

# The Effect of the Preparation Condition of TiO<sub>2</sub> Colloids on Their Surface Structures

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Hydrothermal synthesis of TiO<sub>2</sub> colloids is based on hydrolysis and pressure treatment of titanium isopropoxide precursor in acidic solutions. The influence of the use of nitric and acetic acids during the synthesis was studied, showing a significant effect on the colloid crystal structure. Both dark-field TEM and phase transformation temperature measurements indicate that the colloids prepared in acetic acid contain more of the {101} face compared with the colloids prepared in nitric acid. The surface structure difference affects the performance of dye-sensitized solar cells that consist of electrodes made from these colloids. Better performance is achieved using the colloids prepared in nitric acid, indicating the importance of controlled colloid fabrication for higher conversion efficiencies.

## Introduction

The high light-to-energy conversion efficiencies achieved with dye-sensitized solar cells may be attributed to the nanoporous TiO<sub>2</sub> electrodes.<sup>1–3</sup> These electrodes consist of nanosize TiO<sub>2</sub> colloids that are sintered on a transparent conducting substrate. The sintering process forms electrical contact between the various colloids and between the colloids and the substrate.<sup>2,4</sup> The electrodes have a porous geometry and a very large surface area. When 10–20 nm colloids are used, for example, the surface area of a 10- $\mu$ m thick electrode is approximately a thousand times larger than the area of the substrate.<sup>5</sup>

The nanoporous semiconductor electrode is one of the more puzzling components of the dye-sensitized solar cell. Various studies were aimed at a basic understanding of its operation in the cell. These studies address topics such as the mobility of photoinduced electrons in the porous film,<sup>6–10</sup> the bands position at the film–TCO interface,<sup>11</sup> and the potential distribution across the film.<sup>12</sup> Other high surface area semiconductors such as SnO<sub>2</sub>,<sup>13,14</sup> ZnO,<sup>15</sup> SrTiO<sub>3</sub>,<sup>16</sup> and Nb<sub>2</sub>O<sub>5</sub><sup>17</sup> were tested in order to achieve better understanding of the system and better energy conversion efficiencies. However, despite the high level of activity, a comprehensive fundamental understanding of the system has not been achieved yet.

It is generally accepted that the properties of the nanoporous electrodes depend on the properties of the colloids used to fabricate them.<sup>4,2,11,18</sup> This dependence includes the size, shape, crystal structure, and energetics of the colloids. The size and shape of the colloids from which the electrodes are made determine the porosity and the surface area-to-thickness ratio of the electrodes.<sup>19</sup> The energetics of the colloids, that is, the flat band and band gap potentials, affect the energetics of the electrodes.<sup>20–22</sup> And finally, the colloids crystal structure determines the activity of the nanoporous electrodes.<sup>18,2,23</sup> Therefore, when electrodes are made from colloids that have

the same size, shape, crystal structure, and energetics they are considered to be similar.

We report here measurements of a new factor that has to be considered when comparing the TiO<sub>2</sub> colloids: the surface structure. Colloids that were synthesized under different conditions but have the same size, shape, and crystal structure differ from each other by the ratio between the different surface structures. This difference affects the anatase-to-rutile phase transformation temperature in agreement with reported calculations.<sup>24</sup> In addition, the surface structure difference affects the performance of dye-sensitized solar cells that consist of electrodes made from these colloids. The results suggest that the efficiency of dye-sensitized solar cells can be improved by a controlled synthesis of colloids that contain more of the preferred surface structure.

## Experimental

**Colloid Synthesis.** Two sets of TiO<sub>2</sub> colloids were prepared using the standard hydrothermal method reported previously.<sup>25</sup> This method includes titration of titanium isopropoxide into acid followed by aging and hydrothermal processing. The major difference between the two preparations relates to the type of acid used: nitric acid in one case and acetic acid in the other. To achieve the same crystal size in both preparations, small changes in the pH and the autoclaving temperature were performed.

Two aliquots of 11.5 mL of titanium (IV) isopropoxide (Ti[OCH(CH<sub>3</sub>)<sub>2</sub>]<sub>4</sub>, Aldrich, 99.9%) in 11.5 mL of dry 2-propanol were slowly added into 15.4 mL of pH 2 nitric acid and 15.4 mL of pH 3 acetic acid solutions under vigorous stirring to obtain a white precipitate. The solutions were subjected to aging at ambient temperature for 12 h. The resulting solutions were heated at 82 °C for 2 h to evaporate the 2-propanol. The nitric and acetic acid TiO<sub>2</sub> sols were then subjected to hydrothermal condensations at 250 °C and 280 °C (oven temperature), respectively, for 13 h in separate titanium autoclaves (Parr Instruments).

