



Size and surface groups effects in decahedral anatase nanoparticles for photocatalytic applications

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ARTICLE INFO

Keywords:

Anatase
Nanoparticles
DFT
Quantum size effect
Electronic absorption spectra
Charge carriers

ABSTRACT

A large set of decahedral anatase nanoparticles with the size from 1.1 to 2.7 nm, shape approximately corresponding to maximal photocatalytic activity with $S_{001}/S_{101} = 0.55 \pm 0.14$ and diverse surface composition and structure have been considered to investigate quantum size effect, positions of photogenerated electrons and holes as well as absorption of light. There was a clear quantum size effect for electronic band gap E_g inside each group of nanoparticles with constant types of surface groups and their location. Photogenerated holes and electrons were distributed over atoms of surfaces (101) and (101) + (001), respectively, in majority of cases. For three cases of dehydroxylated nanoparticles, holes and electrons were distributed in (001) and (101) facets, correspondingly, in agreement to experimental observations on micrometer-sized particles. The presence of surface states caused a decrease in E_g to 2.6 eV for hydroxylated and to 2.3 eV for dehydroxylated nanoparticles in extreme cases. Absorption of visible light was significant for dehydroxylated particles while hydroxylated nanoparticles showed little absorption due to the presence of a smaller number of admixture states inside the band gap. Our results show the way to obtaining stoichiometric anatase nanoparticulate photocatalysts with visible light activity and provide insights into UV–vis spectra for anatase prepared at different calcination temperature and different extent of surface dehydroxylation.

1. Introduction

Anatase nanoparticles are considered as very interesting materials since they are active and stable photocatalysts [1–3] and can carry out the majority of photocatalytic reactions [4–6]. Modern methods of preparation allow obtaining anatase nanoparticles in a variety of shapes ranging from spherical that are typical for the widely used P25 photocatalyst to cubic, decahedral, dodecahedral and many other [3,7,8]. Among different shapes, decahedral anatase nanoparticles have the natural equilibrium shape [9,10] and demonstrate an increased activity in many photocatalytic reactions [11].

Photocatalytic deposition of metallic platinum and lead dioxide via reductive and oxidative processes, respectively, can reveal the location of reduction and oxidation sites. For decahedral anatase nanoparticles, photodeposition of Pt proceeded over (101) facets while PbO_2 over (001) facets [12]. Thus, the location of photogenerated holes and electrons was ascribed to (001) and (101) facets, respectively [7]. The high oxidative activity of (001) facet is confirmed by the increased activity of nanoparticles having a high fraction of this facet on their surface [13]. The tendency of separation of photogenerated electrons

and holes on different facets was observed for rutile nanoparticles also that showed reduction on (110) and oxidation over (111) facets [14].

A number of experimental studies dealt with size dependent electronic properties of anatase nanoparticles. The size of nanoparticles is controlled using different time hydrothermal treatment or calcination temperature and time. It was reported that the optical direct band gap of anatase nanoparticles first decreased and then increased with an increase in the nanoparticles size or changed irregularly [15]. This contrasts with the traditionally used Effective Mass Model (EMM) that predicts smooth decrease of the band gap with an increase of the nanoparticles size. The disagreement with EMM could be caused by Ti^{3+} admixture levels and defects that are introduced or removed during the thermal treatment and removal of surface chemisorbed water molecules [16,17]. Indeed, in an earlier study [18], the band gap widening was found only for TiO_2 nanoparticles with diameter below 2 nm, with other particles up to the size of 60 nm having demonstrated ± 0.1 eV variations in the band gap. We suppose that different surface composition of anatase nanoparticles caused different values of the band gap at their same size.

