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PRODUCTION OF ANATASE TiO_2 NANOCRYSTALS USING FREEZE-DRY PROCESS

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ABSTRACT

TiO_2 nanoparticles are often used as a photoanode material in dye-sensitized solar cells. Sintered together, the TiO_2 particles are often conducted at 500°C, to provide porous TiO_2 thin films. Anatase TiO_2 nanoparticles with the dimensions of around 20-30 nm are routinely used to facilitate better electron transport and high dye-adsorption capacity in the film. Prior experiments on the solution synthesis of TiO_2 suggested that dimethylformamide (DMF) plays a crucial role in the formation of DMF-containing amorphous TiO_2 precursors in solution, adaptable for creating size-controlled TiO_2 nanoparticles in the following high temperature process. It was observed that subsequent sintering process of the precursor at 500°C produced Anatase TiO_2 nanoparticles with the sizes of around 20 nm. The purpose of this research is to discover a method of obtaining Anatase TiO_2 semiconductor nanocrystals using low-temperature process without using a high temperature oven. The amorphous TiO_2 precursors were prepared at 40°C using an aqueous $TiCl_4$ solution as a Titanium compound and DMF as a structure directing agent. A new method involved the creation of the semiconductor nanoparticles through freeze-dry the resultant TiO_2 antecedents in order to produce a crystalline powder. The size, shape and crystal phase of TiO_2 particles were also characterized using a transmission electron microscope (TEM) and X-ray diffraction (XRD). It was found that Anatase nanoparticles formed with freeze-dry process of amorphous TiO_2 precursors. This allowed us to produce crystalline TiO_2 at a low temperature.

KEY WORDS: Anatase, TiO_2, nanoparticles, dye-sensitized solar cells, low temperature

1. INTRODUCTION

In an effort to gain independence from fossil fuels, there is much research into renewable and sustainable energy. An increased emphasis on further refining the technology currently available would make it more amenable to adoption and widespread use. Solar cells are a source of interest and have much room for improvement. The Grätzel cell, a dye sensitized solar cell (DSSC), is of particular interest for its simplicity of design. Focused on the excitation and release of electrons from dye molecules when exposed to light, the efficiency of this cell increases when electron transport is increased and when the amount of dye molecules present is increased [1]. A major limiting factor is the low surface area of the scaffolding material that fixes the dye in place. A lower surface area means that less dye can be attached. Because of this, research into the enhancement of anatase titanium dioxide (TiO_2) by means of increasing surface area and porosity are significant for furthering the body of work of improving the viability of non-silicon-based semiconductors. One of the drawbacks to the DSSC is the need for a substrate that enables the dye molecules to have a thick layer; a formulation for a highly porous structure with ample surface area would provide placement and structure for the dye. One technique for producing anatase TiO_2 is a hydrothermal reaction, a process that requires an aqueous solution. In an experiment by Chu et al. [2], a two-step hydrothermal synthesis was used, starting with a sodium hydroxide (NaOH) and titanium (Ti) solution. The solution received heat treatment in

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an autoclave: first at 210°C and again at 200°C, with a hydrochloric acid (HCl) wash in between. After washing with ethanol, the sample dried overnight. The resulting powder was the anatase TiO_2 [2]. It was determined that washing H-titanite nanowires in a solution of NH_4F was the deciding factor between TiO_2 particles with random shapes and products with uniform shape and size. Without the NH_4F wash, the particles lacked morphological uniformity. When tested, the condition that received the wash produced an efficiency of 7.03% [2].

A study by Qiu et al. also used a hydrothermal reaction to test the efficacy of a doubled photoanode, one with small nanospindles and the other with large nanospindles. When tested, it resulted in an efficiency of 8.3% [3]. Both types of nanospindles were produced using an initial solution of 80% anatase TiO_2 and sodium hydroxide, which was stirred, heated in an autoclave for 20 hours at 150°C and cooled to ambient room temperature. The remaining material was stirred with HCl to obtain a pH between 1-2; it was subsequently filtered and washed with distilled water. The resulting hydrogen titanite was either introduced to a water/ethanol solution or a water/ethylene glycol solution to produce large or small nanospindles, respectively. Both samples were stirred with dimethylamine and then heated in an autoclave at 180°C for 10 hours. Cooling to room temperature was sufficient for evaporating the ethanol for the large nanospindles, but the sample of small nanospindles required additional washing with water to remove the ethylene glycol. Using SEM, the morphology of the particles was confirmed and the variation in diameters (6 to 45nm) and lengths (20 to 200nm) of the nanoparticles was observed [3].