**Colloid Characterization.** X-ray diffraction patterns were used to determine the identity, quantity, and crystallite size of

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**TABLE 1: Summary of the Properties of the Colloids Prepared in Nitric and Acetic Acids Showing Similar Size, Shape, Crystal Structure, and Impurities**

	nitric acid	acetic acid
structure	92.6% anatase 7.4% brookite	93.2% anatase 6.8% brookite
average size (TEM)	12.9 nm (SD 2.8)	12.4 nm (SD 4.5)
average size (XRD)	12.8 nm	12.3 nm
surface area	119 m <sup>2</sup> /g	118 m <sup>2</sup> /g
aggregation	3002 nm	2990 nm
C, H <sub>2</sub> , N <sub>2</sub> (450 °C)	No	No

each phase present. The powder XRD patterns were recorded using an X-ray diffractometer (Rigaku 2028) with Cu K $\alpha$  radiation. The average crystallite size,  $D$ , of the hydrothermally prepared powders was calculated from the Scherrer formula.<sup>26</sup> The extent of transformation to rutile was calculated using the ratios of areas under background-subtracted {101} anatase and {110} rutile peaks.<sup>27</sup> The agglomerated particle size was measured by photon correlation spectroscopy using Coulter N4plus. Surface area measurements of the powders were carried out with a standard BET surface area analyzer (Micromeritics Gemini III 2375). The elemental analysis was carried out using Elemental Analyzer (EA 1110) to check the percentage of carbon and nitrogen. Conventional TEM bright-field imaging and dark-field imaging and electron diffraction were carried out with a Phillips CM-120 microscope, operating at 120 kV. Electron diffraction patterns were taken with or without a selected area aperture; in the cases in which an aperture was used, the aperture diameter was 0.9 mm and the patterns were obtained at a camera length of 900 mm. High-resolution TEM (HRTEM) images were taken at a magnification of 500 000 $\times$  or more using an objective lens of 0.9 mm. Samples for TEM analysis were prepared by dispersing TiO<sub>2</sub> onto TEM copper grids coated with thin amorphous carbon.

**Dye-Sensitized Solar Cells.** Conductive glass substrates (Libby Owens Ford, 8 ohm/square F-doped SnO<sub>2</sub>) were cleaned with soap rinsed with deionized water and dried in a nitrogen stream. The TiO<sub>2</sub> colloid paste was spread over the substrate with a glass rod using adhesive tape as spacers. The films were fired at 450 °C for 30 min in air resulting in 6- $\mu$ m thick films. The dye (*cis*-di(isothiocyanato)-*N*-bis(4,4'-dicarboxy-2,2'-bipyridine) ruthenium(II)) was adsorbed by immersing the electrodes overnight in an 0.5 mM ethanol solution of the dye. The amount of dye adsorbed on the electrode was measured by visible absorption of the electrode using an integrating sphere (Cary 500). The film thickness was measured with a profilometer (Mitutoyo, SurfTest SV 500).

A sandwich-type configuration was employed to measure the performance of the dye-sensitized solar cell having a Pt coated F-doped SnO<sub>2</sub> film as a counter electrode. Illumination of the cell was done using a calibrated Xe lamp and direct sun. An Eco Chemie potentiostat was used to measure the photocurrent and photovoltage.

## Results and Discussion

Two sets of TiO<sub>2</sub> colloids prepared by the hydrothermal process are compared in this paper. The major difference between these sets is the type of acid used during the synthesis, nitric acid in one case and acetic acid in the other. Small pH and autoclaving temperature modifications resulted in colloids that seemed to be similar with respect to the standard characterization parameters that is, size, shape, crystal structure, and impurities.