Several quantum chemical computational studies have been

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devoted to the effect of nanoparticles size on their band gap. Karvinen et al. [19] computed HOMO and LUMO energies with HF/6-31 G(d) for very small anatase nanoparticles with formulas Ti_9O_{18} , $\text{Ti}_{17}\text{O}_{34}$ and $\text{Ti}_{21}\text{O}_{42}$. The band gap changed irregularly for these nanoparticles and was equal to 3.53, 3.42 and 3.75 eV, respectively. Makowska-Janusik et al. investigated quantum size effect in spherical anatase nanocrystals with size 0.6–2.0 nm of stoichiometry $(\text{TiO}_2)_2$ to $(\text{TiO}_2)_{140}$ [20]. Single point pm6 and DFT computations with GGA and hybrid functional were used for obtaining electronic band gap values E_g . The E_g decreased from 6 to 3.2 eV when the size of NP increased from 7 to 12 Å and remained almost same for nanoparticles with size 20 Å. DFT methods gave the same tendency but the values of E_g varied widely with LC-BLYP functional seemed to deliver the best agreement with the experimental value for the largest NP. However, the quantum size effect could not be confirmed for rectangular anatase nanoparticles which electronic and optical band gaps varied irregularly as the size of nanoparticles increased [21] according to pm6 and pm7 [22] methods. The approach applied to obtaining the band gap values using unrelaxed nanoparticles could not be correct since the structure of real nanoparticles deviates from the bulk anatase. Qu and Zhu using B3LYP/6-31 + G(d) studied quantum size effect for very small anatase clusters $(\text{TiO}_2)_n$ for $n = 1$ –10 and found growth of band gap with an increase in the cluster size [23]. A relatively smooth quantum size effect was observed by Li and Liu for decahedral nanoparticles with size 1.2–2.7 nm [24].

Preferential positions of photogenerated electrons and holes were studied computationally for decahedral anatase nanocrystals containing 105, 246 and 465 atoms [25]. It was found that both HOMO and LUMO frontier orbitals are delocalized over many atoms inside the nanoparticle and over (101) facets. Hence, both trapped electrons and holes were suggested to be located as small polarons at the vertices between (101) facets. Even stronger disagreement with experimental data was reported for decahedral nanoparticles of various shape [26]. HOMO was located around the junction of (101) facets while LUMO at or closer to the (001) facets [24].

In the present paper, we report a computational investigation on the influence of decahedral anatase nanoparticles size and surface groups on the band gap and the location of photogenerated electrons and holes as represented by LUMO and HOMO orbitals. The shape of the particles is chosen in such a way so that it represents nanoparticles corresponding to the highest photocatalytic activity [8]. We also consider a nanoparticle with (001) facet after its (1×4) reconstruction. We discover that quantum size effect of a decrease in electronic band gap with a decrease in nanoparticles size is observed if nanoparticles are separated into groups according to their surface composition and structure. The band gap decreases to values well below the E_g for bulk anatase due to the presence of surface states of undercoordinated titanium atoms and surface groups. Introduction of the (001) surface reconstruction does not change localization of photogenerated electrons and holes. A large absorption in the visible light region is observed for many nanoparticles with the completely dehydroxylated surface.

2. Models and methods

While nanoparticles could be produced via global optimization, this method turned out to be too computationally expensive for nanoparticles containing hundreds of atoms [27]. Therefore, we used lattice structures with additional groups to keep the structures stoichiometric. Structure and some properties of decahedral clusters of anatase with different size and different surface groups of the present study have been reported previously [28,29]. These nanoparticles were first cut from bulk anatase lattice and augmented with surface groups to ascertain their charge neutrality and oxidation state of titanium 4+ [30]. Complete geometry optimization was performed with scc-dftb method [31] using Slater-Koster files tiorg-0-1 [32] and mio-1-1 in the program dftb+ [33]. UV-vis absorption spectra were computed with the linear response theory of time-dependent scc-dftb Casida formalism. Enthalpy

of formation of the nanoparticles was computed using pm6 method after complete geometry optimization in MOPAC program.

