

## Synthesis the New Nanostructure $Ti_{0.7}Ir_{0.3}O_2$ via Low Temperature Hydrothermal Process

Tai Thien Huynh<sup>1,2,a</sup>, At Van Nguyen<sup>2,b</sup>, Hau Quoc Pham<sup>2,c</sup>,  
Long Giang Bach<sup>3,d</sup>, Van Thi Thanh Ho<sup>1,c\*</sup>

<sup>1</sup>Hochiminh City University of Natural Resources and Environment (HCMUNRE), Vietnam

<sup>2</sup>Bach Khoa University (BKU), Ho Chi Minh City, Vietnam

<sup>3</sup>NTT Institute of Hi-Technology, Nguyen Tat Thanh University, Ho Chi Minh City, Vietnam

<sup>a</sup>httai@hcmunre.edu.vn, <sup>b</sup>nguyenat95@gmail.com, <sup>c</sup>phamquochau11819@gmail.com,  
<sup>d</sup>blgiang@ntt.edu.vn, <sup>e</sup>httvn@hcmunre.edu.vn

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**Abstract.** Noncarbon materials were recognized as the catalyst support to increase the durability of Proton Exchange Membrane Fuel Cells (PEMFC). One of the most noncarbon materials studied to be an emerging candidate for Pt nanoparticles (Pt NPs) support on the cathode side of PEMFC was M doped- $TiO_2$  due to the highly stable structure of  $TiO_2$  and the good conductivity of M-doped  $TiO_2$ . In this paper, the novel nanostructure  $Ti_{0.7}Ir_{0.3}O_2$  was prepared for the first time via low temperature hydrothermal process. The synthesis process for the new nanostructure  $Ti_{0.7}Ir_{0.3}O_2$  was studied in detail in this work. The impact of hydrothermal temperature as well as the reaction time on the dominant phase formation is extensively investigated in this work. We found that the  $Ti_{0.7}Ir_{0.3}O_2$  nanoparticles exist in both rutile and anatase phase. We found that the  $Ti_{0.7}Ir_{0.3}O_2$  nanoparticles with an irregular spherical shape with particle size of approximately 20-30nm with high crystallinity. In addition, we also found that the optimal condition to synthesize the  $Ti_{0.7}Ir_{0.3}O_2$  NPs is obtained at 210°C and 10 hours. The result not only introduces a promising catalyst support  $Ti_{0.7}Ir_{0.3}O_2$  for much needed fuel cells, but it also open a new material type of Ir doped  $TiO_2$ .

### Introduction

In recent decades, fuel cell has been considered as one of the most promising energy conversion technology with high efficiency and low environmental impact by converting chemical energy directly to electrical energy [1]. Among many type of fuel cells, Proton exchange membrane fuel cells (PEMFC) is received much attention due to ambient operation condition which is suitable for both stationary systems and mobile devices [2]. Despite enormous achievement in development PEMFC technology, it still remains several challenges, hampering commercial feasibility. Recent approaches tend to improve the durability and reliability of PEMFC as well as reduce the fabrication cost. Catalyst supports, in particular, which is essential part of FEMFC systems, must be durable over a long operation time in aggressive corrosion environment at electrode. In current state of art, Carbon black is the dominant material used for catalyst support because of the high specific surface area, low cost, and outstanding electronic conductivity [3-5] that carbon black offers. However, two major troubles involving the utilization of carbon black as catalyst support prohibit widespread application. First, the weak interaction between catalyst metal (Pt, Ru) and carbon black results in catalyst agglomeration and loss of active site in long term operation [6]. In addition, the corrosion of carbon have revealed to the main factor to catalyst failure due to high electrode potential, resulting in dissolution of catalyst particles [3, 7]. Although several high graphitic character materials such as graphene [8], carbon nanotube [9, 10] has been investigated as catalyst support alternatives, the intrinsic corrosion of carbon at high potential limit its usage for catalyst support. Therefore, several non-carbon support material, especially conductive and semi-conductive oxide [11], have been studied as a promising corrosion resistant catalyst support materials.

