

Polymeric Templating Synthesis of Anatase TiO₂ Nanoparticles from Low-Cost Inorganic Titanium Sources

Manuel Ojeda,^[a] D. Kishore Kumar,^[a] Binbin Chen,^[b] Jin Xuan,^[a] M. Mercedes Maroto-Valer,^[a] Dennis Y.C. Leung,^{*[b]} and Huizhi Wang ^{*[a]}

Abstract: A novel facile and cost-effective synthesis method for anatase TiO₂ nanoparticles has been developed by using poly-acrylic acid hydrogel as template at room temperature. The newly developed synthesis method avoids the use of hazardous reagents and/or hydrothermal steps, and enables production of highly active TiO₂ nanoparticles from low cost inorganic titanium sources. The synthesized TiO₂ nanoparticles have been studied in several applications including dye-sensitized solar cells as a photoanode as well as in organics degradation of methyl orange in aqueous media. Good photocatalytic performances were obtained in both applications.

Introduction

TiO₂-based materials are playing an important role in the areas of energy and environment for its wide application as a photoactive catalyst for solar fuels, environmental remediation, photovoltaics as well as in a broad spectrum of processes connected to heterogeneous photocatalysis.^[1] Among the three crystalline forms of TiO₂ (anatase, rutile, and brookite), anatase is particularly attractive for energy and environmental applications because of its outstanding photocatalytic activity compared to the two other forms.^[2] Anatase titanium dioxide nanoparticles have been produced by a variety of synthetic techniques, which allow the synthesis of elaborated shapes as well as the formation of composite materials.^[3]

Normally, titanium precursors are needed as feedstock to produce TiO₂ nanoparticles. The high initial cost of titanium precursors still hinder the wide practical applications of TiO₂ nanoparticles.^[4] Within the precursors, organic titanium sources (typically titanium alkoxides) are predominantly used in the synthesis processes to obtain anatase TiO₂ nanoparticles,^[5]

which make the products expensive due to its order-of-magnitude higher cost compared to inorganic sources (US\$10,000 per ton of titanium butoxide with 99% purity vs. US\$1,000 per ton of titanium (IV) chloride with 99% purity).^[6] Besides, the preparation method is considered as another important factor to determine the cost of anatase TiO₂ nanoparticles production. In literature, the typical synthesis method of anatase TiO₂ is by hydrothermal preparation,^[7] which involves the use of several reagents and solvents, as well as long periods of heating and controlled pressure. This increases the energy demand to obtain the anatase phase, and also affect the reproducibility due to the multistep protocol.^[8]

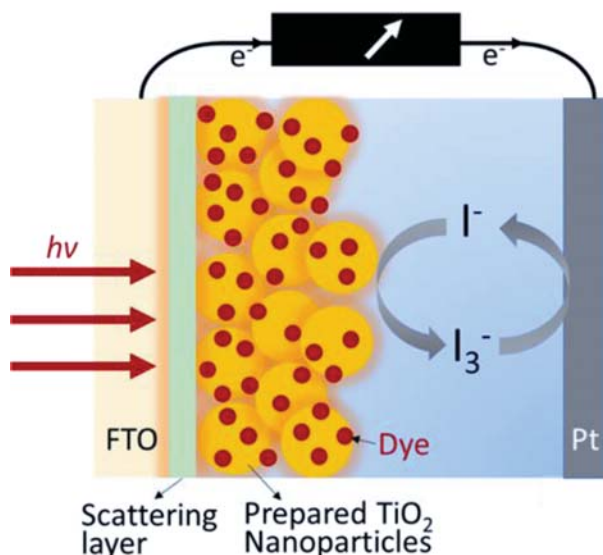
Due to the limitations above, there is an urgent need to develop new methods to synthesize anatase TiO₂ using cheap inorganic sources and simple procedure. Few works can be found in literature on the synthesis of TiO₂ nanoparticles from cost effective inorganic sources such as TiCl₄ as alternative Ti source. The formation of anatase crystalline nanoparticles phase using inorganic sources is sensitive to several factors such as pH control, temperature and additives, making it difficult to control the particle size and purity of the synthesized TiO₂.^[9] Shahi et al. described the synthesis of photoactive nanocrystalline anatase TiO₂ with acid ionic liquids at room temperature. The obtained micropore anatase TiO₂ with particle sizes between 4 and 30 nm that presented high efficiency on the degradation of methyl orange under ultraviolet light.^[10] Liu et al. reported the synthesis of carbon-titanium nanocomposites by using an organic triblock copolymer as template by a hydrothermal process.^[11] Other methods using inorganic sources have been also described such as wet chemical process, thermolysis in strongly acidic media, chemical vapour deposition, *etc.*, all of which entail complex steps among the utilization of hazardous reagents such as strong acids.^[12]