One other study by Wu et al. has demonstrated hydrothermal synthesis of TiO_2 nanoparticles [4]. In their study, a mixture consisting of $K_2TiO(C_2O_4)_2$, DI water, and diethylene was transferred to a Teflon liner. TiO_2-coated FTO glass was placed at an angle on the wall of the Teflon liner, which was then placed in an autoclave at 180°C for 9 hours. This promoted the growth of vertical anatase hierarchical TiO2 nanowires (AHTNW) on the FTO glass. For the synthesis of the macro-porous TiO_2 (MPT), 0.4 ml of butyl titanite was mixed with 20 ml of ethanol with stirring for 2 hours, then 4 ml PS aqueous solution was added and stirred for 12 hours. The TiO_2-covered polystyrene was rinsed with ethanol and distilled water, then dispersed in ethanol with an ultrasonic bath. It was then dripped with a pipet onto the AHTNW/FTO substrate surfaces, which were then calcined in a box furnace at 500°C for 1 hour to remove the PS templates and form the double-layered AHTNW/FTO photoanode. The morphology of the nanoparticles was observed with a FE-TEM and FE-HRTEM. The AHTNW consisted of TiO2 nanowire trunks with 250 nm diameters and many nanorod branches with 50-60 nm diameter and 50-150 nm lengths. The nanoparticles were tested in DSSCs, including conventional TiO2 nanoparticles (TNP), which achieved efficiencies as follows: AHTNW achieved an efficiency of 7.83%, AHTNW+MPT achieved an efficiency of 8.96%, AHTNW+MPT+HTS achieved and efficiency of 10.06%, AHTNW+MPT+HTS-branches achieved an efficiency of 11.01%, and TNP achieved an efficiency of 7.62%.

Experiments using sol-gel based methods are also of considerable interest. The “gel” part produces a structure for the oxide growth that prevents excessive aggregation or the particles sticking together [5]. Lee et al. made a base solution of Ti^{4+} (0.5M) mixed with titanium (IV) isopropoxide (TIP) with triethanolamine (TEOA) [5]. From this they made two samples, one with perchloric acid $HClO_4$, the other with NaOH, taking the solution from the initial pH of 9.5 to 8.5 and 10.5, respectively. Ethylenediamine (ED) was also added. The samples were subjected to two heat treatments in an autoclave: the first at 100°C for 24 hours and the second at 140°C for 72 hours. In order to remove undesired compounds from the particles, all samples relied upon a rigorous schedule of washing and centrifuging the particles: six times with NaOH, two times with HNO_3, and four times with distilled water. Using TEM and XRD, Lee et al. found an assortment of morphologies were exhibited among the different sample conditions and included rods and spheres. The spherical nanoparticles, upon testing in a DSSC, demonstrated an efficiency of 5.3% [5].

Synthesis using the hybrid solvothermal method has produced interesting results. This reaction retains the characteristics of the hydrothermal reaction, but begins with a non-aqueous precursor. Chen et al. used the sol-gel technique to produce a small, smooth precursor material and built upon those in a solvothermal method to create large beads of TiO_2 with enhanced porosity and surface area [6]. After the beads were collected, the experimenters tested three samples of the beads against washing with different amounts of ammonia. The

concentration of ammonia was negatively correlated to specific surface area and positively correlated to the pore sizes. In this study, the first phase was producing the precursor material by mixing hexadecylamine (HAD), ethanol, and potassium chloride (KCl) solution. Isopropoxide (TIP) was added and the mixture was stirred. After standing at room temperature for 18 hours, the material was filtered and further washed with ethanol and then dried in ambient temperature [6]. The next phase, the solvothermal process, was initiated by adding ethanol, di-ionized water and ammonia in differing amounts to the precursor material. The samples were added to an autoclave at 160℃ for 16 hours, after which they were collected, washed with ethanol, dried and then calcined for 2 hours at 500℃. The final, powered product was then inspected using an SEM and XRD. When prepared and tested in a DSSC, an efficiency of 7.2% was exhibited [6].