Titanium dioxide  $TiO_2$ , existing in three crystal forms include anatase, brookite and rutile, is a common catalyst support in various reaction systems due to its unique properties such as good

affinity to metal catalyst particles, chemically stable in aggressive electrochemical condition, high surface area and so on [4, 12-14]. Nonetheless, the extremely low electrical conductivity of  $\text{TiO}_2$  is an obstruction, diminishing the electron transfer between noble metal catalyst (Pt, Ru, Rb) and  $\text{TiO}_2$  catalyst support [3]. As a result, it is not suitable for catalyst support in electrochemical field. Modifying electrical conductivity of  $\text{TiO}_2$  by inserting foreign element into  $\text{TiO}_2$  crystalline lattice is promising approach to adapt the electronic conduction requirement. A number of metal doped  $\text{TiO}_2$  have been fabricated recently revealed that metal doped  $\text{TiO}_2$  not only enhances electronic conductivity by excessing charge carrier, but it also improves the chemical stability of  $\text{TiO}_2$  by diminishing lattice defect [3]. Moreover, several support materials also offer a cocatalyst activity such as  $\text{Ti}_{0.7}\text{Mo}_{0.3}\text{O}_2$  [6],  $\text{Ti}_{0.7}\text{Ru}_{0.3}\text{O}_2$  [5],  $\text{Ti}_{0.7}\text{W}_{0.3}\text{O}_2$  [15].

According to previous research,  $\text{IrO}_2$  has been known as corrosion-resistant material under electrochemical reaction as well as promising catalyst for ORR in PEMFC [16, 17]. However, the ease of  $\text{IrO}_2$  as well as the high cost of iridium precursor limit its application. The similarity of ion radius of  $\text{Ti}^{4+}$  (0.605Å) and  $\text{Ir}^{4+}$  (0.625Å) is expected to lead to well integrated Ir into  $\text{TiO}_2$  lattice resulted in enhancing the intrinsic low electrical conductivity of  $\text{TiO}_2$ .

Here, we demonstrated a novel robust catalyst support  $\text{Ti}_{0.7}\text{Ir}_{0.3}\text{O}_2$  to adapt the requirement of catalyst support for its utilization in long-term PEMFC applications by using low hydrothermal process without utilizing any surfactant or stabilizer. This novel nanostructure is expected to sustain under high corrosion environment and offer cocatalyst activity.

## Experiment

**Chemical.** All reagents and solvents are commercially available and used without further purification. Iridium trichloride hydrate ( $\text{IrCl}_3 \cdot 3\text{H}_2\text{O}$ , 99.9%) was purchased from Sigma - Aldrich, titanium tetrachloride ( $\text{TiCl}_4$ , 99%) was purchased from Aladdin, and hydrochloric acid (37%) was obtained from Merck. Deionized water was used throughout experiments.

## Experimental Procedure.

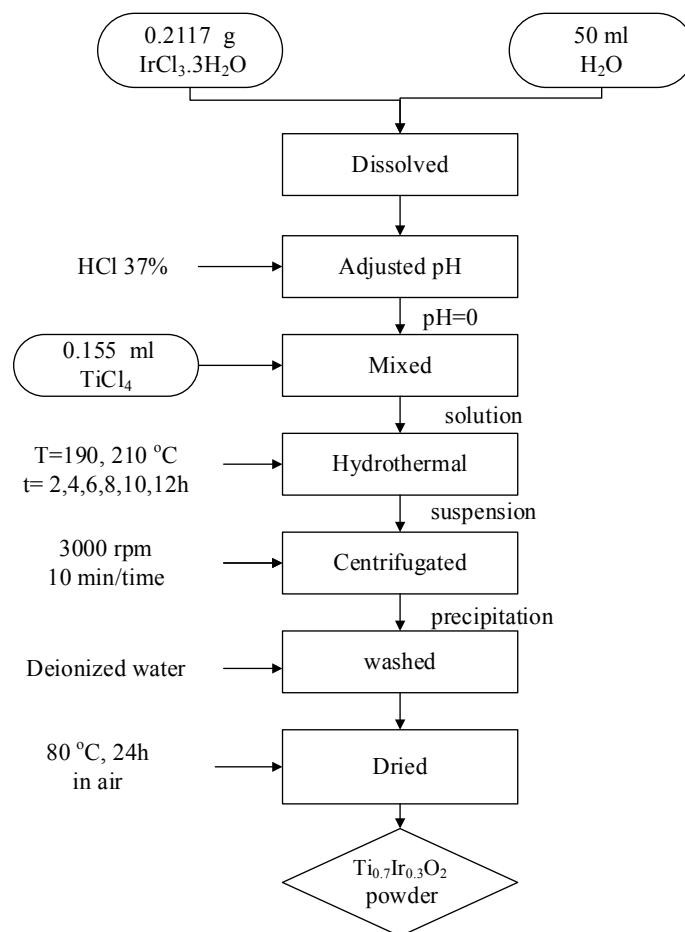
**Synthesis of  $\text{Ti}_{0.7}\text{Ir}_{0.3}\text{O}_2$  nanoparticle.**  $\text{Ir}_{0.3}\text{Ti}_{0.7}\text{O}_2$  nanoparticles were fabricated via one-step hydrothermal process, at low temperature that did not employ a surfactant or stabilizer. In a typical experiment, an aqueous precursor solution containing 12mM  $\text{IrCl}_3$  and 28mM  $\text{TiCl}_4$  (Ir:Ti molar ratio is 3:7) was prepared at pH=0. The precursor solution was transferred to a Teflon-lined autoclave with stainless steel shell. The hydrothermal reaction was carried out at 190 and 210°C for 2, 4, 6, 8, 10, 12h in the oven and then cooled naturally to room temperature. Product was washed with deionized water and centrifuged several times until the pH of washing is neutral. The precipitates were dried at 80°C in oven overnight for further analysis.

