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Author(s)	魏, 久焱
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論文内容の要旨

氏　名　（　魏久焱　）	
論文題名	Study of charge state of Au nanoclusters on anatase TiO_2(101) surface by atomic force microscopy and Kelvin probe force microscopy with density functional theory (原子間力顕微鏡及びケルビンプローブ力顕微鏡と密度汎関数理論によるアナターゼTiO_2(101)表面上のAuナノクラスターの電荷状態の研究)

論文内容の要旨

Surface photocatalysis on noble metal nanocluster-supported metal oxides enhances catalytic efficiency through plasmonic enhancement, improved charge separation, and additional active sites, with applications in environmental remediation and energy conversion. Anatase TiO_2 (101) has garnered significant attention as an important photocatalytic surface due to its higher electron-hole separation efficiency and superior photogenerated electron mobility. However, the catalytic reactants have still remained investigation topics, and the catalytic mechanism has not been fully understood yet. Therefore, it is of high importance to clarify the active sites and charge properties of the anatase TiO_2 surface, experimentally and theoretically. In this work, charge states of steps and Au nanoclusters on the anatase TiO_2(101) surface are studied by noncontact atomic force microscopy (nc-AFM)/Kelvin probe force microscopy (KFPM) with DFT calculations. Nc-AFM and DFT clarify the cause of image modes in atomic resolution. Furthermore, we investigate the Au nanocluster adsorption and the charge states on the anatase TiO_2(101) surface, which provides valuable insights into enhancing surface reactivity.

In chapter 1～2, the research background and purpose of this paper are described. The principles of AFM and KPFM are introduced.

In chapter 3～4, the simulation methods for nc-AFM and TiO_2 are described in detail. The principles of the classical force method/quantum solution and models of TiO_2 are introduced.

In chapter 5, the structure and charge states of steps were experimentally clarified, and the new step B II was confirmed by combining DFT calculation for the first time. We distinguished four types of steps on anatase TiO_2(101) surface along different orientations. By in situ measurements of current and contact potential difference (CPD) information, we found that step B II exhibits the highest charge state, followed by step C and D, which have the same structure, and step A with the weakest charge state. This finding challenges the conventional understanding that step C possesses the highest charge state. By incorporating DFT calculations, we confirmed that step B II possesses a higher charge state.

In chapter 6, the image modes on the anatase TiO_2(101) surface with atomic resolution were investigated by nc-AFM at 78K and DFT calculations. From the AFM, the image modes are identified as the neutral mode with 90% and the protrusion mode with 10%. Through DFT analysis, a stable protrusion mode, characterized using the Ir-Ti_xO_y-H tip apex, indicates the different force curve tendencies at the oxygen (O_{2c}) and titanium (Ti_{5c}) sites. Moreover, we found that the neutral mode, observed by the Ir-H tip apex, and the protrusion mode, observed with the Ir-Ti_xO_y-H tip apex, are significantly influenced by the dipole moments arising from tip-sample charge redistribution, which in turn affects the image mode.

In chapter 7, the adsorption and charge states of Au nanoclusters on the anatase TiO_2(101) surface were investigated by nc-AFM/KPFM and DFT calculations. The Au atom prefers to adsorb on step A while Au nanoclusters prefer to adsorb on steps compared to the terrace. We find the charge state of Au on step B is the highest, which aligns with the trend of step B having a higher charge state, implying greater reactivity. Combined with DFT calculations, we found that Au2 exhibits higher activity compared to Au1, generating stronger intermediate states within the band gap. This results in step B having higher reactivity compared to step C and the terrace.

In chapter 8, the conclusions of this study and future prospects are discussed.

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論文審査の結果の要旨及び担当者

氏　名　（ 魏　久焱　）

論文審査担当者		（職）	氏　名
	主 査	准教授	李　艶君
	副 査	教授	桑原　裕司
	副 査	教授	菅原　康弘
	副 査	主任研究員	湊　丈俊　（自然科学研究機構　分子科学研究所）

論文審査の結果の要旨

Surface photocatalysis on noble metal nanocluster-supported metal oxides enhances catalytic efficiency through plasmonic enhancement, improved charge separation, and additional active sites, with applications in environmental remediation and energy conversion. However, despite some experimental and theoretical investigations, a significant amount of research on catalytic reactants remains ongoing, and the catalytic mechanism hasn't been fully understood. Therefore, it is important to clarify the active sites, size effect of Au nanocluster and charge properties on the surface experimentally and theoretically. This doctoral dissertation summarizes the achievements of three research tasks. (1) investigation of the charge state of the steps by simultaneously measuring the topographic, current, and contact potential difference (CPD) images (2) identification of the image modes and clarification of their origin. (3) investigation of the charge state of adsorbed Au nanoclusters on anatase $TiO_2(101)$ surface using atomic force microscopy (AFM) and Kelvin probe force microscopy (KPFM) at 78K with density functional theory (DFT).

Firstly, the steps and their charge state by simultaneously measuring the topographic, current, and CPD images using the multipass method and AFM/KPFM were investigated. The four types of steps on anatase $TiO_2(101)$ surface along different orientations were identified. By multipass method, the charge state of the steps was precisely investigated, and the step B was the strongest charge state was found, which challenged the conventional research. Combining DFT calculation, the new step B model was proposed, in which the under-coordinated Ti atom provides a mid-gap state implying the stronger charge state promoting adsorption and reaction.

Secondly, the image modes with atomic resolution and their origin were clarified on anatase $TiO_2(101)$ surface by AFM and DFT. The image modes were identified as the neutral mode with 90% and the protrusion mode with 10%. By DFT calculation, the stable protrusion mode was found by the Ir-TixOy-H tip apex. The reason was the dipole moments arising from tip-sample charge redistribution led to the protrusion mode using Ir-TixOy-H tip apex.

Finally, the adsorption and charge states of Au nanoclusters on the anatase $TiO_2(101)$ surface were investigated using AFM/KPFM with DFT. It was found Au atoms and nanoclusters preferentially adsorb on steps rather than terraces on the surface. Using 2D CPD mapping with KPFM and DFT calculations, the charge state order of Au on steps was found as step B> step C(=step D)> step A. Au dimers on step B generated a stronger mid-gap state and activate adjacent O atoms were confirmed using DFT calculations. From the DOS of Au on steps, the charge state order of the Au nanocluster on steps was successfully determined as step B> step C(=step D)> step A. This research has identified the charge states of steps and the adsorption characteristics of Au nanoclusters, thereby laying a robust foundation for future studies on photocatalysis on anatase TiO_2 (101) surface.

As mentioned above, this doctoral dissertation is a new study of charge state on anatase $TiO_2(101)$ surface by AFM/KPFM with DFT. This doctoral dissertation is not only fundamental but also application, and contribute to environmental remediation applications, especially in the field of photocatalysis. Therefore, this thesis is recognized as valuable as a doctoral dissertation.