A simple and straightforward synthesis of titanium dioxide nanoparticles from low-cost inorganics sources, at the same time avoiding the presence of hazardous reagents and additives could be cost-competitive and environmental-friendly. However, such method has not been developed to date. In this work, a simple, cost-effective, and highly reproducible protocol is reported for the synthesis of anatase titanium dioxide nanoparticles at room temperature in two simple steps: preparation of the titanium precursor gel and subsequent calcination to obtain the titanium dioxide anatase crystalline form. In order to compare the properties of the synthesized titanium, two different sources have been utilized, e.g. organic (Ti(OC₄H₉)₄) and inorganic (TiCl₄). The obtained nanoparticles were tested in different applications,

[a] Dr. M. Ojeda, Mr. D.K. Kumar, Dr. J. Xuan, Prof. M.M. Maroto-Valer, Dr. H. Wang
School of Engineering and Physical Sciences
Heriot-Watt University
Edinburgh, EH14 4AS, (United Kingdom)
E-mail: H.Wang@hw.ac.uk

[b] Mr. B. Chen, Prof D.Y.C. Leung
Department of Mechanical Engineering
The University of Hong Kong
Pokfulam Road, (Hong Kong)

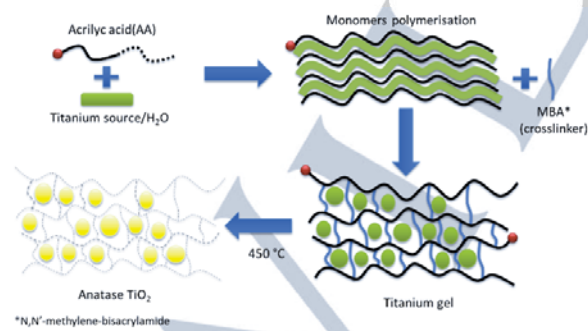
including dye-sensitized solar cells –DSSCs- (Scheme 1) as well as photocatalytic dye degradation of methyl orange in aqueous media under UV radiation.



Scheme 1. DSSC configuration.

Results and Discussion

Anatase titanium dioxide nanoparticles were obtained by a simple two-step method: preparation of the titanium precursor gel and subsequent calcination to obtain the titanium dioxide anatase crystalline form and removal of the organic phase (Scheme 2). Two different sources of titanium, which are titanium (IV) butoxide ($\text{Ti}(\text{OC}_4\text{H}_9)_4$) and titanium (IV) chloride (TiCl_4), denoted as Ti-B and Ti-C respectively, were used in order to compare the properties of the synthesized titanium nanoparticles.



Scheme 2. Synthesis of TiO_2 nanoparticles by using a polymer gel agent at room temperature.

The phase composition and the crystalline size of the TiO_2 materials were studied by XRD. Figure 1 represents the pattern of TiO_2 nanoparticles obtained after calcination at 450 °C,

prepared from both precursors, i.e. titanium butoxide and titanium (IV) chloride which clearly correspond to anatase structures with peaks at 2θ equal to 25.5, 37.4, 37.9, 40.5, 48.1, 53.9, 55.3, 62.6, 68.8, 70.5, and 75.5 degrees, corresponding to (101), (103), (004), (112), (200), (105), (201), (204), (116), (220) and (215) reflexes, respectively, and in good agreement with JCPDS files #21-1272.^[13]

