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研究課題名（和文）水分解反応を目的としたテーラーメイド共役系高分子によるIrO₂の電子状態精密制御研究課題名（英文）Precise tuning of electronic state of IrO₂ by tailor-made conjugated polymer substrate for water electrolysis

研究代表者

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研究成果の概要（和文）：本研究において、研究代表者は酸素発生反応（OER）の効果的な触媒を開発し、高分子支持体の効果やIrO₂ナノ粒子と高分子支持体との配位結合が酸素発生反応の活性と耐久性に及ぼす影響を理解するに至った。これらの結果は極めて有望なものであった。

研究成果の学術的意義や社会的意義

Our methodology will be effective in developing efficient catalyst for green hydrogen production. Further there will be at least 50% of low Ir loading in our catalyst compared to commercial catalyst that enable cost reduction up to 50% with enhanced activity and durability.

研究成果の概要（英文）：we have designed and developed a novel catalyst using the fundamentals of organic-inorganic chemistry using a coordination linkage. In this study we have systematically characterized the material that we developed and understood the effect of polymer substrate along with the effect of coordination linkage between IrO₂ nanoparticles and polymer substrate with coordination linkages. These linkages act as anchoring sites that will reduce the dissolution of diffusion of nanoparticles over several hours of OER reaction effecting the durability. Alongside we have also found that this coordination linkage efficiently changes the electronic structure of the Ir (IV) catalytic centers. From XPS we found that there is a shift in the electron cloud from the polymer to nanoparticles through coordination bonding. This shift of electrons will modulate the bond length of intermediate ions and help in their easy mass transfer resulting in higher activity, low overpotential and very high durability.

研究分野：Materials Chemistry

キーワード：OER Water splitting Polythiophene Iridium oxide Acidic medium

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様式 C-19、F-19-1、Z-19 (共通)

1. 研究開始当初の背景

Current hydrogen production methods include methods by reforming fossil fuels and methods from refining by-product gas from steel mills and soda industry. All of these emit CO₂ during hydrogen production. With the spread of fuel cells for automobiles and homes, the amount of hydrogen supplied is expected to increase, and it is essential to establish a clean hydrogen production method that does not emit CO₂. Attention is being paid to electrochemical water splitting, in which water is split by applying electrical potential to water, and hydrogen is generated at the cathode and oxygen is generated at the anode. Thermodynamically splitting of water into hydrogen and oxygen needs ~1.23 V. But in practical due to internal resistance of several components and complex oxygen electrochemistry it needs higher voltages than theoretical potential. This difference between the experimental potential and theoretical potential is called overpotential. Further, oxygen evolution reaction (OER) is a multi-electron process which thermodynamically and kinetically more demanding. Hence, in order to generate hydrogen more efficiently, it is necessary to increase the kinetics of oxygen evolution OER. IrO₂, one of the only OER catalysts, that has excellent stability under acidic conditions. The key problems associated with IrO₂ catalysts are its cost and high overpotential. In the past, several attempts have been made to tune the catalytic activity, durability and overpotential by changing the morphology and electronic structure. The high surface area nanostructures could achieve decent activity but the overpotential and durability are still at stake. Norskov et al., showed a linear relation between metal oxide d band centre and binding energies to O (intermediates) to the surface (ΔE_0) which play a key role in determining the overpotential of the system. Hence, tuning of electronic structure by doping with other metals like Ru, Ni, Co, Pb, Y, Se, Sn, Sr etc or with fluorine¹ was found to be trending in recent years. But the leaching of alloying metals (durability) and precise tuning of electronic structure are not achieved. Recently our group has come up with a novel strategy of tuning the electronic structure of IrO₂ nanoparticles (nps) by (a) using electrochemically stable carbon and doped carbon substrates (b) very strong metal substrate interaction and (c) changing the electronic structure of IrO₂. By using 10 at% nitrogen doped graphene, overpotential was reduced to 260-270 mV with very high durability. There is always a limit for heteroatom doping using conventional ways. Further very less works on precise tuning of electronic structure and anchoring of IrO₂ nanoparticles to substrate gives a scope of research. The current work deals with the tuning of electronic structure of IrO₂ nanoparticles electronically linked with diimine ligands on the thiophene based polymer substrate and understand its effect on electrochemical OER catalytic activity and durability.

