgart basis set for representing the valence electrons of the atoms mentioned above. A triple zeta basis set was used to describe hydrogen atoms [53]. For carbon, oxygen, and nitrogen a *d* type polarization function ($\alpha_d = 0.80$) [54] was added, and for the hydro-

Download English Version:

<https://daneshyari.com/en/article/5392377>

Download Persian Version:

<https://daneshyari.com/article/5392377>

[Daneshyari.com](https://daneshyari.com)