平成２３年度　新潟大学プロジェクト推進経費研究成果報告書

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本年度の交付を受けたプロジェクト推進経費について，下記のとおり報告いたします。

プロジェクトの種目：奨励研究
プロジェクトの課題：Development of efficient photoanodes for oxygen evolution using nanoporous titanium oxide materials
プロジェクトの代表者：所属 産学地域人材育成センター 職名 研究員 氏名 Debraj Chandra 分担者人
プロジェクトの成果：（別紙可） Please see the attached sheets.

（注）報告書は２枚以上とする。別紙による場合も同じ。

プロジェクト成果の発表（論文名，発表者，発表紙等，巻・号，発表年等）（別紙可）

1. **Debraj Chandra**, Naoto Abe and Masayuki Yagi
Fabrication of chrome doped mesoporous TiO_2 based photoanodes using new structure directing agents: Visible light driven photoelectrochemical properties
(*Manuscript under preparation*)

(Title)

Development of efficient photoanodes for oxygen evolution using nanoporous titanium oxide materials

(Purpose)

Design and development of an efficient photoanode for water oxidation to evolve O_2 for an artificial photosynthesis device is highly desired for future clean energy providing systems. Purpose of the research work, carried under this project was to expand the challenge to development of a competent photoanode for water splitting based on various nanotextured porous TiO_2-based electrodes. The ultimate goal was to develop an efficient water splitting system that is able to produce H_2 and O_2 from water in economically viable way.

(Experimental)

1. Transparent and well ordered mesoporous TiO_2 films (mesopore dimension ~ 10 nm) having high surface area have been fabricated using a triblock copolymer F127 [poly(ethylene oxide)-*b*-poly(propylene oxide)-*b*-poly(ethylene oxide), $EO_nPO_mEO_n$] as a mesoporous structure directing agent (SDA). Synthesis procedure has been optimized to obtain better quality crack-free films with improved mesoporous properties.
2. Optically uniform TiO_2 films composed of small mesopore system (~ 2-3 nm) have been designed and synthesized using laboratory made long chain alkyl-2-pyridinylmethylamines (PAL2-*n*, *n* = 16 and 12) as SDAs. Small mesopore systems were examined due to its slim pore wall which increases possibility of more active surface for water oxidation.
3. Photoelectrochemical performance of different mesoporous TiO_2 based photoanode has been investigated. TiO_2 photoanode has been modified by electrochemical deposition of chrome species (act as inorganic sensitizer) over the mesoporous surface to improve visible light absorption property.

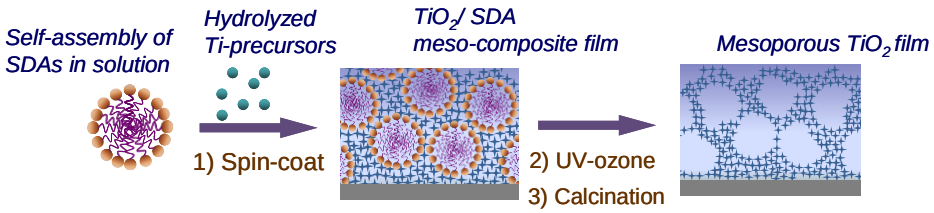

Figure 1. Generalized scheme for formation of mesoporous TiO_2 electrode using self-assembly of SDAs

(Results)

1. Characterization of bidentate long chain alkyl-2-pyridinylmethylamines SDAs

Long chain alkyl-2-pyridinylmethylamines (PAL2-*n*, *n* = 16 and 12) SDAs were characterized by ^{1}H NMR and FT-IR spectroscopy. 1H NMR spectra of these SDAs are shown in Figure 2. Schiff base condensation of the aromatic aldehyde and alkyl amine results the long-chain imines in almost quantitative yield. The resulting imine on borohydride reduction yielded the secondary amines. N atoms located in the pyridine ring and in the side chain could donate their respective lone pair of electrons to the framework Ti^{IV} species and thus could act as SDAs to stabilize the nanostructure.