Li et al**.** also used a solvothermal method with the intention of building hierarchical microstructures due to impressive reported rates of efficiency [7]. The solvothermal method employed produced TiO_2 structures that exhibited high crystallinity, which improves the performance of "light harvesting" compared to non-hierarchical TiO_2 particles. To produce these hierarchical TiO_2 microstructures (HM-TiO_2) by mixing tetra-n-butyl titanite (TBT) with a solution of N,N-dimethylformamide (DMF) and acetic acid (HAc) and stirring before being added to an autoclave at 200℃ for 12 hours. After the heat treatment, the material was removed from the autoclave, centrifuged and washed with ethanol. It was set to dry at 60℃ overnights. Inspection with an SEM and XRD revealed the nanoparticles to be spheres with thin spikes or needles pointing out from the center. Subsequent testing in a DSSC yielded a light conversion efficiency of 9.79% [7].

Another form of TiO_2 is rutile. As opposed to the spherical shape of anatase, rutile TiO_2 is rod-shaped. Rutile TiO_2 can be synthesized using similar methods. Studies by Oh et al. [8], Yu et al. [9], Lin et al. [10], and He et al. [11] have demonstrated hydrothermal methods for synthesizing rutile TiO_2. The hydrothermal method is the same for synthesizing rutile TiO_2 as it is for synthesizing anatase TiO_2 in that it involves a high-temperature reaction using an aqueous solution. Similarly, rutile TiO_2 can also be synthesized using solvothermal methods, as demonstrated by studies by Feng et al. [12] and Li et al. [13]. Both methods require a high-temperature reaction, which can be expensive.

In contrast to these prior researches of using high-temperature autoclaves and ovens, a low-temperature reaction-based strategy to form anatase TiO_2 has not been fully established to date. Therefore, a novel powder synthesis of anatase TiO_2 particularly at low-temperatures is a challenging issue. This is not only for the development of cost-effective powder production, but also for promoting new perspectives in the fields of photovoltaic technologies.

2. EXPERIMENTAL

Aqueous Ti(IV) chloride solution (Ti: 16.0~17.0%) and dimethylformamide (DMF) were purchased from Wako and used as purchased. Methanol (CH_3OH, Primepure, 99.9%) and sodium hydroxide (NaOH, 97%) were used as purchased from KANTO CHEMICAL. A water purification system (Milli-Q®) was used to generate di-ionized water (H_2O), (resistivity: 18.2 MΩ•cm) adapted for TiO_2 synthesis.

1.879 g of NaOH pellets was added to 50 mL of ultrapure H_2O at room temperature. The mixture, in a 100mL beaker, was mixed in a sonic bath (Fig. 1) until the NaOH was dissolved.

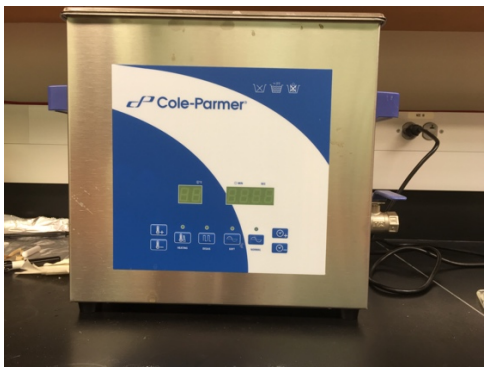


Fig. 1 Sonic bath used to dissolve NaOH and H_2O

150 mL methanol (CH_3OH) was measured in a graduated cylinder and added to a 1 Liter flask along with the NaOH solution and gently mixed with a magnetic stirrer. 100 mL of Dimethylformamide (DMF) was added to the flask's mixture, next 56.56 g $TiCl_4$ were added to the flask (Fig. 2).

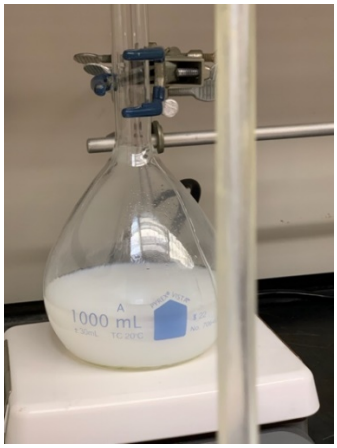


Fig. 2 The mixture of NaOH, MeOH, DMF and $TiCl_4$.