**Material characterization.** Powder X-ray diffraction (XRD) patterns of  $\text{Ti}_{0.7}\text{Ir}_{0.3}\text{O}_2$  nanoparticles were obtained by D2 PHASER diffractometer using  $\text{Cu K}_\alpha$  radiation and Ni as filter at 30 kV and 100 mA. The particle sizes of  $\text{Ti}_{0.7}\text{Ir}_{0.3}\text{O}_2$  nanoparticles were evaluated by transmission electron microscopy (TEM) on an FEI-TEM-2000 microscope operated at an accelerating voltage of 3800 V.

## Results and Discussion

The color of obtained suspension (Fig. 2) have varied from white to dark grey with respect to the increase of reaction time for 2 hours, 4 hours, 6 hours, 8 hours, respectively. These phenomena could be explained by the hydrothermal time requirement. The hydrothermal time lower than 4 hours are insufficient to complete reaction resulted in the low substitution of Ir ions to  $\text{Ti}^{4+}$  in  $\text{TiO}_2$  lattice. Therefore, the majority of solid was  $\text{TiO}_2$  nanoparticles in white color. The longer reaction time accelerates the doped probability and thus resulting in dark grey powder (Fig. 2.(c),(d)). As comparison with other researches, Ir doped  $\text{TiO}_2$  requires higher energy consumption than other metals doped  $\text{TiO}_2$ . For example, synthesizing  $\text{Mo}_{0.3}\text{Ti}_{0.7}\text{O}_2$  took place at 200 °C for 2h [6]. The phenomena could be illustrated by the discrepancy of ionic radii of  $\text{Ir}^{4+}$  (0.625Å),  $\text{Ir}^{3+}$  (0,68Å) and

$\text{Ti}^{4+}$  (0.605 Å) are larger than that of  $\text{Mo}^{5+}$  (0.61 Å) and  $\text{Ti}^{4+}$ . As the result, it requires higher reaction time and temperature to incorporate Ir ions into  $\text{TiO}_2$  lattice.



Scheme 1. Scheme of synthesis  $\text{Ti}_{0.7}\text{Ir}_{0.3}\text{O}_2$  by solvothermal method.