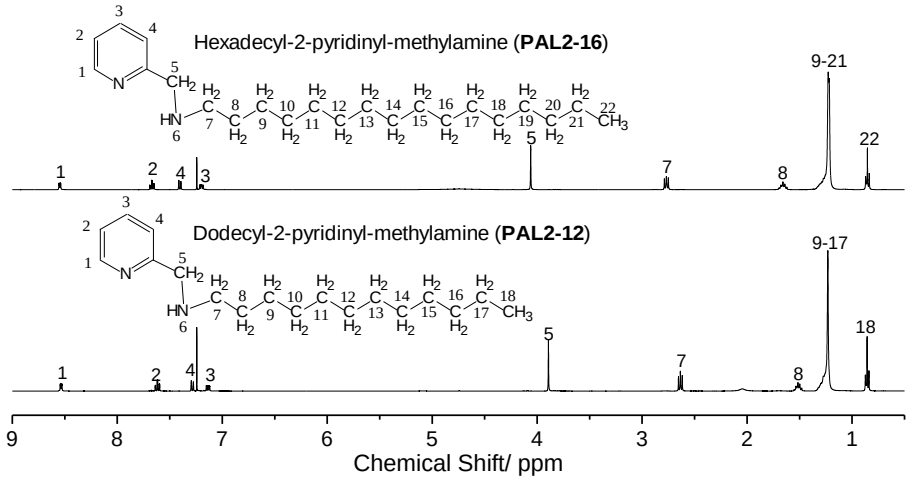

Figure 2. 1H NMR spectra of bidentate SDAs

2. Characterization of different nanoporous TiO_2 based photoanodes

Mesoporous structures of the different TiO_2 films have been characterized in detail by small angle X-ray scattering (SAXS), X-ray diffraction (XRD) measurement, scanning electron microscopy (SEM) and UV-visible spectroscopy.

Representative SAXS patterns (Fig. 1) of TiO_2 film prepared by triblock copolymer F127 as SDA as-made and calcined at 450 ºC shows formation of mesopore of dimension around ~10 nm. Wide angle XRD patterns (not shown here) confirm the formation of anatase phase upon crystallization of the films at 450 ºC. Variation and effect on mesoporous structure of the films by changing the concentration of F127 and different block-copolymer has been also investigated.

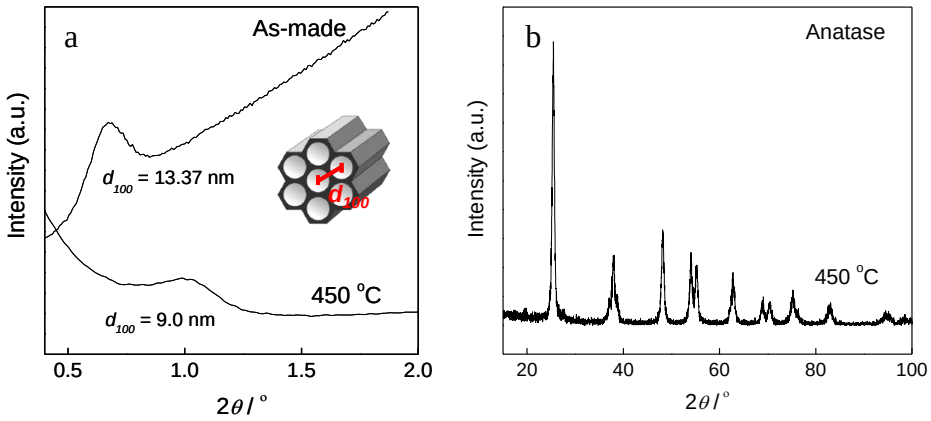

Figure 3. SAXS and wide angle XRD patterns of different TiO_2 films prepared by F127 as SDA

Formation of mesoporous structures of TiO_2 films prepared by PAL2-16 and PAL2-12 have confirmed from low angle XRD measurement. Single diffraction peaks were obtained at low 2θ having d ~ 2-4 nm for both the films, suggesting the formation of disordered mesoporous materials with no long range mesoscopic ordering. Both these samples show noticeable diffraction peak after calcination followed by UV-ozone treatment. Results show the exceptional stability of the small mesopores during crystallization of the framework due to formation of carbon layer during UV-ozone treatment.