2. 研究の目的

The purpose of the current work is to tune the electronic structure of IrO₂ nanoparticles electronically linked with ligands on the polymer substrate by varying the functional groups and understand its effect on electrochemical OER catalytic activity and durability.

3. 研究の方法

Synthesis of Bisiminoasenaphthenquinone with thiophene structure:

Acenaphthenquinone (1.20 g, 6.6 mmol) and methyl 2-aminothiophene-3-carboxylate (2.23 g, 14.2 mmol) were stirred in acetonitrile overnight in reflux conditions to synthesize the desired product (BIAN-Thiophene). (Yield - 2.64 g, 5.87 mmol, 88%) (Scheme 1).

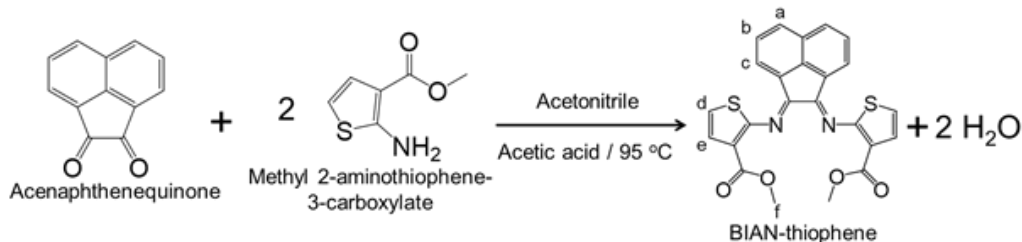
¹H-NMR (DMSO-d₆, 400Hz): δ (ppm) 3.61 (6H, f), 7.72-7.74 (2H, e), 7.80-7.85 (2H, d), 7.88-7.93 (2H, b), 8.07-8.10 (2H, a), 8.38-8.40 (2H, c)

Preparation of vertically aligned Titanium Dioxide Nanotube array (TNT):

The TiO₂ nanotubes array was prepared using a standard anodization method. Fig. 1 shows a diagram of the anodizing method apparatus. The cleaned Ti chip was anodized at a DC voltage of 50 V with constant ultrasonication for 2.5 h in an aqueous ethylene glycol solution containing 0.5 wt.% NN₄F using a platinum as the cathode. After anodizing, Ti chip was washing with methanol and sintered at 300 °C to prepare the TiO₂ as a single phase and eliminate all the organic contaminants.

Production of Polymer/TNT: Polymer / TNT was prepared by electro-polymerization technique. TNT chip was used as the working electrode, Ag/Ag⁺ electrode was employed as a reference, and a platinum chip was used as the counter electrode. Thiophene or

BIAN-Thiophene (0.1 M) was electropolymerized from a solution in acetonitrile with 0.1 M aq HClO₄. The potential was cycled between -2 V and 0 V vs Ag/Ag⁺ at a scan rate of 50 mVs⁻¹. This cycling was carried out 50 times.



Scheme.1 BIAN-Thiophene synthesis

Formation of Ir complex:

Ir complex was formed by immersing BIAN-Thiophene/TNT in a water: methanol (15mL:5mL) mixture containing IrCl₃·nH₂O (0.30 g, 0.05 M) for 2 days.

Preparation of IrO₂/Polymer/TNT:

IrO₂/Polymer/TNT was prepared by hydrothermal synthesis method as follows.

(1) Preparation of reaction Solution and Preprocessing

Hydrothermal synthesis was carried out using a Teflon coated autoclave. 4.5 mL of Ethanol and 0.5 mL of H₂O (9:1 volume ratio) were added to the autoclave using a micropipette. Thereafter, 0.5 mL of H₂IrCl₆·nH₂O solution (3.65 mg/ml) were added. The polymer/TNT was immersed in this solution for 3 hours.

(2) Hydrothermal synthesis

Hydrothermal synthesis was carried out in the atmosphere using an electric furnace at 150 °C for 6 hours in order to decorate IrO₂ on the surface of the TiO₂ nanotube. In total we have prepared 4 different electrodes ① IrO₂ decorated on TNT ② IrO₂ decorated on conventionally polythiophene-TNT composite ③ IrO₂ decorated on poly-BIAN/TNT with complexation ④ IrO₂ decorated on poly-BIAN/TNT without complexation.

