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研究課題名（和文）Dye-sensitized mesoporous Ta3N5 photocatalysts for water splitting under visible light with longer wavelengths up to ~600 nm

研究課題名（英文）Dye-sensitized mesoporous Ta3N5 photocatalysts for water splitting under visible light with longer wavelengths up to ~600 nm

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研究成果の概要（和文）：結晶性メソポーラスTa205にさまざまな窒化処理を行い、結晶性メソポーラスTa3N5を合成した。窒素吸着の結果によると、700度、処理時間24時間の結晶質のメソポーラスTa3N5の表面積が最も大きく（27.1m2/g、細孔サイズ21.3nm）、良い結晶化度であることがわかった。幾通りかの結晶構造のメソポーラスTa3N5を、更なる光触媒性能の確認と、異なる手順で処理されたTa3N5のサンプルの性能の関係を更に明らかにするために、CoOxのような異なる共触媒を添加し準備した。これらの実験結果をまとめて、結晶性メソポーラス Ta3N5合成最適化と光触媒の活性進化ついて論文を発表する予定である。

研究成果の概要（英文）：On the basis of sol-gel method, high surface area mesoporous Ta205 (117 m2/g) and crystalline mesoporous Ta3N5 (44 m2/g), which can adsorb visible light up to 600 nm, has been successfully synthesized. For the crystalline mesoporous Ta205, the photocatalytic performace demonstrated three times higher than that of noporous courtpart. For the Ta3N5, however, the performance are not ideal. Although the surface area of mesoporous Ta3N5 were dramatically increased comparing with bulk counterparts, the crystallinity was still low, which is disadvantage and easily results in the combination of photo-induced electron and hole. Several organic dyes have been used to improve the charge separation and photocatalytic activity of the catalysts. Some interesting phenomena was observed, although the overall water splitting has not be achieved. The correponding results will be published in near future. Now, I am trying to increase the crystallinity of the as-synthesized mesoporous Ta3N5.

研究分野：catalysis

キーワード：photocatalysis

１．研究開始当初の背景

Hydrogen will play an important role to power our society due to it is an ultimate clean energy and it can be used in fuel cells. Directly splitting water into hydrogen and oxygen using a photocatalyst and sunlight is a very attractive candidate for future hydrogen production. Long ago, natural plants figured out how to activate small molecules and store solar energy by photosynthesis. Now, we and other investigators worldwide target the hydrogen production by water splitting, which is the mimic of photosynthesis.

Water splitting using a powdered photocatalyst is advantageous for its simplicity and easily large-scale application. To achieve the water splitting, the bottom of conduction band must locate at a more negative potential than the reduction potential of H^+ to H_2, while the tops of valance band must locate at a more positive potential than the oxidation potential of H_2O to O_2. The minimum photon energy thermodynamically requires to drive the water splitting is 1.23 eV, corresponding to a wavelength of ca. 1000 nm. Accordingly, it would be possible to utilize the entire spectral range of visible light, which makes up the majority of sunlight. To efficiently utilize sunlight, the photocatalysts can be responsive longer wavelengths (such as up to ~ 600 nm, more than 35% of the sunlight can be utilized). Some photocatalysts (such as $LiTiO_2N$ and Ta_3N_5) with the potential to split water by absorbing light with wavelengths up to ~600 nm, however water splitting has not yet been achieved by these 600 nm-class photocatalysts, which is very likely that defects formed during preparation processes degrade their final performance.

The photocatalytic reaction for water splitting consists of three crucial steps: the photocatalyst absorbs photon energy greater than the band gap energy and generates photoexcited electron-hole pairs; the photoexcited carriers separate and migrate to the surface without recombination; and the surface reaction for H_2 and O_2 evolution. Based on the characteristics of crystalline mesoporous Ta_2O_5 (thin crystalline pore wall (short charge migration distance) and high surface area (more reaction sites)), three times that of nonporous Ta_2O_5 water splitting rate have been achieved according to our recent experimental results.

Ta_3N_5 with a band gap of 2.1 eV (absorption edge at 600 nm) has proper level of conduction and valence bands for H^+ reduction into H_2 and H_2O oxidation into O_2. However, water splitting has not yet been achieved on Ta_3N_5. Ta_3N_5 can generate both H_2 and O_2 individually from H_2O in the presence of sacrificial agents by absorbing visible light up to ~600 nm. Notably, the H_2 generating activity is much lower than the O_2-generating one, so it is considered more important to enhance the former.

Our group has found $KTa(Zr)O_3$ modified by proper organic dye can greatly facilitate the charge separation and promote H_2 generating. The LUMO level of the dye is more negative than the conduction-band level of $KTa(Zr)O_3$ and the HOMO level is a little positive than the evolution potential of oxygen to avoid the dye degradation by hole oxidation. At the same time, the valance band of $KTa(Zr)O_3$ is positive enough for the formation of O_2. The energy levels of the organic dye and $KTa(Zr)O_3$ satisfy the configuration of the Z-scheme model.