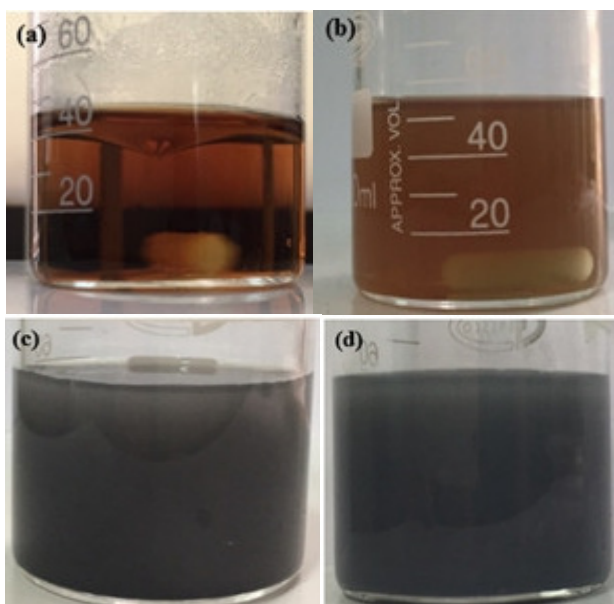


Fig. 1. The color of (a)  $\text{IrCl}_3$  solution; (b)  $\text{IrCl}_3$  solution after adding  $\text{TiCl}_4$ ; (c) suspension after hydrothermal 6h, 210 °C; (d) suspension after hydrothermal 8h, 210 °C.

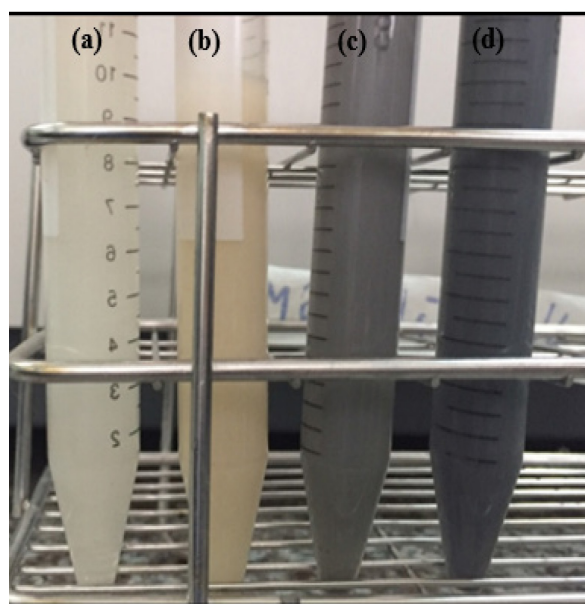


Fig. 2. Suspension color of different samples carrying hydrothermal reaction at 210 °C for (a) 2 hours; (b) 4 hours; (c) 6 hours; (d) 8 hours.

The crystal structure of  $\text{Ti}_{0.7}\text{Ir}_{0.3}\text{O}_2$  samples were confirmed by XRD analysis. Fig. 3 depicts the XRD pattern of  $\text{Ti}_{0.7}\text{Ir}_{0.3}\text{O}_2$  samples with different hydrothermal time at 6h, 8h, 10h, 12h at 210 °C as well as the standard XRD pattern of  $\text{TiO}_2$  (anatase and rutile phases) and  $\text{IrO}_2$ . As we can observed from the graph, the absence of unique peaks of  $\text{IrO}_2$  at (28°, 34.5° and 54°) and existence of  $\text{TiO}_2$  peaks in all samples indicate that the formation of solid solution. The XRD pattern of sample (a) (210 °C, 12h) having a single rutile phase shows a high level of crystallinity. Whereas, sample (b),(c),(d) with respect to hydrothermal time for 10h, 8h, 6h introduce the formation of two phase of  $\text{TiO}_2$  including anatase and rutile. According to previous study, under the high HCl concentration condition, the rutile phase, indexing at 2theta angles 27.3, 35.6, 38.9 corresponding to plane (110), (101), (200) [18] have high tendency to form rather than anatase phase. The phase transformation from anatase phase to rutile phase could be interpreted by the effect of increasing reaction time. This results are appropriate with previous research [19]. Furthermore, the low reaction time provides insufficient energies to complete hydrothermal reaction resulting in lower crystallinity. For instance, sample (c) prepared at 210 °C and 8 hours possesses lower diffraction peak intensities compared to that of sample (b) at 210 °C and 10 hours.

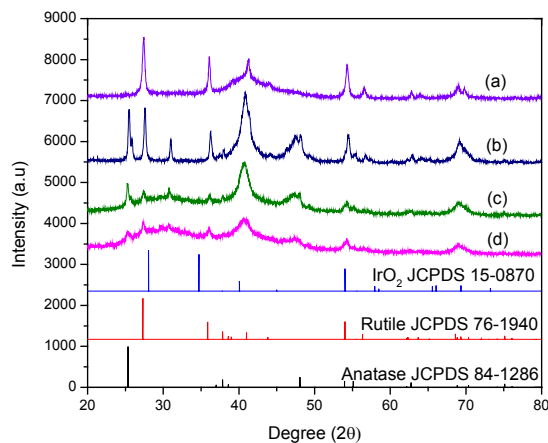


Fig. 3. XRD patterns of Ir doped  $\text{TiO}_2$  NPs samples prepared via hydrothermal method at 210 °C with various hydrothermal time (a) 12h; (b) 10h; (c) 8h; (d) 6h.