Optical band gap of decahedral anatase nanoparticles was estimated using Tauc plots [34]. The UV-vis absorption spectra were replotted as $(\alpha h\nu)^{1/r}$ versus $h\nu$, where α is the absorption coefficient, $h\nu$ is the quantum energy, r is equal to 0.5 for direct allowed transitions, 1.5 for direct forbidden transitions, 2 for indirect allowed transitions, 3 for indirect forbidden transition and 1 for nanocrystalline direct allowed transitions [35]. The best linearization was obtained with $r = 2$. The ratio S_{001}/S_{101} of the surface areas of facets (001) and (101) was calculated by assuming rectangular shape of (001) facets and equilateral trapezoid shape of (101) facets.

3. Results and discussion

3.1. Stability of decahedral anatase nanoparticles with different arrangements of surface groups

Decahedral anatase nanoparticles of the present study contain equal number of elementary cells in directions x and y and a selected number of atomic layers in direction z to make the size in all three dimensions as similar as possible. Fig. 1 shows atomic structures of the optimized nanoparticles of the present study. The clusters presented in Fig. 1(a)–s) were optimized with semiempirical method pm6 and clusters t) and u) were optimized with scc-dftb. Structure of clusters Ti22r1–Ti55r5 optimized with scc-dftb has been reported previously [28]. The methods of optimization pm6 and scc-dftb provide somewhat different structure of nanoparticles. Pm6 leads to almost straight geometry of Ti–O–H groups and scc-dftb provides cell parameters that are significantly closer to the experimental values. Nevertheless, pm6 method was calibrated for enthalpy of formation and these values can be trusted. Hence, geometric properties are taken from the results of optimization with scc-dftb method, while enthalpy of formation is provided by pm6 method for comparison of the clusters stability.

Table 1 presents data of stoichiometry, enthalpy of formation and energy for all the clusters of the present study. Comparison of clusters can be made only for the same stoichiometry. Thus, all the decahedral nanoparticles can be organized into groups with additional groups represented by hydroxyl groups, or by oxygen atoms. Titanium atoms with excessive electrons are located at the edges between facets (001) and (101) as well as at the vertices between four adjacent facets (101). Therefore, hydroxyl groups are attached either to titanium atoms at the (001)/(101) edges as in nanoparticles Ti22r1, Ti33r1, Ti44r1, Ti55r4, Ti551.5r and Ti551.5rR, to titanium atoms at (101)/(101) vertices and at (001)/(101) edges as in nanoparticles Ti22r2, Ti55r3, Ti33r2, Ti33r3, Ti33r3, Ti44r2, Ti44r3 and Ti55r5. For the nanoparticles with hydroxyl groups, the highest stability is obtained for the geometries with hydroxyl groups at the (001)/(101) edges according to both methods used, pm6 and scc-dftb. Nanoparticles Ti22r2, Ti22r3 and Ti33r2, Ti33r3 represent pairs of stereoisomers with different symmetry of OH groups location at opposite (001) facets. Their stability is very similar according to both pm6 and scc-dftb methods.

Nanoparticles Ti44r2 and Ti44r3 differ by location of OH groups at (001)/(101) edges. In Ti44r2 they are located at the vertices formed by (001) and two (101) facets, while in Ti44r3, OH groups are located near each other. This last type of geometry is more stable.

Nanoparticles with additional oxygen atoms can also have different distribution of these oxygens over titanium atoms with excessive electrons with a large number of alternatives. These oxygen atoms can be situated at (001)/(101) edges as in nanoparticle Ti33r4, Ti44r6, Ti44r7, Ti55r2 and Ti55r3, or at (101)/(101) corners as in Ti33r5. Stability of the nanoparticle with oxygen atoms at (001)/(101) edges is higher. For nanoparticles with oxygen atoms at (001)/(101) edges, stability should be determined individually for each case, as closely situated oxygens can be less stable as for Ti44r6 or more stable as for nanoparticle Ti55r3.

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