２．研究の目的

Splitting water into hydrogen and oxygen using a photocatalyst and sunlight is a very attractive route for future hydrogen production. To achieve the grand vision, the primary subject is the phtotocatalysts that can achieve water splitting with visible light of longer wavelengths. The research will target water splitting with visible light of longer wavelengths (~600 nm) using organic dye sensitized crystalline mesoporous Ta_3N_5 as the photocatalyst.

３．研究の方法

This research is to fabricate the organic dye sensitized mesoporous Ta_3N_5, which can achieve water splitting by utilizing sunlight with wavelengths up ~ 600nm. To achieve the goal, three close related research parts will be sufficiently implemented.

Part 1: Optimized crystalline mesoporous Ta_3N_5 synthesis; Various nitridation treatments have been utilized, the

as-synthesized Ta_3N_5 samples have been characterized by various characterization techniques especially the recently developed atom resolution technique in order to clarify the mechanism of defects formation in Ta_3N_5. The purpose of above described research is to finally synthesize optimized mesoporous Ta_3N_5 with low defects level and thin crystalline pore wall.

Part 2: Synthesis of ideal dye with proper LUMO and HUMO level to match the band level of Ta_3N_5; two points will be paid attention. One is the as-synthesized organic dye should have proper LUMO (more negative than the conduction band of Ta_3N_5) and HUMO (a little positive compare with the evolution potential of oxygen) level, which can well match the band structure of Ta_3N_5. The other is the dye can be well modified or tightly coated onto the surface of Ta_3N_5. Adjustment of ligand and center metal ion will be the way to satisfy the two points. The dyes synthesis and screening will start on the basis of our former research

Part 3: Interface optimization among dye, Ta_3N_5 and co-catalysts and water splitting evaluation using dye modified Ta_3N_5.

４．研究成果

In this project, crystalline mesoporous Ta_3N_5 has been synthesized by different nitridation treatments on the crystalline mesoporous Ta_2O_5. The nitridation procedures were adjusted by changing temperature from 700 to 850 ^oC and the time from 14 to 48 hours. At the same time, the NH_3 flow rate was fixed at 200 cm3/min. X-ray diffraction (XRD), X-ray photoelectron spectrum, high resolution scanning electron microscope (SEM), transmission electron microscopy (TEM), UV/vis diffuse reflectance spectra and Nitrogen sorption and so on have been used for the characterization of the as-synthesized samples. In summary of the all the results, the crystalline mesoporous Ta_3N_5 have been successfully synthesized by directly nitridation treatments on the mesoporous Ta_2O_5. The longer time and higher temperature of the nitration treatments are good for the crystal structure transformation from Ta_2O_5 to Ta_3N_5 on the basis of the XRD results. According to the UV/vis diffuse reflectance spectra, the higher temperature treatments resulted in higher level of the defects. In addition, all the as-synthesized mesoporous Ta_3N_5 showed clear and well crystalline structure according to the high resolution TEM images. Some special sample preparation may be needed to get very thin sample for the clear atom resolution image to identify the atom defects, which is still under research. The Nitrogen sorption results showed the crystalline mesoporous Ta_3N_5 treated at 700 ^oC for 24 h had the highest surface area (27.1 m^2/g and the pore size is 21.3 nm) and also good crystallinity. Several series crystalline mesoporous Ta_3N_5 have been prepared by loading different co-catalysts, such as CoO_x, in order to further check the photocatalytic performance and further elucidate the relationship of performance and different procedure treated Ta_3N_5 samples. Finally, one manuscript will be prepared to summarize the all results for publication.
Several organic dyes have been used to improve the charge separation and photocatalytic activity of the catalysts. Some interesting phenomena was observed, although the overall water splitting has not been achieved. The corresponding results will be published in near future. Now, I am trying to increase the crystallinity of the as-synthesized mesoporous Ta_3N_5.

５．主な発表論文等
（研究代表者、研究分担者及び連携研究者には下線）

〔雑誌論文〕（計　1　件）

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〔学会発表〕（計　4　件）

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2. Limin Guo, Water oxidation on mesoporous Ta_3N_5 photocatalysts under visible light, The International Chemical Congress of Pacific Basin Societies 2015, 2015-12-15, Honolulu,

USA.

3. Limin Guo, Direct access to crystalline mesoporous Ta_2O_5, Ta_3N_5, and their photocatalytic activity for overall water splitting, Materials Research Society of USA, 2014-12-04, Boston, USA.

4. Limin Guo, Soft-templating method to access crystalline mesoporous tantalum oxide/nitride, 2014 International Conference for Top and Emerging Materials Scientists, 2014-07-20, Zhuhai, China.

6. 研究組織

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