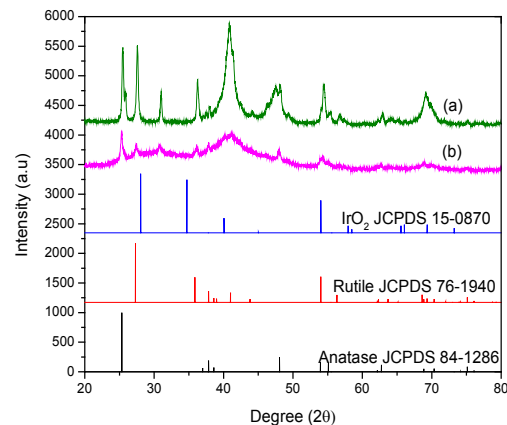


Fig. 4. XRD patterns of Ir doped  $\text{TiO}_2$  NPs samples prepared via hydrothermal method (a) 210 °C, 10h; (b) 190 °C, 10h.

The XRD patterns showed in Figure 4 demonstrates the impact of hydrothermal temperature on the crystallinity of sample. Regardless to the similarity of hydrothermal time for 10 hours, the lower temperature 190°C assigned to the majority of anatase phase shows low crystallinity after hydrothermal treating (Fig. 4(e)). Low temperature demands longer reaction time. However, it accelerates the particle agglomeration possibility declining surface area for anchoring catalyst metals in the platinized step. For that reason, 210 °C is a suitable hydrothermal temperature to obtain good crystallinity sample as describing bellow.

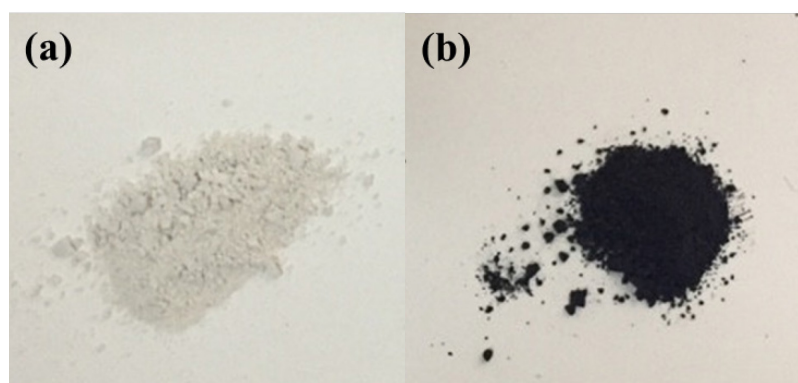


Fig. 5. Color of (a) undoped  $\text{TiO}_2$  (b)  $\text{Ti}_{0.7}\text{Ir}_{0.3}\text{O}_2$  prepared at 210 °C, 10h.

The color of  $\text{Ti}_{0.7}\text{Ir}_{0.3}\text{O}_2$  powders synthesized at 210 °C for 10 hours are black. Whereas, the original color of pure  $\text{TiO}_2$  materials are white. The combination of powder color changes and XRD results provide preliminary evidence for the formation of solid solution instead of mixing oxides in which the substitution of Ir to  $\text{TiO}_2$  framework changes the color of powders.