Finally, 238 mL ultrapure H_2O was added (Fig. 3)

Fig. 3 The solution after the addition of ultrapure water.

The flask was subsequently covered, placed into a bath (Fig. 4) set at 40°C and was allowed to sit, stirred continuously, for 5 days.

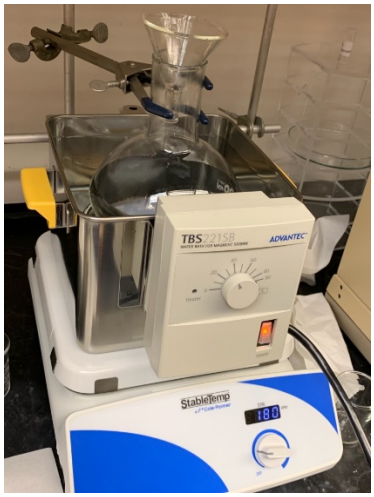


Fig. 4 Water bath where the mixture will sit at a constant temperature for 5 days

After the allotted time, the reaction mixture thickened and was removed from the bath, separated into tubes and centrifuged (Fig. 5) at 4000 rpm for 15 minutes. After centrifugation, the colorless liquid that had separated from the white TiO_2 was disposed of.

Fig. 5 Post-water bath, the mixture is divided into bottles (left) and centrifuged (right) to separate the particles from the liquid (center).

The remaining gel containing the TiO_2, was placed into tubes flash frozen in a bath of liquid nitrogen (Fig. 6).

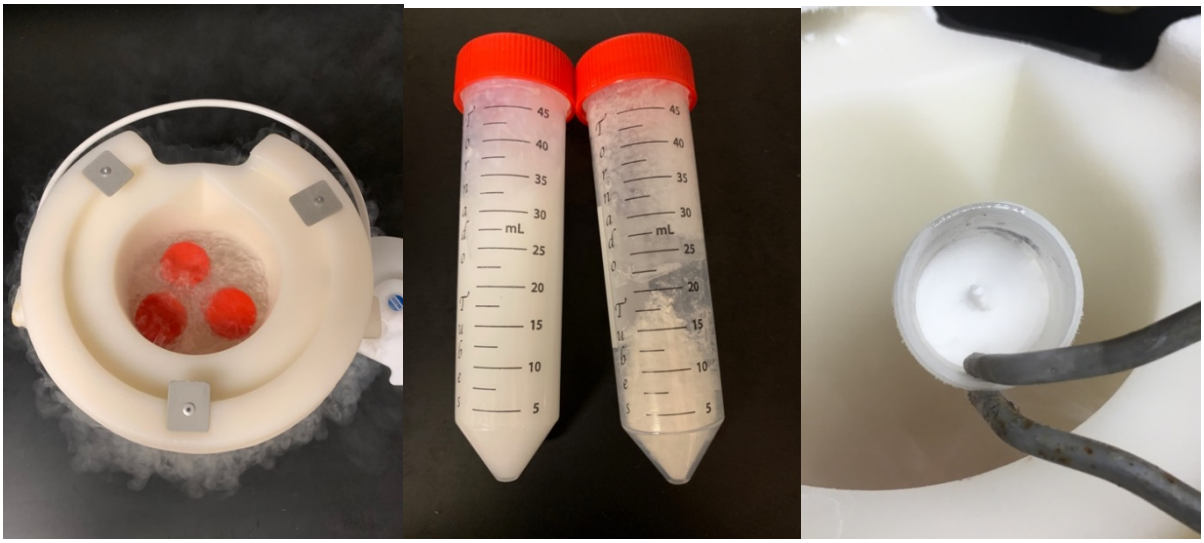


Fig. 6 The liquid nitrogen bath (left). Tubes of frozen TiO_2 (center). Closeup of TiO_2 after freezing (right).

When removed from the liquid nitrogen, the caps removed from the tubes, and were covered with chem-wipes (or filter paper), place into a jar and placed into a freeze-dry vacuum device (Bench Top Pro with Omnitronics, VirTis SP Scientific) (Fig. 7) at 200mTorr for 24 hours.

