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論文の内容の要旨

In the catalytic field, the Au/TiO_2 plays an important role due to an extraordinary high activity for low-temperature catalytic combustion, partial oxidation of hydrocarbons, hydrogenation of unsaturated hydrocarbons, and reduction of nitrogen oxides and so on. Studying the electronic states of the Au/TiO_2 interface is vital to explore the catalytic mechanism. Many researchers already studied the electronic structure of the Au/TiO_2 (110) interface by several microscopic or optical technique such as scanning tunnelling microscope (STM), transmission electron microscope (TEM), UV-Vis spectroscopy, and so on . However, the observation of the electronic states of the Au/TiO_2 interface and stepped and flat TiO_2 surface by second harmonic generation (SHG) method is very limited. For this reason, I intended to observe the electronic states of the Au/stepped TiO_2 interface using SHG method. SHG is a well-established surface-specific probe of centrosymmetric media. In the dipole approximation, SHG is forbidden in the bulk of a medium having inversion symmetry, while it is allowed at the surface where inversion symmetry is broken. Because of the symmetry selection property, the SHG method can be one of the ideal methods to measure the contribution of the step structure, while other surface tools such as XPS, TEM, STM, UV-Vis spectroscopy and microscopy technique cannot do because the number of steps are normally lower than the terrace atoms. In this research, stepped bare TiO_2 (320) single crystal surface was used as a substrate and Au thin film with the thickness of 2 nm was deposited on the surface in a UHV chamber at a pressure of $2x10^{-7}$ Torr. This Au/TiO_2 (320) interface may act as an active sites for showing the catalytic behaviour. As it is well known, surface defects such as steps and kinks play an important role in generating active sites for catalytic reactions, so it is vital to study the structure and the electronic states of such surface defects. Thus, it would be very informative to analyse the SHG response from the interface of TiO_2 stepped surface decorated by Au. Au/TiO_2 steps should generate an SHG signal due to broken symmetry at the interface.

The SHG response from the Au/TiO_2 (320) interface and bare TiO_2 (320) surface was

investigated with the incident photon energies of 1.17 eV and 2.33 eV generated by using a pulsed Nd^{3+}:YAG laser. The isotropic response was found from both samples at the incident photon energy of 1.17 eV. In contrast, we observed the anisotropic response from both Au /TiO_2 (320) and bare TiO_2 (320) at the incident photon energy of 2.33 eV. From the Au/TiO_2 (320) sample, an anisotropic structure was observed to the $[\bar{2}30]$ direction for Pin/Pout polarization combination. Here, the Pin denotes the input polarization mode of the incident light and Pout corresponds to the output polarization mode of the SHG light. From the experimental data, I theoretically decomposed the nonlinear susceptibility elements ($\chi_{ijk}^{(2)}$). Here, i, j and k denote the axis direction of the sample coordinate. I found that there were two groups of the nonlinear susceptibility elements corresponding to step and terrace contribution. More precisely, I have calculated SHG intensity patterns for Au/TiO_2 (320) and bare TiO_2 (320) based on the terrace and step contributions fitted to the experimental results with photon excitation energies of 2.33 eV. The anisotropic responses were observed due to the contributions of both the step and terrace groups of nonlinear susceptibility elements. From the calculated results of the step and terrace groups of $\chi_{ijk}^{(2)}$ elements, it was found that the step contribution of the Au/TiO_2 (320) is different from that of the bare TiO_2 (320) sample for the Pin/Pout polarization combination. In order to discuss the possible reasons for this difference, I considered the four possible mechanism candidates as an origin of the signal enhancement from the Au/TiO_2 (320) interface. This four candidates are (a) Enhancement of the incident electric field by surface defects (b) Electronic resonance of Au/TiO_2 interface step (c) Surface plasmon effect on SHG enhancement (d) Fresnel factor effect on SHG enhancement.

I found that Au deposited TiO_2 (320) surface contains island structure by the observation of AFM and SEM with EDX and these islands might act as “hot spot” and make the SHG intensity stronger. However, this effect should have an isotropic nature with respect to the rotation of the sample around its normal because these islands are randomly distributed. The effect would be similar if I consider the enhancement occurring due to the random steps on the surface. This is not the case when I see the SHG pattern for Pin/Pout polarization combination. So, this candidate should be eliminated.

An electronic resonance may occur at the step region of the Au/TiO_2 interface and it is the most possible candidate for the enhancement of the SHG signal considering this case. In this study I observed the enhanced SHG signal correlated with the existence of the Au/TiO_2 (320) interface steps. Hence this interface step electronic state is a credibe candidate of the origin of the enhanced signal.