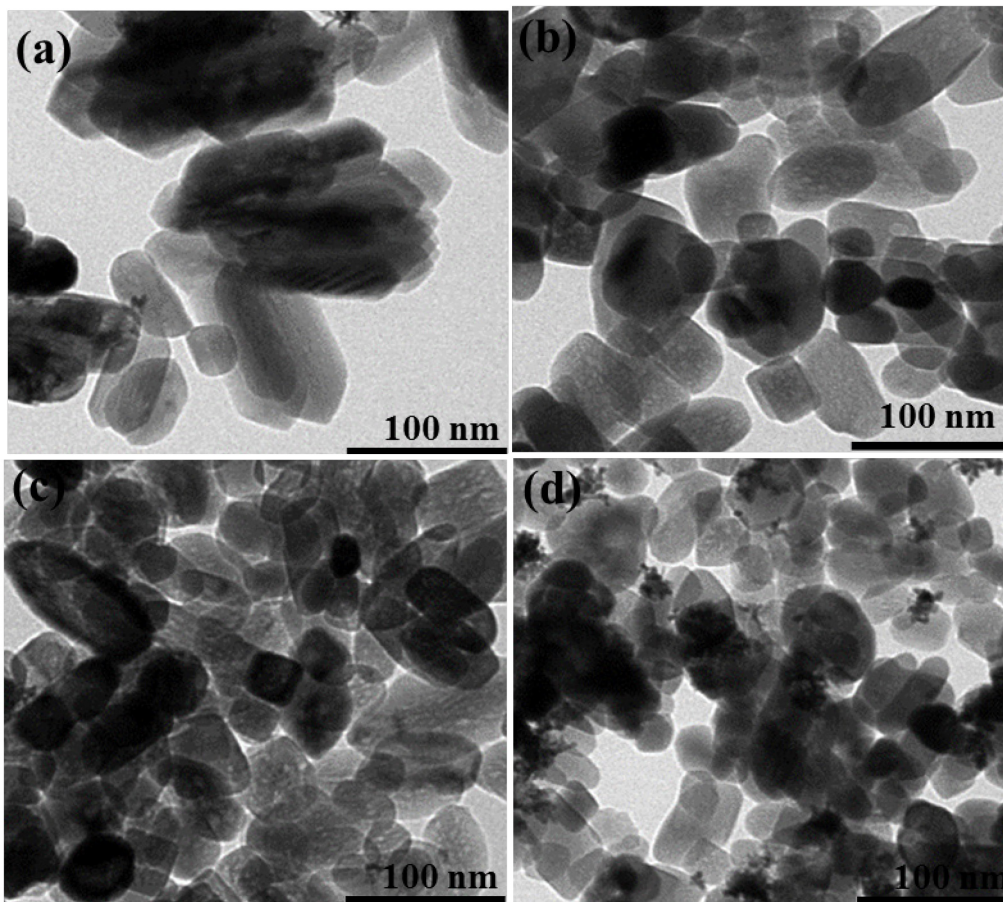


Fig. 6. TEM images of sample Ir doped  $\text{TiO}_2$  210 °C at (a) 12h; (b) 10h; (c) 8h; (d) 6h.

The morphology of  $\text{Ti}_{0.7}\text{Ir}_{0.3}\text{O}_2$  samples prepared at different time is shown at scale 100nm. There are two types of particle shape including sphere and rod. The ratio between two types of morphology depends on the reaction time. It is well know that the rod-like shape materials own lower surface area than that of spherical shape materials. So that, in our research we choose reaction condition at 210 °C and 10h to avoid the formation of bar shape particles. As low reaction time, spherical particles are dominant types. However, the increasing of solvothermal time lead to the transformation of spherical to rod-like particles due to the (110) facet orientation. Particles shapes of sample (a) prepared at 210 °C for 12h are rod associating with rutile  $\text{TiO}_2$  phase have high tendency to agglomeration resuting in low surface areas. On the other hand, samples synthesized at 210 °C for 6 hours, 8 hours and 10 hours show the low agglomeration degree. As for low reaction time for 6 hours, the appearance of small particles cluster can be attributed to the formation of amorphous  $\text{TiO}_2$  phase [20].

Size and general morphology of Ir doped  $\text{TiO}_2$  (Ir:Ti molar ratio is 3:7) synthesized via hydrothermal method at 210 °C, 10h were investigated using TEM (Fig. 7). The bar-shape particles indicated the formation of rutile phase is 50-80nm in length and 20nm in width. Whereas, the spherical nanoparticles of approximately 25nm in diameter attributed to the formation of anatase phase. The existence of a mixed anatase/rutile phase in accordance to XRD pattern. However, As the reaction time reached 10 hours, rutile phase become the dominant phase.