Electrochemical characterization: To understand the electrocatalytic activity of catalysts prepared, cyclic voltammetry, linear-sweep voltammetry (LSV) and chronopotentiometry was studied in conventional 3 electrode system. TNT chip with catalyst was used as working electrode, Pt mesh was used as counter and Ag/AgCl (saturated KCl) was used reference electrode and later referenced to reversible hydrogen electrode (RHE). Nitrogen saturated 0.5M H₂SO₄ was used as electrolyte.

4. 研究成果

Characterization of composite electrodes

The morphological, elemental, and electronic states of all the IrO₂ composite electrodes were studied using TEM, scanning transmission electron microscopy equipped with high angle annular dark field detector (STEM-HAADF), X-ray photoelectron spectroscopy (XPS). The particle size, crystallinity of IrO₂ supported by the composite electrodes was observed with a transmission electron microscope (TEM). Elemental mapping was studied using STEM-HAADF characterization. Further, several other characterizations were done to understand the materials like SEM, SEM-EDS, Thermogravimetric analysis etc. Figure 1 shows the HAADF-STEM images of novel IrO₂-BIAN-TNT with complexation as an example.

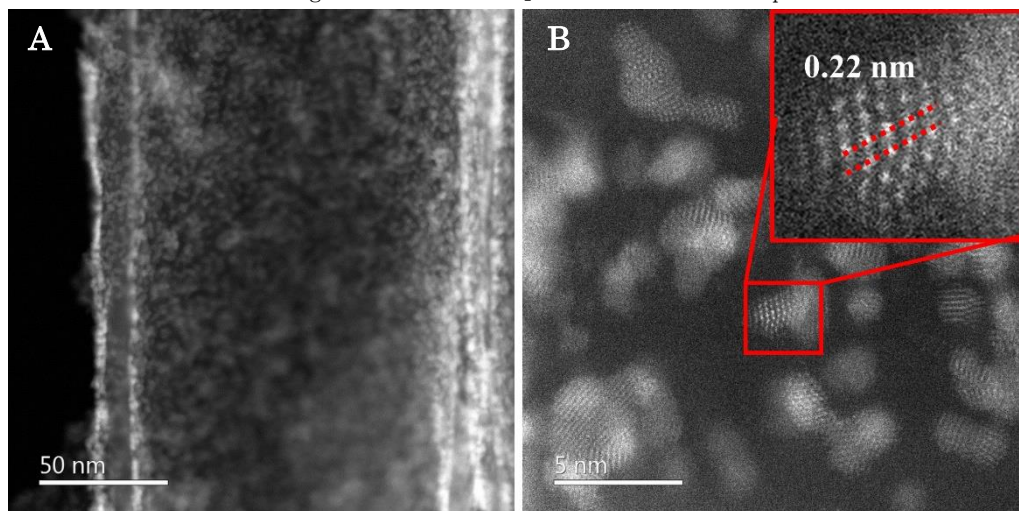


Figure 1: HAADF-STEM images of IrO₂-BIAN-TNT

Fig 1A shows that the entire surface of the TNT was decorated with IrO_2 nanoparticles of <2 nm. We also found that the nanoparticles were found to be both inner and outer surface of the nanotube. Further the Fig 1B and inset shows that the nanoparticles are very crystalline and the lattice spacing was found to be 0.22 nm representing the (020) plane of the IrO_2 rutile structure. Similar features were seen even in other catalysts too. Fig 2 shows the EDS elemental mapping of 3 catalysts showing that IrO_2 nanoparticles were very uniformly distributed all over the substrate. Further in TNT-PTh and TNT-BIAN samples carbon was also uniformly distributed confirming the uniform polymerization over the TNT surface.