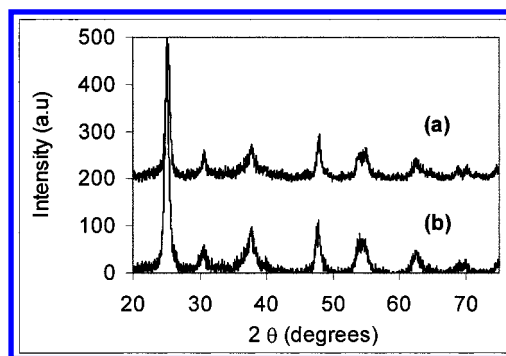
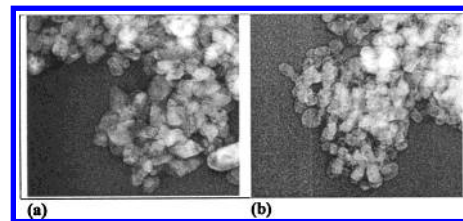
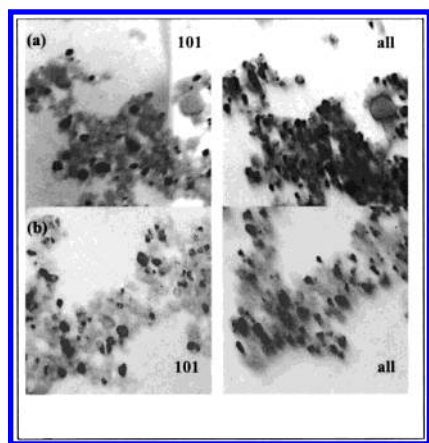
**Figure 1.** X-ray diffractograms of the two sets of colloids prepared by the hydrothermal process in (a) nitric and (b) acetic acids.**Figure 2.** TEM pictures of the two sets of colloids prepared by the hydrothermal process in (a) nitric and (b) acetic acids.

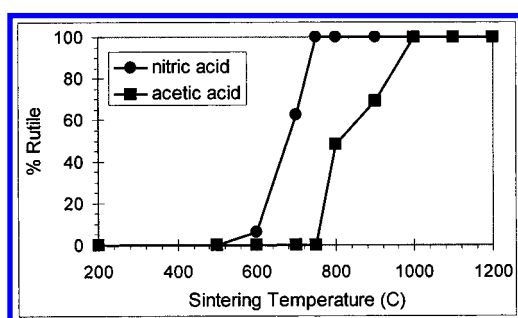
Table 1 and Figures 1–2 summarize the characterization of the TiO<sub>2</sub> colloids. The X-ray diffractograms of the two sets of colloids presented in Figure 1 show that in both preparations, the dominant crystal structure of the colloids is anatase. Both samples contain ca. 7% of the brookite structure that disappears during the high-temperature sintering treatments. The TEM pictures of the two sets presented in Figure 2 show that comparable colloid shapes are produced in both preparations. The average colloid sizes presented in Table 1 are similar in both preparations differing slightly by their size distribution values. The average sizes were calculated from the X-ray diffractograms by the Scherrer formula and from the TEM pictures counting 200 particles.<sup>26</sup> Table 1 further presents the similarity in the colloidal powder surface area (BET measurement) and the size of colloidal aggregates (photon correlation spectroscopy). Finally, nitrogen and carbon impurities were not found in either the nitric acid or the acetic acid based colloids. The elemental analysis measurements were done after 450 °C heat treatment, which was used throughout the research.

Despite the similarities found using the standard characterization methods, the crystals prepared in the different solutions differ by surface structure. The calculated most stable TiO<sub>2</sub> crystal is a cleaved bipyramid.<sup>23,24</sup> According to this calculation, the surface structure of the colloids should consist of the {101}, {001}, and {221} surfaces with a specific ratio between them.<sup>24</sup> Experimental reports suggest that other surface structures such as {111}, {103} and {100} also exist in TiO<sub>2</sub> colloids.<sup>19,28</sup> The difference in surface structures is evident from TEM analysis and from measurements of the colloid anatase-to-rutile phase transformation temperature.

Dark-field TEM was employed to differentiate the {101} diffraction of the colloids from the total of all other diffractions. Further differentiation is beyond the resolution of the microscope used in this investigation. Figure 3 presents two sets of dark-field TEM pictures showing just the {101} diffraction of the colloids and then showing the total of all the other diffraction. Dividing the number of colloids present in the {101} picture by the number of colloids in the parallel “all diffraction” picture provides a value (denoted F101) that is proportional to the fraction of the {101} face in the overall colloid surface area. It



**Figure 3.** Dark-field HRTEM pictures of the colloids prepared by the hydrothermal process in (a) nitric and (b) acetic acids. The corresponding {101} diffraction and all the other diffractions are marked in the figure.



**Figure 4.** The percentage of rutile present in the TiO<sub>2</sub> sample after treatment at the relevant temperature for 3 h (measured by XRD).

is important to note that F101 is sensitive to many factors, such as preferred orientation, thus it is used here only for comparison between the two comparable colloid sets. The F101 values calculated for the nitric acid and acetic acid based colloids are 0.27 and 0.78, respectively. These results suggest that the colloids prepared in acetic acid contain ca. 3 times more of the {101} face structure in comparison with the colloids prepared in nitric acid.