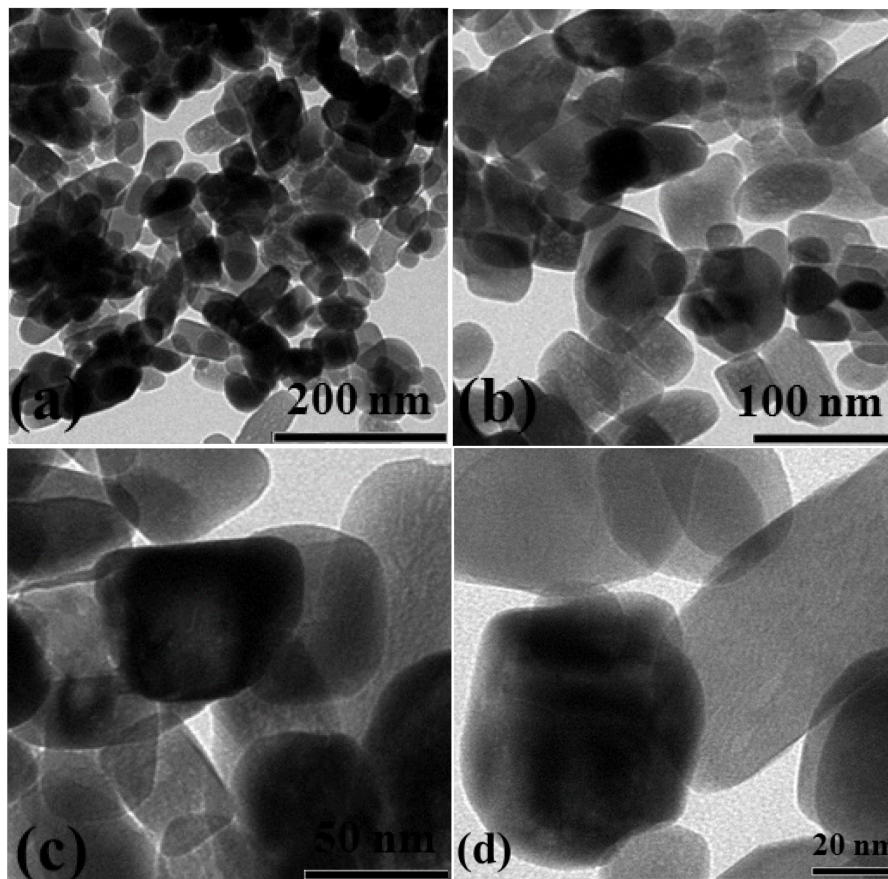


Fig. 7. TEM images of sample  $\text{Ti}_{0.7}\text{Ir}_{0.3}\text{O}_2$  prepared at 210 °C, 10h with different scale bar.

## Conclusions

In conclusion, novel catalyst support  $\text{Ti}_{0.7}\text{Ir}_{0.3}\text{O}_2$  has been fabricated successfully via facile hydrothermal method without using any surfactant and stabilizer. Novel material shows better electronic conductivity compared to that of undoped  $\text{TiO}_2$ . This results offer a promising materials used for catalyst support in PEMFCs tacking the intrinsic electronic insulation of  $\text{TiO}_2$  and exploring the high durability of  $\text{TiO}_2$ . In addition,  $\text{Ti}_{0.7}\text{Ir}_{0.3}\text{O}_2$  nanoparticles exhibit small particle size approximately 25-30 nm. As a result,  $\text{Ti}_{0.7}\text{Ir}_{0.3}\text{O}_2$  catalyst support is anticipated to be appropriate to anchor noble metal on its surface as well as provide cocatalyst activity will be investigated in our following research.

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## References

- [1] U. Lucia, Overview on fuel cells. *Renew. Sustain. Energy Rev.* 30 (2014) 164-169.
- [2] C. Wang, et al., Multimetallic Au/FePt<sub>3</sub> nanoparticles as highly durable electrocatalyst. *Nano Lett.* 11(3) (2011) 919-926.
- [3] Y. J. Wang, D. P. Wilkinson, and J. Zhang, Noncarbon support materials for polymer electrolyte membrane fuel cell electrocatalysts. *Chem. Rev.* 111(12) (2011) 7625-7651.