Absence of traces of the precursor materials in the diffractogram shown in Figure 1 confirms the synthesized TiO_2 nanoparticles as anatase phase with minimal concentration of crystalline impurities (less than 2-4 wt%). Nanoparticle size was calculated by Debye-Scherrer's formula using the (101) peak and it was ca. 8-10 nm for both Ti-C and Ti-B, which is in good agreement with TEM images of the titanium nanoparticles (Figure 2). TEM micrographs show that titanium materials present spherical-like morphology with uniform size distribution in both titania materials. In literature work with typical synthesis procedures, TiO_2 nanoparticles sizes were usually reported to be larger than 10 nm when high-temperature treatments is involved during the hydro/solvo-thermal preparation or the postsynthesis annealing to achieve crystalline TiO_2 nanoparticles,^[14] due to the sintering of the titanium nanoparticles.^[15]

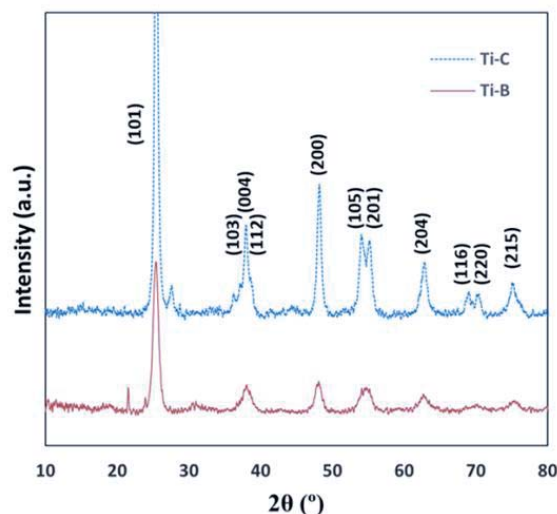


Figure 1. XRD patterns of TiO_2 nanoparticles.

Therefore, our newly developed strategy to incorporate titanium source into the gel network represents significant advantage in controlling nanoparticle size (< 10 nm), by preventing the sintering/growth of larger nanoparticles in the annealing step to form the crystalline phase.

Textural properties such as specific surface area and pore volume of the anatase TiO_2 materials were studied by using the N_2 adsorption isotherms. Discernible pores are present at the space between the nanoparticles, indicating that the mesoporosity is due to the interparticle space. Ti-B and Ti-C showed values of BET surface area of 78.68 and 64.28 m^2/g ,

respectively, both higher than commercial Degussa P25 (ca. 50 m²/g).

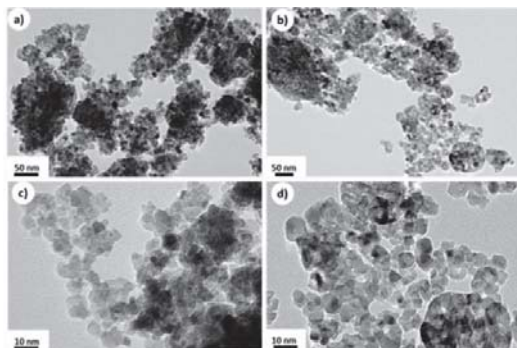


Figure 2. TEM micrographs of: a) and c) Ti-B; b) and d) Ti-C.

Further investigations on surface composition of the materials by XPS (Figure 3) clearly confirmed Ti and O as the main elements. The C 1s and N 1s peaks could be due to the presence of undecomposed organic hydrogel after calcination at 450 °C. Figure 3a shows the Ti 2p spectra of TiO₂ nanoparticles, with a similar profile for both materials Ti-B and Ti-C. The Ti 2p_{3/2} and 2p_{1/2} peaks appear at 458.7 and 464.6 eV, which are attributed to the Ti 2p peaks of O-Ti-O.^[16] The peaks indicate the presence of Ti(IV) oxide.^[17]