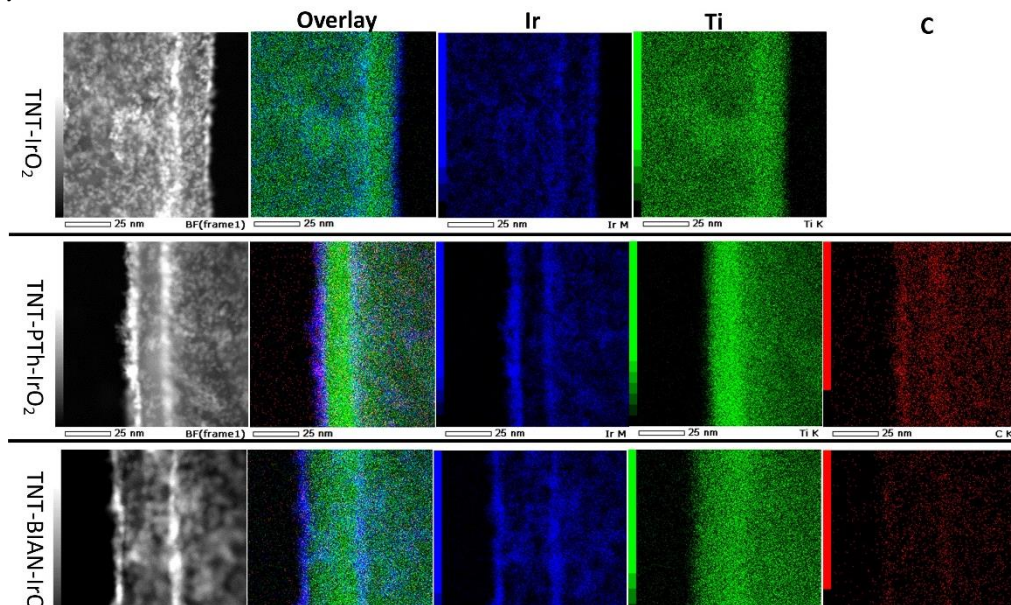


Figure 2: STEM-HAADF and EDS mapping showing uniform elemental distribution of catalysts.

XPS was studied to analyze the effect of complexation and structure of polymer on the electronic structure of IrO_2 nanoparticles. As per the proposal and our novel strategy the effect of complexation using diimine linkages was indeed reflected in our XPS analysis.

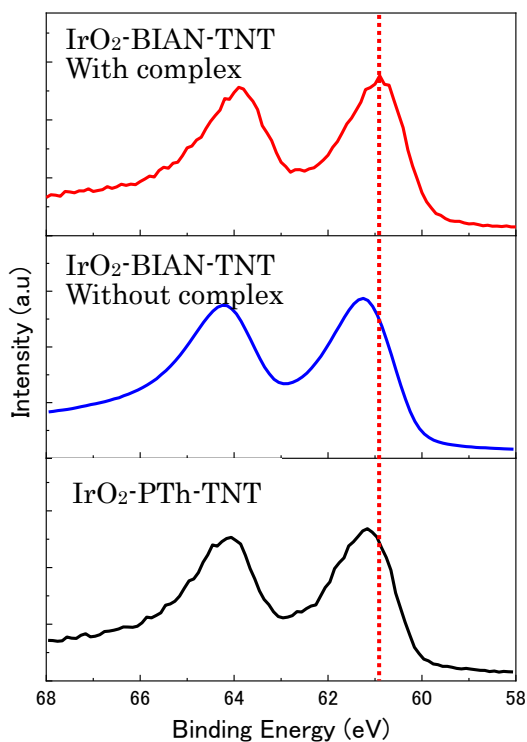


Figure 3: XPS spectra of Ir 4f of IrO_2 -BIAN-TNT with & without complex and IrO_2 -PTh-TNT

Figure 3. Shows the XPS Ir 4f spectra of IrO_2 -BIAN-TNT with complex and without complex along with IrO_2 -PTh-TNT. Of these, binding energy for IrO_2 complexed with BIAN was found to be much lower (60.9 eV) than that of other two materials. This confirms that 1) High electron density was achieved by anchoring Ir nanoparticles with the polymer substrate using α -diimine ligand. 2) Without prior complexation there seems to be very less interaction between polymer substrate and IrO_2 nanoparticles. This shift of electrons will modulate the bond length of intermediate ions and help in their easy mass transfer leading to higher activity & low overpotential.