- [4] J. Parrondo, et al., Platinum supported on titanium-ruthenium oxide is a remarkably stable electrocatalyst for hydrogen fuel cell vehicles. *Proc. Nat. Acad. Sci. U. S. A.* 111(1) (2014) 45-50.
- [5] V. T. Ho, et al., Robust non-carbon  $\text{Ti}_{0.7}\text{Ru}_{0.3}\text{O}_2$  support with co-catalytic functionality for Pt: enhances catalytic activity and durability for fuel cells. *Energ. Envir. Sci.* 4(10) (2011) 4194.
- [6] V. T. Ho, et al., Nanostructured  $\text{Ti}_{0.7}\text{Mo}_{0.3}\text{O}_2$  support enhances electron transfer to Pt: high-performance catalyst for oxygen reduction reaction. *J. Am. Chem. Soc.* 133(30) (2011) 11716-11724.
- [7] D. A. Stevens, et al., Ex Situ and In Situ Stability Studies of PEMFC Catalysts. *J. Electrochem. Soc.* 152(12) (2005) A2309.
- [8] R. Kou, et al., Stabilization of Electrocatalytic Metal Nanoparticles at Metal–Metal Oxide–Graphene Triple Junction Points. *J. Am. Chem. Soc.* 133(8) (2011) 2541-2547.
- [9] M. M. Shaijumon, S. Ramaprabhu, and N. Rajalakshmi, Platinum/multiwalled carbon nanotubes-platinum/carbon composites as electrocatalysts for oxygen reduction reaction in proton exchange membrane fuel cell. *Appl. Phys. Lett.* 88(25) (2006) 253105.
- [10] S. Ghosh, S. Mondal, and C. Retna Raj, Carbon nanotube-supported dendritic Pt-on-Pd nanostructures: growth mechanism and electrocatalytic activity towards oxygen reduction reaction. *J. Mater. Chem. A*, 2(7) (2014) 2233-2239.
- [11] Y. Shao, et al., Novel catalyst support materials for PEMfuelcells: current status and future prospects. *J. Mater. Chem.* 19(1) (2009) 46-59.
- [12] S. Y. Huang, et al., Development of a Titanium Dioxide-Supported Platinum Catalyst with Ultrahigh Stability for Polymer Electrolyte Membrane Fuel Cell Applications. *J. Am. Chem. Soc.* 131(39) (2009) 13898-13899.
- [13] P. Dhanasekaran, et al., Rutile  $\text{TiO}_2$  Supported Pt as Stable Electrocatalyst for Improved Oxygen Reduction Reaction and Durability in Polymer Electrolyte Fuel Cells. *Electrocatal.* 7(6) (2016) 495-506.
- [14] P. Mazúr, et al., Non-conductive  $\text{TiO}_2$  as the anode catalyst support for PEM water electrolysis. *Int. J. Hydr. Energ.* 37(17) (2012) 12081-12088.
- [15] C. V. Subban, et al., Sol–Gel Synthesis, Electrochemical Characterization, and Stability Testing of  $\text{Ti}_{0.7}\text{W}_{0.3}\text{O}_2$  Nanoparticles for Catalyst Support Applications in Proton-Exchange Membrane Fuel Cells. *J. Am. Chem. Soc.* 132(49) (2010) 17531-17536.
- [16] I. Jang, I. Hwang, and Y. Tak, Attenuated degradation of a PEMFC cathode during fuel starvation by using carbon-supported  $\text{IrO}_2$ . *Electrochim. Acta*, 90 (2013) 148-156.
- [17] E. Antolini, Iridium As Catalyst and Cocatalyst for Oxygen Evolution/Reduction in Acidic Polymer Electrolyte Membrane Electrolyzers and Fuel Cells. *ACS Catal.* 4(5) (2014) 1426-1440.
- [18] Y. Zheng, et al., Hydrothermal Preparation of Nanosized Brookite Powders. *J. Am. Ceram. Soc.* 83(10) (2000) 2634-2636.
- [19] S. Bakardjieva, et al., Transformation of brookite-type  $\text{TiO}_2$  nanocrystals to rutile: correlation between microstructure and photoactivity. *J. Mater. Chem.* 16(18) (2006) 1709.
- [20] K. Yanagisawa, and J. Ovenstone, Crystallization of Anatase from Amorphous Titania Using the Hydrothermal Technique: Effects of Starting Material and Temperature. *J. Phys. Chem. B*, 103(37) (1999) 7781-7787.