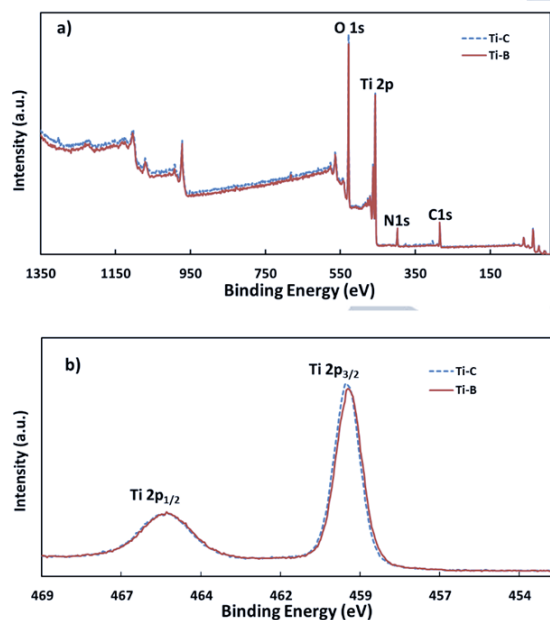


Figure 3. XP spectra of TiO₂ nanoparticles a) survey, and b) Ti 2p.

Figure 4a shows the transmission spectra of TiO₂ films. It is observed that the Ti-C and Ti-B materials show the similar optical properties. The Tauc-plots of the films are shown in Figure 4b. The optical band gap for Ti-C and Ti-B film is found to be 3.32 eV and 3.33 eV, respectively, which correspond to the band gap of normal anatase TiO₂.

The photovoltaic performance of TiO₂ nanoparticles was studied as a photoanode in DSSC. Figure 5 shows the photocurrent-voltage curves for the titanium nanoparticles-based DSSCs (by using Ti-C and Ti-B) under AM 1.5G light illumination of 100 mW/cm².

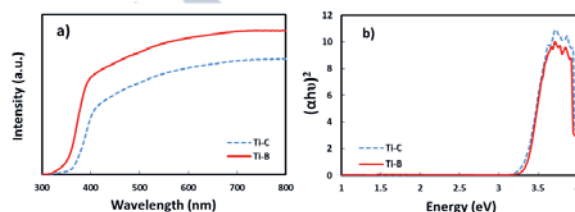


Figure 4. a) Transmittance spectra; and b) Tauc plots of TiO₂.

The behaviour of Ti-C and Ti-B in DSSC are quite similar in both titanium materials. Photovoltaic parameters such as open circuit voltage (V_{oc}), short-circuit current density (J_{sc}), fill factor (ff%) and photoconversion efficiencies (η%) are summarized in Table 1. The results indicate that anatase TiO₂ prepared from inorganic source exhibited a similar performance as compared with those obtained from organic source, with an efficiency slightly higher for Ti-C device (5.2%). The cell efficiency obtained in this study is also comparable to those cells reported in recent literatures using different pre-formed anatase TiO₂ nanoparticles with spherical morphology and N719 solution as dye (4~7 %).^[18]

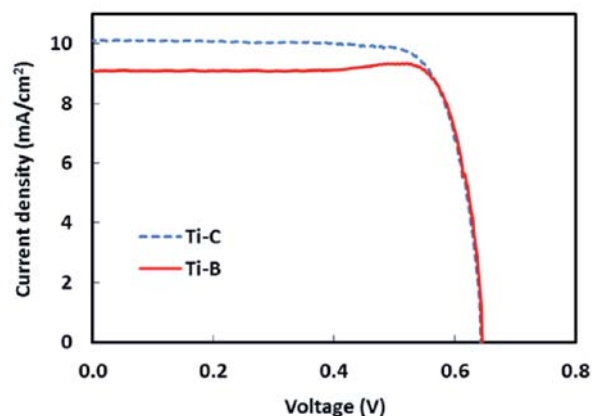


Figure 5. J-V characteristics of DSSC recorded with Ti-C and Ti-B.

Table 1. Photovoltaic parameters of the DSSC made from Ti-B and Ti-C.