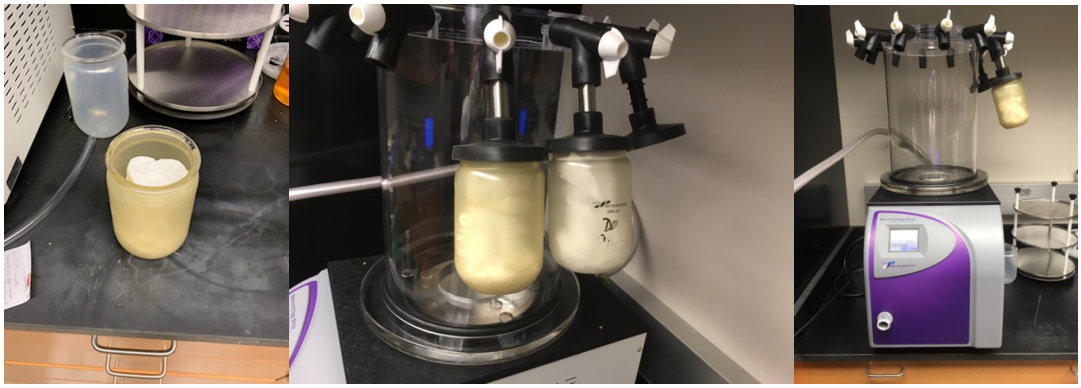


Fig. 7 Uncapped tubes covered with a filter (left). Jars containing frozen TiO2 attached to dry-freeze vacuum (center, right).

After which, it is removed from the freeze-dry equipment and set aside. The resulting TiO_2 nanoparticles are white crystals (Fig. 8). At this point, a transmission electron microscope (TEM) is necessary to observe the finished product.

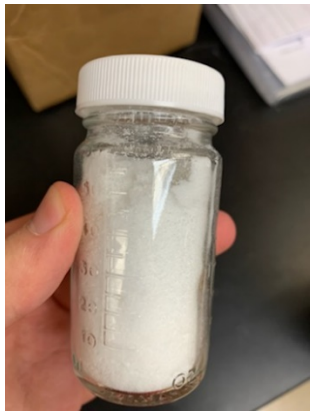


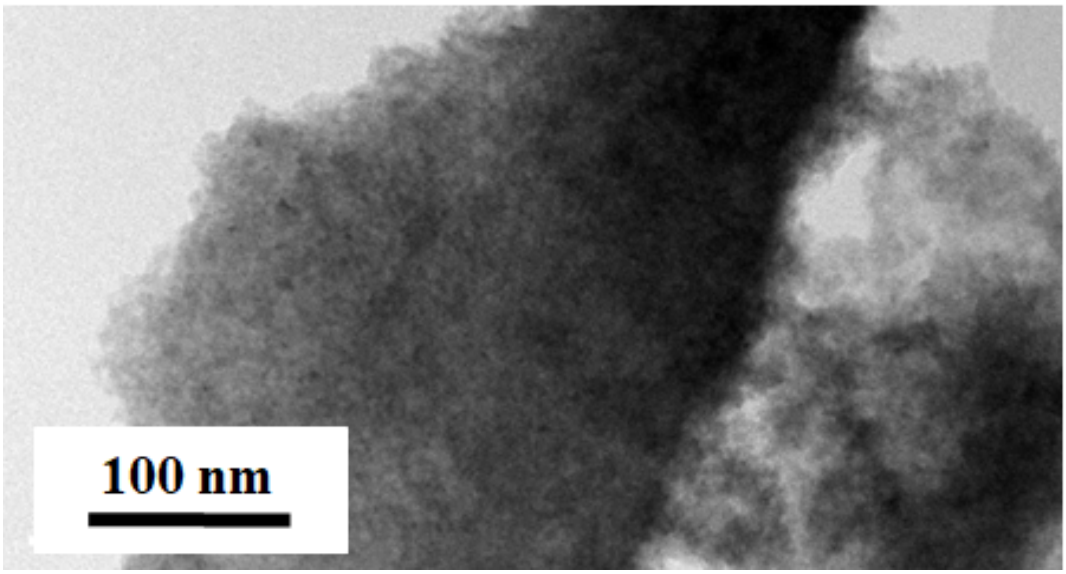
Fig. 8 The white, crystalline product.