A similar trend was obtained when HRTEM was employed to differentiate the {101} face from all other faces. The colloids prepared in both acids were imaged by HRTEM, and the surface structure to each of the colloids was assigned by the distance between fringes. Calculating the F101 value for 25 colloids of each preparation shows that the colloids prepared in acetic acid contain ca. 4 times more of the {101} face structure in comparison with the colloids prepared in nitric acid.

The preparation-induced surface structure difference of the TiO<sub>2</sub> colloids is also evident from their anatase-to-rutile phase transformation temperature. Figure 4 presents the anatase-to-rutile transformation curves of the two types of colloids. Each point on the graph represents the percentage of rutile present in an anatase sample that was sintered for 3 h at the indicated temperature. The extent of transformation was calculated using the ratios of areas under the {101} anatase and {110} rutile peaks. Figure 4 shows that the colloids prepared in nitric acid experience phase transformation at a lower temperature compared with the colloids prepared in acetic acid. Since this trend may result from size effects caused by the size distribution, similar measurements were done for particles of various average sizes. Regardless of size, in the range of 9–20 nm all the colloids prepared in nitric acid show lower transformation temperatures compared with the colloids prepared in acetic acid.

**TABLE 2: A Comparison between Dye-Sensitized Solar Cells that Contain Electrodes That Were Fabricated from the Colloids Prepared in Nitric and Acetic Acids**

	nitric acid	acetic acid
Voc (mV)	625	605
Jsc (mA/cm <sup>2</sup> )	14.9	11.9

The different transformation temperatures may be attributed to variance in either the surface or the bulk of the colloids.<sup>29,30</sup> Careful examination of the XRD and HRTEM show no evidence of defects in the colloids that might affect the phase transformation temperature. The X-ray diffractograms are similar to reported ones of pure TiO<sub>2</sub>, and no disorders in the crystal fringes imaged by HRTEM were found. The fact that the average size calculated from the X-ray diffractograms equals the size measured from the TEM pictures also supports this hypothesis. The different transformation temperature is, therefore, attributed to the variance in the surface of the colloids that results from the preparation conditions. The surface structure/surface energy has a significant influence on the overall colloid stability for small colloids, in which a large fraction of the atoms are at the surface.<sup>23,29</sup>

Oliver et al. calculated the surface energy of all the possible surfaces of TiO<sub>2</sub> colloids showing that {101} and {001} are the most stable surface structures.<sup>24</sup> Colloids consisting of these surface structures are thus expected to be more stable. The results presented in Figure 4 show that the colloids prepared in acetic acid are more stable, suggesting that their surface contains more of the {101} and {001} structures. This finding is in line with the dark-field measurements described above that show a higher fraction of the {101} face in the colloids prepared in acetic acid.

The ability to control the surface structure of the TiO<sub>2</sub> colloids is important in all the applications that are based on processes occurring at the colloid surface. One such application is the dye-sensitized solar cell that consists of nanoporous TiO<sub>2</sub> electrode. A comparison between the photovoltaic performance of two cells containing electrodes that were fabricated from the two types of colloids shows that the colloids made in nitric acid are preferable for dye-sensitized solar cells (Table 2). The compared cells were fabricated using similar procedures and measured under similar conditions in order to extract the contribution of the surface structure. Both the nitric acid and acetic acid based electrodes were fabricated as described in the Experimental Section. Absorption measurements showed that they were coated with the same amount of dye. The measurements were done with an integrating sphere accessory in order to avoid light scattering effects. Both electrodes had similar surface areas and thicknesses as measured by BET and a profilometer. The electrolyte used in both solar cells was 0.5M LiI/0.05M I<sub>2</sub> in dry acetonitrile, so that large cation effects are not expected. The unavoidable small difference in size distribution and colloid shape should, however, be noted.

The mechanism for the superior performance of dye-sensitized solar cells that consist of the colloids prepared in nitric acid is not yet known. It may relate to the effect of the surface structure on many processes that take place in the cell, including the injection, recombination, electron mobility, and energetics. Further experiments to clarify this mechanism are in progress.

## Conclusions

The surface structure of TiO<sub>2</sub> colloids prepared by hydrothermal synthesis is affected by the type of acid used in the process. Colloids that were prepared in acetic acid contain more

of the {101} structure face in comparison with the colloids prepared in nitric acid. This difference affects the performance of dye-sensitized solar cells that consist of nanoporous electrodes made from these colloids. A comparison between operating cells shows that the colloids prepared in nitric acid should be preferred for these cells.

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