In the case of a thin gold film deposited on pre-patterned TiO_2 substrate, local field enhancement may result from the surface plasmon resonance (SPR). I measured the linear optical reflectivity in order to confirm whether there is any influence of surface plasmon resonance and Fresnel factor for the enhancement of the anisotropic SHG signal obtained from the Au/TiO_2 (320) interface. From the reflectivity data of the Au/TiO_2 (320) interface, it was observed that, the reflectivity for P- and S- polarized light are almost

the same at the azimuthal angle, φ = 0^{O} and 180^{O}. This result indicates that the linear optical process at frequency ω occurs almost in the same way at φ = 0^{O} and 180^{O} and it means that even if the SPR occurred, there is no effect on the enhanced SHG signal due to the different response from the φ = 0^{O} and 180^{O}. This discussion is also true for the Fresnel factors. Therefore, there is no influence of Fresnel factors on the enhancement of SHG signal.

From the above discussion of four candidates, it seems that electronic resonance at the Au/TiO_2 (320) interface step is feasibly responsible for the enhancement of the SHG. The other three mechanism candidates can be eliminated due to their less feasibility.

Keywords: Second harmonic generation (SHG); Photocatalyst; Au/TiO_2 (320) interface; Electronic states; Nonlinear susceptibility elements.

論文審査の結果の要旨

金微粒子を担持した酸化チタン(Au/TiO_2)触媒は、一酸化炭素や炭化水素化合物の酸化、不飽和炭化水素化合物の水素化などの触媒として重要で代表的な触媒である。本論文ではそのTiO_2(320)面上の原子ステップをAu膜で修飾し、光第二高調波発生(SHG)応答の、原子ステップによる対称性のやぶれの成分のみを分離することに成功した。まず、作成した質量膜厚2nmの厚さのAuを蒸着したTiO_2(320)試料のモフォロジーと元素分布を、原子間力顕微鏡と走査型電子顕微鏡およびエネルギー分散型X線分析装置を用いて評価した。その結果、Auは局所的に数百nmの島状構造を作るが、TiO_2表面全体を覆っていることがわかった。また、質量膜厚2nmの厚さのAuを蒸着したTiO_2(320)と修飾しないTiO_2(320)面の、SHG応答の波長依存性、試料方位角依存性、入射出射偏光依存性を調べた。その結果、1.17eV励起の時は、いずれの試料についても、方位角依存性に異方性は認められなかった。一方2.33eV励起の時は、両方の試料について、方位角依存性に異方性が認められた。そして2.33eV励起の時の方位角依存性パターンは、２つの試料で非常に異なった形を示すことがわかった。そこでこれらの試料の非線形光学係数を分析するために、本研究では試料の法線方向の座標(3)を奇数個添字に含む非線形感受率およびステップの方向座標(2)を奇数個含む非線形感受率にわけて、方位角依存性パターンを分解した。ここで前者はファセット表面のテラス面からの寄与と考えられ、後者はステップ構造からの寄与であると考えられる。ここでステップ構造からの寄与と思われる異方的なSHG応答の起源について、以下の４つの可能性を挙げて検討した。その可能性とは(1)試料表面の構造的な粗さによるもの、(2)試料のフレネル因子の異方性によるもの、(3)金の微粒子構造による局所プラズモンの異方的な励起によるもの、(4)AuとTiO_2ステップの界面の電子状態によるもの、である。(1)の候補は特にAuの島状構造によるシグナルの増強を引き起こすが、この効果は試料回転に対して異方的

に働くとは考えられないので除外した。(2)(3)の可能性を検討するために、白色ランプを用いた当該試料の線形反射率測定を行った。その結果、SHGでは異方性が認められた２つの方位角の間で、線形反射率のスペクトルの違いはまったく検出できず、フレネル因子は局所プラズモン励起による電場の増強効果は少なくとも等方的であることから、SHG応答の異方性は(2)(3)の理由によるものではないことがわかった。したがって、検出されたSHG応答の異方性は(4)のAuとTiO_2(320)上のステップの間の電子準位に起因することが推測された。今後、波長可変光源を用いてステップからの寄与の成分のエネルギースペクトルを求めることにより、触媒反応に関連する電子準位のスペクトルが求められることが期待される。以上、本論文は代表的な触媒材料について非線形表面分光学的に新しい探求法を提示したものであり、学術的に貢献するところが大きい。よって博士（マテリアルスサイエンス）の学位論文として十分価値あるものと認めた。