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

令和　元 年　 ６ 月 ２５ 日現在

機関番号：３２６８９
研究種目：基盤研究(C)（一般）
研究期間：2016～2018
課題番号：１６Ｋ０５９２２

研究課題名（和文）Photo-electrochemical water-splitting on conducting polymer composite materials

研究課題名（英文）Photo-electrochemical water-splitting on conducting polymer composite materials

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交付決定額（研究期間全体）：（直接経費）　　3,400,000円

研究成果の概要（和文）：Metal-free polythiophene derivatives was developed as high-rate photocatalysts for hydrogen and H2O2 production at high pH; achieved by structure control during a solid state polymerization process.

研究成果の学術的意義や社会的意義
The realization of efficient and practical production of “solar fuels” is crucial for transfer from fossil sources to renewable ones. The discovery that simple organic semiconductors acts as combined light harvesters and highly efficient photocatalysts can guide the research towards practical usage.

研究成果の概要（英文）：Metal-free polythiophene derivatives was developed as high-rate photocatalysts for hydrogen and H2O2 production at high pH; achieved by structure control during a solid state polymerization process.

研究分野：応用化学

キーワード：Water splitting　Conducting polymers　Hydrogen　Electrochemistry

様　式　Ｃ－１９、Ｆ－１９－１、Ｚ－１９、ＣＫ－１９（共通）

１．研究開始当初の背景

The practice, established over more than 100 years, of relying on energy sources that have been built up and stored underground over millions of years has to be changed to a situation where the global energy requirement is produced more or less “in situ”. This change of the energy landscape has already started; the installed wind turbine capacity is accelerating, various solar-energy collecting systems are commercial and ethanol from crops, bio-diesel, etc. are already on the market as alternatives in the transport sector. One limitation is the significant mismatch between the form of energy coming from most of the non-fossil sources – electricity – and that currently the main energy consumption is in form of fuels. In particular, for transportation and industrial purposes it will be virtually impossible to convert to use only electricity.

The conversion of energy from non-fossil sources can either be as a conversion of electricity to fuel or as a direct conversion of e.g. sunlight to hydrogen or an active metal. Thus the ability to effectively convert energy between e.g. an electric and a chemical state or from photons to a chemical state is becoming crucial. The development of efficient (photo-)electrocatalysts is at the core of these technologies and has been the focus of extensive research over many years. Despite these efforts no robust and efficient technology is currently available for the direct light-assisted conversion of solar energy to fuel, e.g. hydrogen.

２．研究の目的

For the transformation towards non-fossil energy sources (solar, wind etc.) there is an urgent need for technologies that can convert these sources into fuels, which currently account for >70% of the global energy consumption, rather than electricity. The current research study proposed to develop robust organic catalysts for electrochemical and photo-electrochemical hydrogen production through water-splitting. At the core of the research has been the use of conjugated polymers and composites thereof as combined light harvesters and catalytic centers.

３．研究の方法

The main research method employed has been to investigate, understand and optimize the photo-electrocatalytic properties of thiophene based compounds. Thereby the project has established an understanding of the fact that these compounds only are electro-catalytic active under light i.e. that not only the reaction rate is depending on light but also the catalytic functionality itself is relying on the molecule being in its excited state. Understanding this concept on the molecular level has allowed for designing more efficient structures. The project has been using both known and new polythiophene derivatives, to further explore, explain and optimize the underlying photo-electrocatalytic events.

４．研究成果

I_2 has successfully been identified as ideal replacement oxidant for polymerization of polyterthiophene (I_2-PTTh) and similar thiophene-containing "ter-mers". The polymerization occurs while the monomers are in the solid (crystalline) state, i.e. below the melting point of the monomers, and this particular property of the polymerization method gives additional possibilities of structural control of the polymer. While illuminated I_2-PTTh reached H_2 evolution rates of 330 mmol h^{-1} g^{-1}, other derivatives achieved up to 600 mmol h^{-1} g^{-1} at 0V vs RHE. This difference in performance (catalytic current density) is believed to be due to a combination of chemical composition and structural differences (i.e. increased surface area and thereby increased number of catalytic sites).

The maximum photo voltage has been found to depend on the position of the HOMO level of the polymer derivatives and for poly(phenyl–1,4 dithiophene) (PDTB) a photo voltage higher than the thermodynamical limit for water-splitting (1.23 V) was obtained, which facilitated complete light-driven water-splitting at pH 12 using MnOx as anode catalyst.

A particular important finding has been that the catalytic activity of all polymers investigated is not following the expected Nernstian dependency of pH, but rather shows an *increase* in onset potential at higher pH, which make them an ideal match for traditional oxygen evolution electrodes like MnOx.

The use of I_2 as oxidant for a "universal" metal-free polymerization platform for thiophene containing "ter-mer" derivatives efficiently focused the research to a limited range of possible derivatives. The incorporation of hydrophilic groups in the polymers, through synthesis of novel ter-monomers, has not resulted in improved performance for the H_2 evolution. This is suggesting that the hydrophobic character of the polymers is not limiting the performance, rather optimization of morphology has been identified crucial for the H_2 evolution, leading to current densities in the mA/cm^2 range.

Two significant additional outcomes of the research activities have been:

I. Some of the poly-thiophene derivatives synthesized are also applicable for the photo(electro)chemical reduction of oxygen to hydrogen peroxide (H_2O_2) both in dark and under illumination; hereby light-driven H_2O_2 production was achieved. H_2O_2 has very recently been shown to have the potential of being an efficient energy carrier ("solar fuel"), highlighting the importance of simple photocatalysts to produce H_2O_2 by the reduction of oxygen.

II. By using blends of different ter-mer derivatives for the I_2 vapour polymerization, well-ordered co-polymers could be obtained as a result of the co-crystal structure of the monomers. This technique opens for synthesizing a range of new ordered conjugated co-polymers. Notably, these co-polymers have catalytic properties similar to their parent polymers.

５．主な発表論文等

〔雑誌論文〕（計 5 件）

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〔学会発表〕（計 1 件）
① Bjorn Winther-Jensen, “Diverse composites of metal-complexes and PEDOT facilitated by vapour assisted complexation near the melting-point of the ligands”. IUPAC 17th International Symposium on Macromolecular Complexes (MMC-17), 28 August 2017 - 31 August 2017.

〔図書〕（計　　件）

〔産業財産権〕
○出願状況（計　　件）

名称：
発明者：
権利者：
種類：
番号：
出願年：
国内外の別：

○取得状況（計　　件）

名称：
発明者：
権利者：
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番号：
取得年：
国内外の別：

〔その他〕
ホームページ等

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