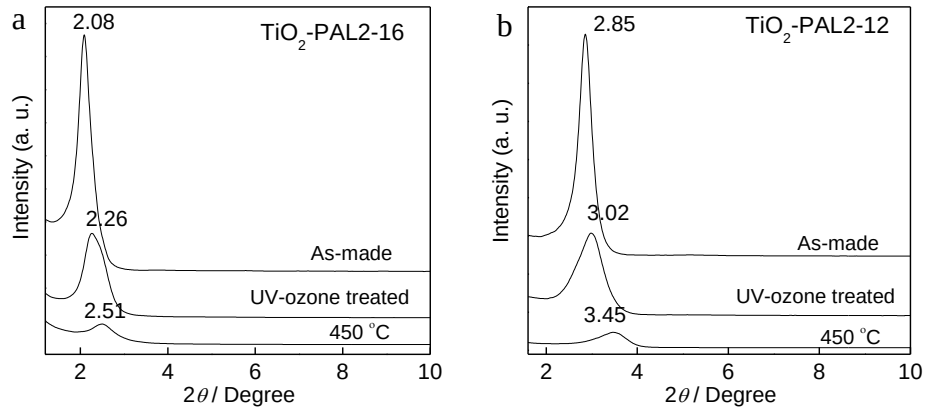

Figure 4. XRD patterns of TiO_2 films prepared by PAL2-16 (a) and PAL2-12 (b) as SDAs

3. Study of photoelectrochemical properties of different TiO_2 based photoanodes

Photoelectrochemical measurement of different TiO_2 based films (doping or without doping of chrome species) have been studied in detail. Cyclic voltammetric (CV) measurements have been performed in single compartment electrochemical cell using Ag/AgCl as reference electrode and Pt as counter electrode. Under visible light irradiation the photoanodic current was highly induced due to water oxidation. Chrome doped sample has more visible light absorption and photo-response compared to the undoped films (Figure 5a). However, more interestingly undoped TiO_2 films have significant visible light response on photocurrent generation (Figure5b), which are quite unique and interesting features of these mesoporous films.

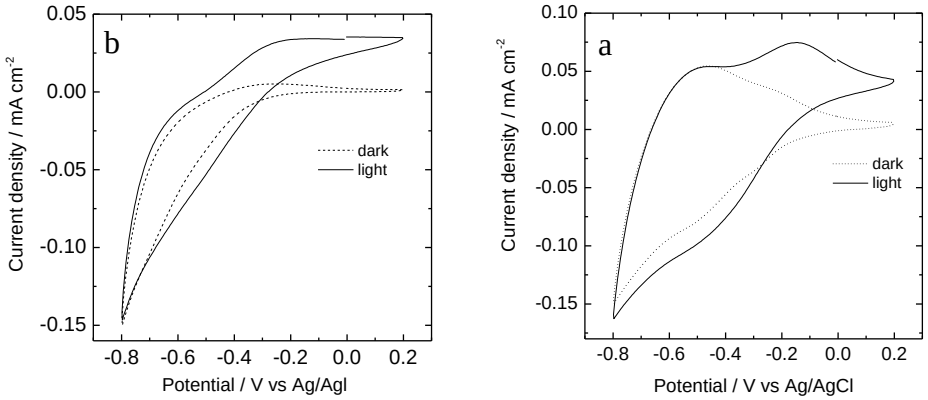

Figure 5. Cyclic voltammograms (CV) of FTO/ F127-TiO_2 films calcined at 450 ^{0}C before (a) and after (b) Cr doping

収支決算書

単位：円

配分額：　600000　円

費目別収支決算表

設備備品費	消耗品費	旅　　費	謝金・賃金	そ の 他	合　　計
488250	111750				600000

設備備品費内訳

設備備品名	仕様・型式等	数　量	単　価	金　額
ブランソン社超音波ホモジナイザー		1	488250	488250
計				488250

消耗品費内訳

品　　目	数　量	単　価	金　額
Alfa Aesar Tin(Ⅳ) oxide,15% in H20 coll	1	17356	17356
ALD Amberlite IRA-400 塩化物フォーム	1	4485	4485
酢酸パラジウム(Ⅱ)特級 1ｇ	1	5670	5670
TCI Phosphorus(Ⅴ)Chloride	1	1344	1344
スクリューキャップ　他	1	12442	12442
プランジャーASSY　送料	1	1000	1000
特級 N,N ジメチルホルムアミド(DMF)　他	1	5107	5107
ガラス電極	1	2100	2100
特級 ジエチルエーテル　他	1	8379	8379
酸化コバルト(Ⅱ)100ｇ	1	5670	5670
特級　アセトン　他	1	8525	8525
tert-ブチルヒドロペルオキシド　他	1	22176	22176
真空シールセット	1	9922	9922
工業用アセトン	1	7560	7560
RIA 用テストチューブ	1	14	14
計			111750

旅　費　内訳

事　項　・　出張先	回　数	単　価	金　額
計			

謝金・賃金　内訳			
事　　項	員　数	単　価	金　額
計			

そ　の　他　内訳			
事　　項	員　数	単　価	金　額
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