

FABRICATION OF TIO<sub>2</sub> NANOTUBE ARRAYS BY ANODIZATION AND ITS  
APPLICATIONS IN PHOTOREDUCTION OF CHROMIUM(VI)

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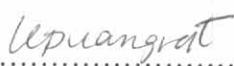
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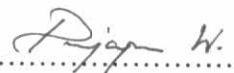
  
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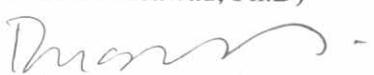
  
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วิจัยวรรณ จันทร์มณี: การขึ้นรูปไททาเนียมโดยออกไซด์แบบท่อนาโนด้วยวิธีอะโนไดเซชัน และการประยุกต์ใช้ในปฏิกิริยาไฟฟ้ารีดักชันของโครเมียม(FABRICATION OF TIO<sub>2</sub> NANOTUBE ARRAYS BY ANODIZATION AND ITS APPLICATIONS IN PHOTOREDUCTION OF CHROMIUM (VI)) อ. ที่ปรึกษา : รศ. ดร. พวงรัตน์ ขจิตวิชานุกูล, อ. ที่ปรึกษาร่วม: ศ. ดร. คริสแนน ราเจษฐวา. 165 หน้า.

งานวิจัยนี้มุ่งเน้นศึกษาการขึ้นรูปและวิเคราะห์คุณลักษณะของไททาเนียมโดยออกไซด์แบบท่อนาโนด้วยวิธีอะโนไดเซชัน โดยใช้ความต่างศักย์ไฟฟ้าทั้งบวกและลบบนแผ่นโลหะไททาเนียม ความต่างศักย์ที่ใช้ในการทดลองครั้งนี้มี 2 แบบด้วยกัน กล่าวคือ 20 โวลต์ สลับกับ -4 โวลต์ และ 20 โวลต์ สลับกับ 0 โวลต์ และมีการเปลี่ยนระยะเวลาในการใช้ศักย์ไฟฟ้าลบและศูนย์ตั้งแต่ 2 วินาที ถึง 16 วินาที การขึ้นรูปไททาเนียมโดยออกไซด์แบบท่อนาโนเกิดขึ้นในสารละลายแอมโมเนียมฟลูออไรด์ และส่วนประกอบอื่น ๆ ในสารละลาย (กรีเชอรอล เอธทิลเอ็นไกลคอล หรือโพลีเอธทิลเอ็นไกลคอล) ผลการทดลองพบว่า การขึ้นรูปแบบใช้ความต่างศักย์ไฟฟ้าทั้งบวกและลบนั้น ทำให้ได้ไททาเนียมโดยออกไซด์ลักษณะ เป็นห้องนาคเล็กในระดับนาโนเมตร และมีค่าการตอบสนองต่อปฏิกิริยาเคมีไฟฟ้าสูงกว่าการใช้เพียงศักย์ไฟฟ้าบวกเพียงอย่างเดียวโดยสภาวะที่เหมาะสมที่สุด ในการขึ้นรูปไททาเนียมโดยออกไซด์แบบท่อนาโนคือ การใช้ศักย์ไฟฟ้า 20 โวลต์ สลับกับ -4 โวลต์ และใช้ระยะเวลาในการใช้ศักย์ไฟฟ้าลบ 2 วินาที เนื่องจากศักย์ไฟฟ้าลบทำให้แอมโมเนียมไอออนในสารละลายน้ำติดพิวของไททาเนียมโดยออกไซด์ซึ่งจะทำหน้าที่ป้องกันการถูกทำลายของไททาเนียมโดยออกไซด์จากฟลูออไรด์ไอออนที่มีอยู่ในสารละลายนอกจากนี้ยังมีการศึกษาความสัมพันธ์และการเปลี่ยนแปลงของการตอบสนองต่อปฏิกิริยาเคมี และปฏิกิริยาไฟฟ้ากระแสไฟฟ้าต่ำ เมื่อมีเติมโลหะไอออนและสารประกอบอื่น ๆ ในสารละลาย ซึ่งผลการทดลองพบว่าการเลือกใช้โลหะไอออนกับสารประกอบอื่น ๆ ที่เหมาะสมนั้น สามารถช่วยเพิ่มประสิทธิภาพของไททาเนียมโดยออกไซด์แบบท่อนาโนในการตอบสนองต่อปฏิกิริยาเคมี และปฏิกิริยาไฟฟ้ากระแสไฟฟ้าต่ำ โดยการทดสอบปฏิกิริยาไฟฟ้ากระแสไฟฟ้าต่ำดักชันของโครเมียม ประจำวันที่ 6 ภายใต้การฉายแสงอัลตราไวโอเล็ต ได้ทำการทดสอบทั้งไททาเนียมโดยออกไซด์แบบท่อนาโน และไททาเนียมโดยออกไซด์แบบท่อนาโนที่มีการเติมไอออนโลหะ และกลีเซอรอลให้ค่าอนตัมมิลิวูบงถึง  $3.2 \times 10^{-2}$