3. RESULTS AND DISCUSSION

In recent years, we have demonstrated that brush-shaped TiO_2 nanoparticles can be synthesized at near room-temperature [14, 15]. From TEM measurement, the size of TiO_2 particles was found to range from 100-200 nm consisting of nanowires with an average diameter of ~5 nm. The crystal phase of TiO_2 was assigned to be rutile. This paper focused on generating smaller TiO_2 nanoparticles with anatase crystal phase. Generally, Ti(IV) salts are highly reactive in water, and therefore hydrolysis and subsequent polycondensation reactions are difficult to control for homogenous production of TiO_2 particles. One of the strategies for avoiding the fast hydrolysis is the addition of structure directing agents (SDA) in a reaction mixture, such as citric acids and amino acids, which can stabilize the intermediates of Ti(IV) precursors [16].

We anticipated that the addition of DMF in the reaction mixture can modify the octahedral Ti(IV) coordination environment, being the strong coordination of DMF to Ti(IV) source through the oxygen atom. As a result, this modification of Ti(IV) intermediates could lead to the variation of TiO_2 crystal phase. The details of TiO_2 synthesis are described in Experimental part. The reaction mixture containing DMF at 40 °C started to form chunks of white gel from the 3rd day of the reaction. In order to characterize the Ti(IV) precursor, the sample was freeze-dried after completion of 4 days of reaction. This led to the isolation of the product in a powder form. TEM images the powder sample are shown in Figure 9. The TEM data clearly indicated that TiO_2 nanoparticles of ~5 nm in size were grown in the amorphous moiety. Most importantly, the high-resolution TEM image in Figure 9(b) clearly indicated the lattice fringe in the individual particle and the crystal phase of TiO_2 was assigned to be anatase from the interspacing of $d_{(101)} = 0.35$ nm. The TiO_2 crystal phase was also identified as anatase from XRD pattern, Figure 10. Sintering of these nanoparticles are also in progress to obtain high-performance electrode materials for dye-sensitized solar cells.

(a)



(b)

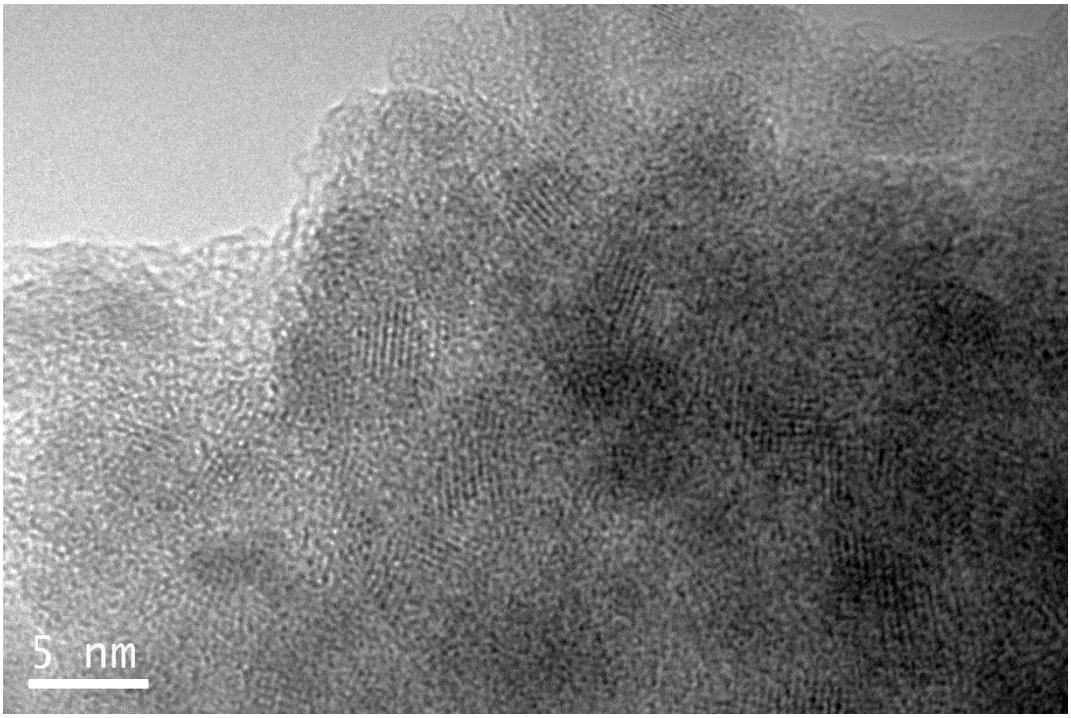


Fig. 9 TEM images of the anatase TiO_2 particles after freeze-drying process. (a) Low magnification TEM image. (b) HR-TEM image of the same sample. The yellow circles present the lattice fringes of TiO_2 particles.