CV characterization of the materials under study showed conventional IrO_2 profiles. Voltammograms didn't show any redox peaks showing the presence of Ir (III)/(IV) peaks confirming the presence of Ir in the form of +4 oxidation state i.e. as IrO_2 . This clearly confirms that the shift in the binding energy is not due to the presence of other oxidation states of Ir. Further, LSV was performed to understand the catalytic activity, overpotential at 10 mA/cm^2 etc. LSV voltammograms (Figure 4 A) showed that IrO_2 -BIAN-TNT with complex showed highest current density of $\sim 130 \text{ mA/cm}^2$

at 1.8 V vs RHE amongst all the catalyst. This was followed by $\sim 60 \text{ mA/cm}^2$ for IrO₂-PTh-TNT and $\sim 5 \text{ mA/cm}^2$ in the case of IrO₂-TNT. Further, IrO₂ decorated on BIAN-TNT support without complexation did not show any reliable current density. These results show that the use of BIAN-TNT as support and growing IrO₂ nanoparticles show nearly 30 times higher activity than TNT and 2 times higher activity than PTh-TNT as substrates. The overpotential at 10 mA/cm² was found to be 260 mV in the case of IrO₂-BIAN-TNT with complex which is on par with the best of the Ir based catalysts known from the literature. IrO₂-PTh-TNT showed $\sim 300 \text{ mV}$ of overpotential at 10 mA/cm² where as IrO₂-TNT failed to reach 10 mA/cm² even with 600 mV of overpotential. LSV results clearly substantiate our claim of the effect of substrate on electronic structure of IrO₂ catalyst that affects the overall activity.

Further to understand the durability of the catalysts, chronopotentiometry (CP) studies were performed. Here the potential was monitored at the anodic current density of 10 mA/cm² for several hours. Figure 4 B shows the CP curves of IrO₂-BIAN-TNT with complex in comparison with IrO₂-PTh-TNT catalyst. IrO₂-BIAN-TNT with complex needed nearly 1.52 V vs RHE whereas nearly 1.63 V vs RHE was needed in case of IrO₂-PTh-TNT catalyst. Further, the voltage response was very stable in the case of IrO₂-BIAN-TNT with complex whereas in the case of IrO₂-PTh-TNT catalyst was unstable. Due to the unstable behaviour the potential response was increasing after few hours of continuous OER. This shows that the overpotential in the case of novel BIAN based coordinative catalyst with strong anchoring was unchanged whereas the overpotential was continuously increased in the case of its counterpart. The CP experiments are in the process to understand the durability of the novel catalyst for more than 24 h of continuous usage. Further, the effect of long term OER on the morphology and electronic structure of IrO₂ nanoparticles will be studied using TEM, EDS and XPS studies to understand the dissolution of Ir metal into the electrolyte during OER.

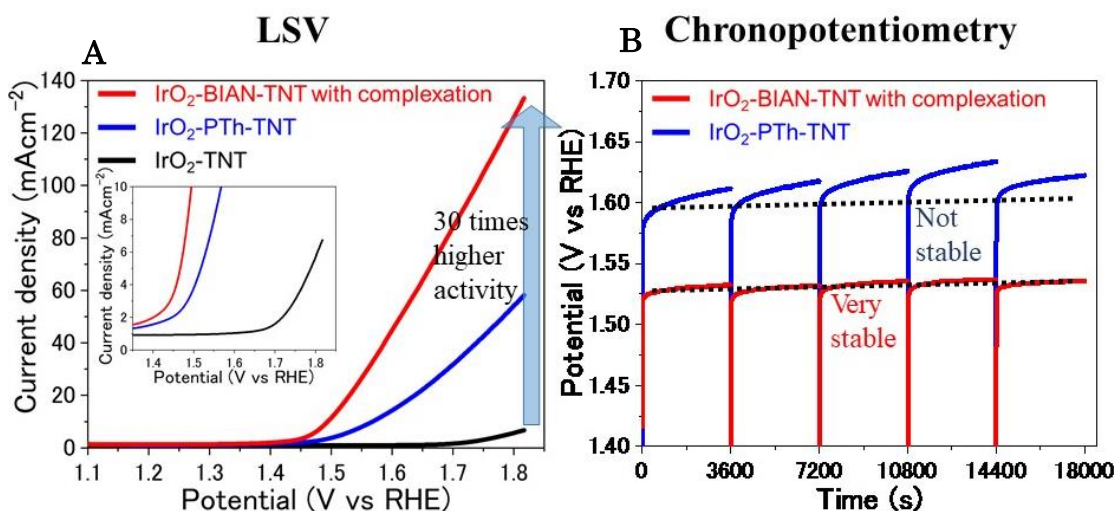


Figure 4: LSV (A) and CP (B) comparison of IrO₂-BIAN-TNT with complex, IrO₂-PTh-TNT, and IrO₂-TNT.

