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研究課題名(和文) Fabrication of plasmonic metal nano-structures for photocurrent generation drawing an innovation for design of thin-film solar cells

研究課題名(英文) Fabrication of plasmonic metal nano-structures for photocurrent generation drawing an innovation for design of thin-film solar cells

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研究成果の概要(和文)：本研究では、金属表面上に形成された有機金属ナノアレイの液相成長メカニズムを研究した。ナノスケールの観察を可能にする走査型トンネル顕微鏡へ表面ラマン分光装置を導入することで、ナノレベルの構造情報と化学組成に関する情報を同時に得ることができる。本手法で金表面に吸着した有機配位子二種類を調査したところ、吸着分子および吸着原子で構成される微細な金属-有機骨格構造体は塩化水素の酸性条件下で形成されることを見出した。詳細な分析によるこのナノアレイは配位子分子と塩化物イオンで構成され、水素結合と金原子間に特有の相互作用による三次元構造の自己集合体であることが明らかになった。

研究成果の概要(英文)：Under the proposed research grant, a solution growth mechanism of metal-organic nanostructured arrays formed on the metal surface has been studied. Nano-scale microscopy combined with Raman spectroscopy set-up has been constructed and used to obtain simultaneously information on the nanoscale order structure and chemical composition of the arrays. Two types of organic ligands adsorbed on the gold surface were investigated. It has been found that well-defined metal-organic framework structures composed by ad-molecules and ad-atoms can be formed in the presence of hydrogen chloride. Detail analysis by both the set-up and computational chemistry revealed that the nanostructures are composed of protonated ligand molecules and a surface chloride compound which guides their self-assembly into three dimensional structures via attractive hydrogen bonding and unique interactions between gold atoms.

研究分野：表面化学

キーワード：金属有機構造体 表面分光 プラズモニクス 自己組織化

1. 研究開始当初の背景

(1) It has been proposed that plasmonic effects such as electromagnetic field and scattering enhancement observed in the vicinity of noble metal nanoparticles could provide a new approach to improve light absorption efficiency of thin film solar cells.

(2) The main challenge however has been in the fabrication of long-range ordered nanostructured metal arrays on solid substrates using cost-friendly solution deposition methods.

2. 研究の目的

(1) The general purpose of the research was to investigate surface chemistry leading to the self-assembly of metal-organic nanostructured arrays from solutions and their characterization at the nanoscale.

(2) The specific aim was to construct an experimental set-up allowing for chemical and structural identification of the arrays with nanoscale resolution.

3. 研究の方法

(1) The growth of long-range ordered metal-organic nanostructured arrays was achieved by deposition of organic ligand onto thin film of Au under acidic conditions.

(2) The resultant structures were characterized on the nanoscale using scanning tunneling microscope (STM) that has been combined with the Raman spectroscopy in a so-called tip-enhanced Raman spectroscopy (TERS) set-up. With this set-up information on chemical composition of the arrays and orientation of molecules could simultaneously be obtained.

(3) On a microscopic level the resultant metal-organic nanostructures have been investigated using conventional Raman and secondary-ion mass spectrometry (SIMS).

4. 研究成果

(1) Under this research project a tip-enhanced Raman spectroscopy (TERS) set-up added on a scanning tunneling microscope (STM) was constructed and was used to study first the molecular arrangement of 4,4'-bipyridine (4,4'-BiPy) and 4,4'-bipyridine N,N'-dioxide (4,4'-BiPyO₂) adsorbed on Au(111). Over a

monolayer of 4,4'-BiPy, in the ambient atmosphere, intense TERS signals were present, involving Au-N stretching vibration at 185 cm⁻¹ (Fig. 1(b)). At the early stage of 4,4'-BiPy adsorption, the Au-N stretching signal was not detected. By the aid of the theoretical calculations of the Raman scattering intensities for each vibrational normal mode, a standing-up, tilted orientation at monolayer coverage and a vertical orientation with the longitudinal molecular axis parallel to the surface at low surface coverage was concluded. Adsorption of 4,4'-BiPyO₂ on Au(111) resulted in formation of a (6 × 9) adlattice. Moderately intense TERS signals were observed, containing the N-O stretching modes and the in-plane ring vibrational modes. Neither Au-O nor Au-N stretching modes were observed. 4,4'-BiPyO₂ was laid with the longitudinal axis parallel to the surface, and the molecular plane vertical to the surface. These results demonstrated for the first time that STM-TERS is an effective method for simultaneous imaging and vibrational analysis, facilitating identification of the adsorbed layers with the nanometer-scale spatial resolution and monolayer sensitivity.