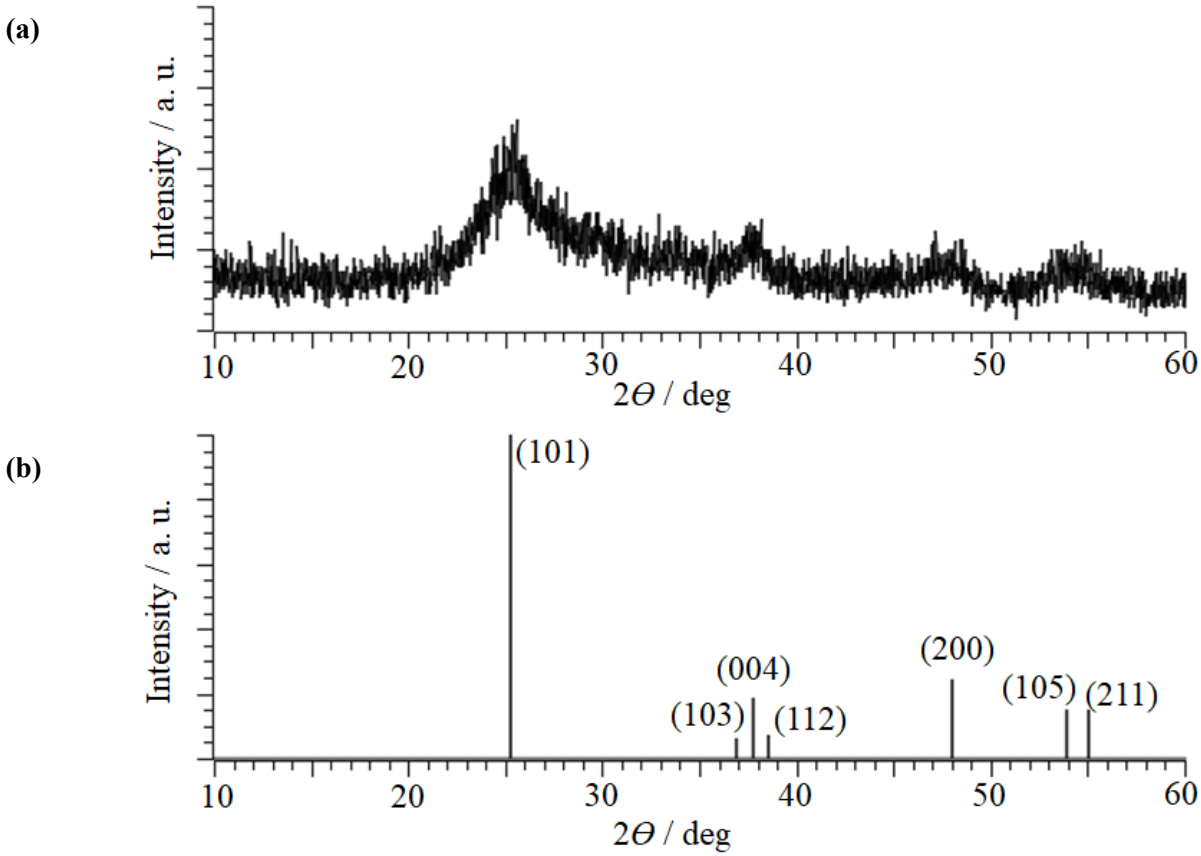


Fig. 10 XRD pattern of synthesized particles (a). The peaks align with the standard XRD graph (b) for anatase TiO_2. The crystal phases of the anatase TiO_2 are also presented.

4. CONCLUSIONS

The aim of this work was to establish the method for synthesizing anatase TiO_2 nanoparticles. This was achieved by freeze-drying of DMF-derived Ti(IV) gel precursors. Most notably, anatase TiO_2 nanoparticles were successfully obtained at temperatures even lower than 40 °C without conventional hydrothermal techniques. Our low temperature synthesis of TiO_2 provides a new method to create versatile semiconductor metal oxides. In addition, our results will not only provide further avenues in the low cost production of TiO_2 powder materials, but also play an important role in the new development of photoenergy conversion technologies such as emerging solar cells and photocatalysts.

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