In conclusion we have designed and developed a novel catalyst using the fundamentals of organic-inorganic chemistry using a coordination linkage. In this study we have systematically characterized the material that we developed and understood the effect of polymer substrate along with the effect of coordination linkage between IrO₂ nanoparticles and polymer substrate with diimine coordination linkages. These linkages act as anchoring sites that will reduce the dissolution of diffusion of nanoparticles over several hours of OER reaction effecting the durability. Alongside we have also found that this coordination linkage efficiently changes the electronic structure of the Ir (IV) catalytic centers. From XPS we found that there is a shift in the electron cloud from the polymer to nanoparticles through coordination bonding. This shift of electrons will modulate the bond length of intermediate ions and help in their easy mass transfer resulting in higher activity, low overpotential and very high durability.

5. 主な発表論文等

〔雑誌論文〕 計0件

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1. 発表者名 Yusaku Asai, Rajashekar Badam, Noriyoshi Matsumi
2. 発表標題 IrO ₂ -polymer Composite for Enhanced Oxygen Evolution Reaction
3. 学会等名 JAIST World Conference 2020; International Symposium for Innovative Sustainable Materials (国際学会)
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1. 発表者名 Rajashekar Badam, Yusaku Asai, Agman Gupta, Noriyoshi Matsumi
2. 発表標題 Effect of Functional Substrate on the Electrocatalytic OER Activity of IrO ₂ Nanoparticles
3. 学会等名 JAIST World Conference 2020; International Symposium for Innovative Sustainable Materials (招待講演) (国際学会)
4. 発表年 2020年～2021年

1. 発表者名 浅井優作, バダム ラージャシェーカル, 松見紀佳
2. 発表標題 効率的な触媒の酸素発生を指向した二酸化イリジウム/ポリマーコンポジット
3. 学会等名 第69回 高分子討論会
4. 発表年 2020年～2021年

1. 発表者名 浅井優作, バダム ラージャシェーカル, 松見紀佳
2. 発表標題 二酸化イリジウム/ポリマーコンポジットの設計と酸素発生反応触媒としての検討
3. 学会等名 第10回 CSJ化学フェスタ
4. 発表年 2020年～2021年

1. 発表者名 浅井優作, バダム ラージャシェーカル, 松見紀佳
2. 発表標題 水分解反応を目的とした共役系高分子によるIrO ₂ の電子構造制御
3. 学会等名 日本化学会第101春季年会
4. 発表年 2021年

1. 発表者名 Rajashekar Badam, Yusaku Asai, Agman Gupta, Noriyoshi Matsumi
2. 発表標題 Effect of Functional Substrate on the Electrocatalytic OER Activity of IrO ₂ Nanoparticles
3. 学会等名 239th ECS Meeting (国際学会)
4. 発表年 2021年

1. 発表者名 Rajashekar Badam, Yusaku Asai, Agman Gupta, Noriyoshi Matsumi
2. 発表標題 Effect of Functional Substrate on the Electrocatalytic Activity of IrO ₂ Nanoparticles for Water Electrolysis
3. 学会等名 Advanced Functional Materials and Devices (AFMD-2021) (招待講演) (国際学会)
4. 発表年 2021年

1. 発表者名 Rajashekar Badam, Yusaku Asai, Agman Gupta, Noriyoshi Matsumi
2. 発表標題 Effect of Functional Substrate on the Electrocatalytic OER Activity of IrO ₂ Nanoparticles
3. 学会等名 India - Japan Web-Symposium on Innovations in Science & Technology for New Issues and Challenges (招待講演) (国際学会)
4. 発表年 2020年 ~ 2021年

〔図書〕 計0件

〔産業財産権〕

〔その他〕

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6. 研究組織

	氏名 (ローマ字氏名) (研究者番号)	所属研究機関・部局・職 (機関番号)	備考
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7. 科研費を使用して開催した国際研究集会

〔国際研究集会〕 計0件

8. 本研究に関連して実施した国際共同研究の実施状況

共同研究相手国	相手方研究機関
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