様　式　Ｃ－１９、Ｆ－１９－１、Ｚ－１９　（共通）

科学研究費助成事業　　研究成果報告書

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研究課題名（和文）Developing efficient inexpensive catalysts for solar driven carbon dioxide-to-fuels conversion towards artificial photosynthesis

研究課題名（英文）Developing efficient inexpensive catalysts for solar driven carbon dioxide-to-fuels conversion towards artificial photosynthesis

研究代表者
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交付決定額（研究期間全体）：（直接経費）　　2,300,000円

研究成果の概要（和文）：Here we developed several cheap iron non-porphyrin complexes, an Fe(bpb) that showed high activity for CO2 reduction with 93% CO faradaic efficiency at a moderate overpotential η = 0.41 V in homogeneous and heterogeneous media.

研究成果の学術的意義や社会的意義
This work is expected to develop the academic and social society in terms of developing systems for the production of renewable fuel based on storage of solar energy in the form of renewable fuels and is expected to reduce the carbon dioxide atmospheric level to reduce its global warming effect.

研究成果の概要（英文）：The current fossil fuels are unsustainable and cause global warming. So, discovering alternative fuels is indispensable. CH3OH is currently proposed as one of the best new fuels. A key factor for efficient CH3OH production is developing efficient catalysts for CO2-to-CO conversion. Here we developed several cheap iron non-porphyrin complexes, an Fe(bpb) that showed high activity for CO2 reduction with 93% CO faradaic efficiency at a moderate overpotential η = 0.41 V in homogeneous CO2-saturated DMF solutions. Moreover, these catalysts were successfully immobilized on a nitrogen-doped graphene (NG) electrode to achieve efficient and selective CO2-to-CO conversion in neutral aqueous NaHCO3 solutions (pH =7.3), generating 6 mA/cm2 current density with very high TOF values of 1120 s−1 at η= 0.47 V. These values are among the highest reported values achieved by molecular catalysts in aqueous solutions.

研究分野：Chemistry, artificial photosynthesis

キーワード：Carbon dioxide reduction

様　式　C－１９、F－１９－１、Z－１９（共通）

1. **研究開始当初の背景**

The current fossil fuels are unsustainable and cause global warming. So, discovering alternative fuels is indispensable. CH_3OH is currently proposed as one of the best new fuels. One promising approach for production of CH_3OH is artificial photosynthesis. In this system, water oxidation and CO_2-to-CO conversion occur at anode and cathode, respectively based on electric power generation by a solar cell. Finally, CO is converted to a methanol fuel by the well-known Fischer-Tropsch method. For designing an efficient artificial photosynthesis system, however, developing efficient catalysts for water oxidation and for CO_2 to CO conversion are inevitable and need further improvements. Among the reported CO_2 RedCs, iron porphyrin monomers and dimers showed the benchmark activity, selectivity, and stability for CO_2 conversion to CO. However, the use of porphyrin ligands might hinder their global scale utilization at a reasonable cost due to the long preparation steps and the very low synthetic yield of porphyrin ligands. Moreover, the strong color of iron porphyrins hinders their integration to *p*-type semiconductor for fabrication of efficient photocathode.

２．研究の目的

a. Developing efficient inexpensive catalysts for CO_2 reduction.
b. Construction of efficient cathode based on these catalysts working in aqueous media.

３．研究の方法

Several planar iron no porphyrin complexes have been prepared and characterized with the traditional spectroscopic methods and their CO_2 reduction performance were investigated by the electrochemical and analytical techniques.

４．研究成果

a) Several Fe(bpc) complexes have been prepared and investigated for the CO2 reduction in non-aqueous DMF solutions. These complexes showed high activity for CO_2 reduction (**Fig. 1a)** with high, 93% CO faradaic efficiency (**Fig. 1b**) at a moderate overpotential η = 0.41 V in homogeneous CO_2-saturated solutions.

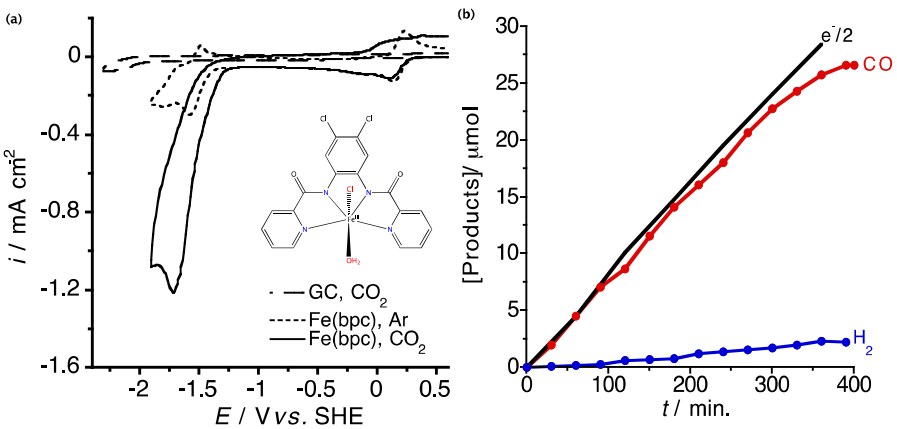

Fig. 1. (a) CVs at 100 mV/s scan rate of Fe(bpc) for CO_2 reduction in DMF solutions. **(b)** products analysis of the catalyst compared to theortical $e^-/2$.

b) These complexes were immobilized on a nitrogen-doped graphene (NG) electrode to achieve efficient and selective CO_2-to-CO conversion in neutral aqueous $NaHCO_3$ solutions (pH =7.3), generating 6 mA/cm^2 current density with very high TOF values of 1120 s^{-1} at η = 0.47 V (Figure 2). These values are among the highest reported values achieved by molecular catalysts in aqueous solutions.