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KEY WORD: TiO<sub>2</sub> / PULSE ANODIZATION / TIO<sub>2</sub> DOPING / PHOTOELECTROCHEMICAL RESPONSE / TITANIUM NANOTUBE / CHROMIUM / ZINC PORPHYRIN / TIO<sub>2</sub> DYE SENSITIZED/ PHOTOCATALYSIS /

WILAIWAN CHANMANEE: FABRICATION OF TIO<sub>2</sub> NANOTUBE ARRAYS BY ANODIZATION AND ITS APPLICATIONS IN PHOTOREDUCTION OF CHROMIUM (VI). THESIS ADVISOR: ASSOC. PROF. PUANGRAT KAJITVICHYANUKUL, Ph.D., THESIS CO-ADVISOR: PROF. KRISHNAN RAJESHWAR, Ph.D., 165 pp.

This research focuses on preparation and characterization of TiO<sub>2</sub> nanotube arrays prepared by anodic oxidation of Ti substrates using pulse voltage waveforms. Voltages were pulsed between 20 V and -4 V or between 20 V and 0 V with varying durations from 2 to 16 seconds at the lower limit of the pulse waveform. Ammonium fluoride were used as the electrolyte with or without added medium modifier (glycerol, ethylene glycol, or poly (ethylene glycol) (PEG 400)) in these experiments. The pulse waveform was optimized to electrochemically grow TiO<sub>2</sub> nanotubes and chemically etch their walls during its cathodic current flow regime. The resultant TiO<sub>2</sub> nanotube arrays showed a higher quality of nanotube array morphology and photoresponse than samples grown via the conventional continuous anodization method. Films grown with a 20 V/-4 V pulse sequence and pulse duration of 2 s at its negative voltage limit afforded superior photoresponse compared to other pulse durations. Specifically, the negative voltage limit of the pulse (-4 V) and its duration promote the adsorption of NH<sub>4</sub><sup>+</sup> species that in turn inhibits chemical attack of the growing oxide nanoarchitecture by the electrolyte F<sup>-</sup> species. The co-doping effects by metal cations on photoelectrochemistry properties were also observed on photocatalysis reduction. Thus, it was found that transition metal doping into photocatalysts with wide band gaps was effective for the development of photoelectrochemical response and photocatalytic activity if a suitable combination of dopant–codopant is chosen. Finally, photocatalytic reduction of hexavalent chromium were studied under ultraviolet light using anodically growth Ti/TiO<sub>2</sub> and metal modified TiO<sub>2</sub> nanotube show quantum yield up to  $3.2 \times 10^{-2}$  obtain by film were prepared with NiF<sub>2</sub> and used glycerol as dopant.

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## NOMENCLATURES

Ti	=	titanium
TiO <sub>2</sub>	=	titanium dioxide
NH <sub>4</sub> F	=	ammonium fluoride
NaF	=	sodium fluoride
N <sub>2</sub>	=	nitrogen gas
O <sub>2</sub>	=	oxygen gas
PEG	=	Polyethylene glycol
EG	=	ethylene glycol
CO <sub>2</sub>	=	carbon dioxide gas
H <sup>+</sup>	=	hydrogen ions
OH <sup>-</sup>	=	hydroxide ion
h	=	hour
min	=	minute
M	=	molar
k <sub>app</sub>	=	apparent rate constant
r <sub>initial</sub>	=	initial reaction rate
t <sub>1/2</sub>	=	half life
Φ <sub>app</sub>	=	apparent quantum yield
j <sub>ph</sub>	=	photocurrent density