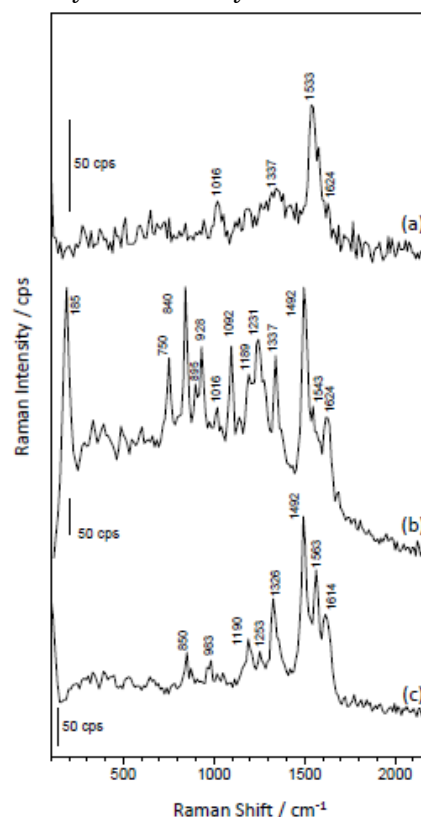


Fig. 1 TERS spectra; (a) after 3 h, and (b) after 3 days immersion into a neutral, 1 mM solution of 4,4'-BiPy (c) after 6 h of immersion time into 1 mM of 4,4'-BiPyO₂.

(2) A growth of a hybrid inorganic-organic layered structure on the Au(111) surface using a one-step solution deposition have been studied. The results showed that the hybrid structure consists of 4,4'-bipyridine [4,4'-BiPyH₂]²⁺ cations, Cl anions and Au adatoms, provided from substrate by means of the adsorbate-induced surface phase transition of a surface reconstruction. STM results revealed a growth of the first [4,4'-BiPyH₂]²⁺ layer on top of the p(3×3)R30° chlorine overlayer formed on the Au(111) surface. These two layers have been found to provide a platform for a following three-dimensional growth facilitated by hydrogen bonding, aurophilic and π-π stacking interactions.

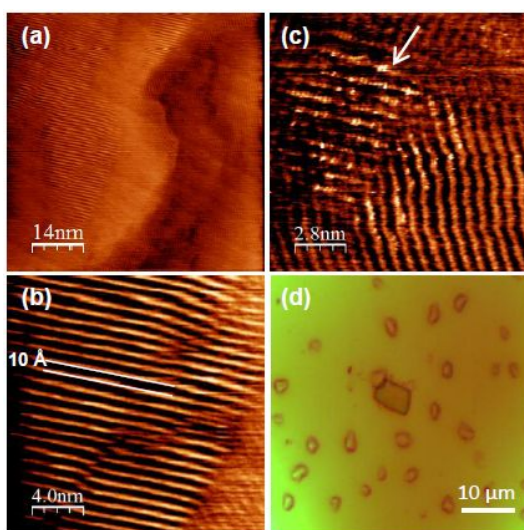


Fig. 2 STM images after prolonged immersion of an Au slide into 1 mM ethanolic solution of 4,4'-BiPy, acidified to pH = 3 with HCl: (a) a 70 × 70 nm image showing a chain structure; (b) a 20 × 20 nm zoomed image of the chain structure; (c) a 14 × 14 nm zoomed image of the chain structure showing development of the next -top layer; (d) a bright-field microscope image of the Au slide showing surface-grown crystals..

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:2 件)

- (1) “Chlorine adlayer-templated growth of a hybrid inorganic-organic layered structure on Au(111)”
I.I. Rzeznicka, H. Horino, K. Yagyu, T. Suzuki, S. Kajimoto, H. Fukumura, Surf. Sci. 2016, in press
<http://dx.doi.org/10.1016/j.susc.2016.03.007>
 (peer review)

- (2) “Tip-enhanced Raman spectroscopy of 4,4'-bipyridine and 4,4'-bipyridine N,N'-dioxide adsorbed on gold thin films”
I. Rzeznicka, H. Horino, A. Morita, N. Kikkawa, S. Sakaguchi, S. Takahashi, T. Komeda, H. Fukumura, T. Yamada, M. Kawai, Surf. Sci. 617, 2013, pp. 1-9,
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 (peer review)

[学会発表] (計:5 件)

- (1) I. Rzeznicka, H. Horino, N. Kikkawa, S. Sakaguchi, A. Morita, S. Takahashi, T. Komeda, H. Fukumura, T. Yamada, M. Kawai,
 The 15th International Conference on Vibrations at Surfaces, San Sebastian, Spain, June 20-26, 2015.
 “Determination of molecular orientation in monolayers adsorbed on metals using STM-based TERS”.
- (2) I. Rzeznicka; Symposium of the Spectroscopical Society of Japan, Division of High Sensitivity Surface and Interface Spectroscopy, Sendai, Japan, March 6th, 2015. “ Raman spectroscopy of surface-grown metal-organic nanostructures”.
- (3) I. Rzeznicka; Tohoku Branch of Chemical Society of Japan, Yonezawa, Japan, September 5-6, 2014.
 “Determination of molecular orientation in monolayers adsorbed on metals using STM-based TERS”.
- (4) I. Rzeznicka, H. Horino, N. Kikkawa, S. Sakaguchi, A. Morita, S. Takahashi, T. Komeda, H. Fukumura, T. Yamada, M. Kawai,
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- (5) I. Rzeznicka, H. Horino, N. Kikkawa, S. Sakaguchi, A. Morita, S. Takahashi, T. Komeda, H. Fukumura, T. Yamada, M. Kawai, The 7th International Symposium on Surface Science, Matsue, Japan, November 2-6, 2014.
 “ Molecular adsorption and orientation of 4,4'-bipyridine and 4,4'-bipyridine N,N'-dioxide in monolayers adsorbed on gold by tip-enhanced Raman spectroscopy”

〔図書〕(計:0件)

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〔その他〕
ホームページ等

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