Sample	Voc (V)	Jsc (mA/cm ²)	ff%	η%
Ti-C	0.659	10.4	75.5	5.2
Ti-B	0.644	9.3	83.5	5.0

Photodegradation of aqueous MO was studied under UV irradiation for 60 min. Degussa P25 was utilised for comparison under the same conditions. Figure 6 illustrates the percentage of degradation of MO at different time intervals using both titanium nanoparticles Ti-B and Ti-C, as well as P25. The percentage was obtained using the following equation:

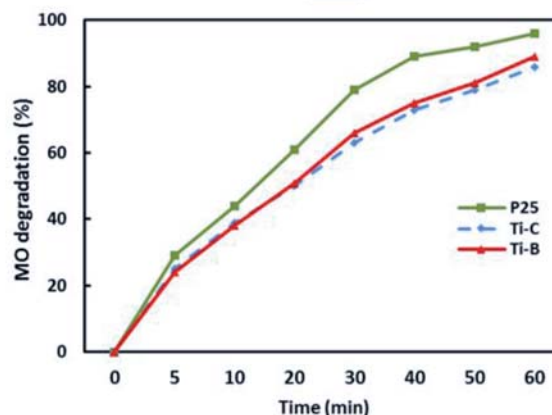
$$\text{Degradation \%} = [(1 - A_t)/A_0] \times 100$$

where A_0 is the initial absorbance and A_t is the obtained absorbance from the different samples after time t . The degradation occurs in a similar rate with both titanium nanoparticles, with almost complete degradation of MO within 1 hour. Commercial Degussa P25 showed a slightly better performance than Ti-C and Ti-B, which could be due to the synergistic effect between anatase and rutile phases as described in literature.^[19] This proposed synthesis method can be scale-up due to its easy, reproducible and cost-effective protocol which allows the utilisation of both organic and inorganic sources for its synthesis.

Conclusions

A new synthesis protocol for TiO₂ nanoparticles has been developed which allows the utilization of either organic or less expensive inorganic sources. This protocol entails two steps: formation of TiO₂ gel by using acrylic acid and its subsequent calcination in order to obtain pure anatase TiO₂ which was corroborated by XRD. These materials showed similar physicochemical properties independently of the titanium source utilized, showing an average nanoparticle size ca. 8-10 nm with spherical shape with uniform size distribution. Textural properties revealed that both materials showed a surface area in the mesoporosity range of 65-80 m²/g.

Upon characterization, the TiO₂ nanoparticles were tested in DSSC devices as a photoanode, showing photoconversion parameters slightly higher using Ti-C when compared with Ti-B. In addition, their utilization in wastewater treatment was carried out by performing the photocatalytic degradation of methyl orange dye, with almost full degradation in both cases after one hour of irradiation, and with similar values to those obtained using commercial TiO₂. The results obtained from this study open up a new direction for synthesis of high performance TiO₂-based material from much cheaper inorganic Ti sources.

Figure 6. Photocatalytic degradation of methyl orange dye in aqueous media.

Experimental Section

The synthesis protocol for the preparation of TiO₂ nanoparticles using a polymeric gel template as well as the different parameters for the characterization techniques are detailed in the SI.

Acknowledgements

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Keywords: Anatase TiO₂ nanoparticles • Dye-Sensitized Solar Cells • Organics Degradation • Polymeric Templating Synthesis

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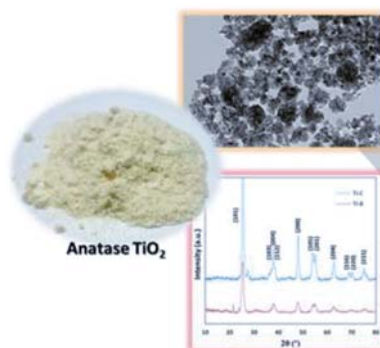
FULL PAPER

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Layout 1:

FULL PAPER

A low-cost, eco-friendly and simple preparation method which allows the utilisation either organic or less expensive inorganic sources to obtain anatase TiO₂ nanoparticles is reported in this work. The as-prepared nanoparticles showed promising results in DSSCs as well as in dye degradation.



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