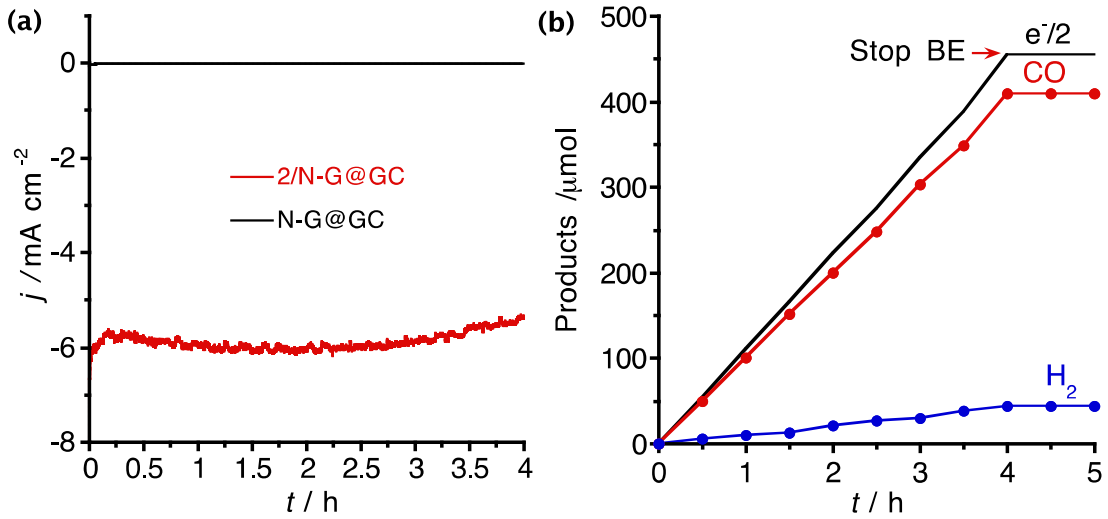

Figure 2. (a) Current density–time profiles in bulk electrolysis at −0.58 V vs. RHE in a CO_2-saturated 0.5 M $NaHCO_3$ solution (pH 7.3) using **2** /N-G@GC (red) and N-G@GC (black). (b) Time courses of the amounts of CO (red), H_2 (blue) evolved and theoretical products (black) calculated from $e^-/2$ of charge required during the bulk electrolysis (BE).

c) We also developed several Ni analogous complexes. When the Fe(bpc) and Ni(bpc) complexes are co-adsorbed on the NG electrode, their performance are much improved, generating 18 mA/cm^2 current density, indicating the cooperative effect of the Fe and Ni centers as that obsereve in the biological systems.

５．主な発表論文等

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２．論文標題 Recent Advances in the Development of Molecular Catalyst‐Based Anodes for Water Oxidation toward Artificial Photosynthesis	５．発行年 2019年
３．雑誌名 ChemSusChem	６．最初と最後の頁 1775-1793
掲載論文のDOI（デジタルオブジェクト識別子） 10.1002/cssc.201802795	査読の有無 有
オープンアクセス オープンアクセスではない、又はオープンアクセスが困難	国際共著 該当する

１．著者名 Chandra Debraj、Li Dong、Sato Tetsuya、Tanahashi Yuki、Togashi Takanari、Ishizaki Manabu、Kurihara Masato、Mohamed Eman A.、Tsubonouchi Yuta、Zahran Zaki N.、Saito Kenji、Yui Tatsuto、Yagi Masayuki	４．巻 7
２．論文標題 Characterization and Mechanism of Efficient Visible-Light-Driven Water Oxidation on an in Situ N2-Intercalated WO3 Nanorod Photoanode	５．発行年 2019年
３．雑誌名 ACS Sustainable Chemistry & Engineering	６．最初と最後の頁 17896～17906
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２．論文標題 Highly Efficient and Selective Electrocatalytic CO2-to-CO Conversion by a Non-heme Iron Complex with an In-Plane N4 Ligand in Heterogeneous Aqueous Media	５．発行年 2020年
３．雑誌名 ACS Applied Energy Materials	６．最初と最後の頁 4114～4120
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2．論文標題 Multi-potential-step chronocoulospectrometry for electrocatalytic water oxidation by a mononuclear ruthenium aquo complex immobilized on a mesoporous ITO electrode	5．発行年 2020年
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1．著者名 Tsubonouchi Yuta、Eo Tatsuya、Honta Junichiro、Sato Taisei、Mohamed Eman A.、Zahran Zaki N.、Saito Kenji、Yui Tatsuto、Yagi Masayuki	4．巻 400
2．論文標題 Molecular aspects, electrochemical properties and water oxidation catalysis on a nanoporous TiO2 electrode anchoring a mononuclear ruthenium(II) aquo complex	5．発行年 2020年
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掲載論文のDOI（デジタルオブジェクト識別子） 10.1016/j.jphotochem.2020.112696	査読の有無 有
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3．学会等名 International Conference on Artificial Photosynthesis-2019（国際学会）
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産業財産権の種類、番号 特許、2019-90888	出願年 2019年	国内・外国の別 国内

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産業財産権の種類、番号 特許、2020-37127	出願年 2020年	国内・外国の別 国内

〔取得〕　計0件

〔その他〕

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６．研究組織

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