Experimental report

15/02/2021

Proposal: **6-07-26** **Council:** 4/2017

Title: Probing the vibrational and local dynamics of conjugated microporous materials for photocatalysis applications

Research area: Soft condensed matter

This proposal is a resubmission of 6-07-13

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Samples: C16H10(C6H4)8
C16H10(C6H4)8 in H2O:CD3OD:(C2D5)3N
D2O:CD3OD:(C2D5)3N
D2O:CD3OD:(C2H5)3N
C16H10(C6H4)8 in D2O:CD3OD:(C2D5)3N
C16H10(C6H4)8 in D2O:CD3OD:(C2H5)3N
H2O:CD3OD:(C2D5)3N

Instrument	Requested days	Allocated days	From	To
IN6-SHARP	0	4	11/04/2018	16/04/2018
IN1 LAG	5	3	02/07/2018	05/07/2018
IN6	6	0		
IN5	5	0		

Abstract:

Conjugated microporous polymers (CMPs) are a new class of materials within the molecular electronic materials family that are promising for solar energy conversion applications, especially hydrogen production from water through photocatalysis. They are typically used in mixture of water/methanol/triethylamine. CMPs exhibit a 3D polymer backbone network and a complex network of micropores and mesopores. They are of amorphous nature as evidenced by XRay diffraction. Modelling suggests that rings of up to 6 monomers can be formed depending on the building blocks and different vibrational signatures are observed by FTIR. We propose to probe the guest (water)/host (CMPs) dynamics by quasi-elastic neutron scattering and further study the vibrational behaviour of CMPs in the aqueous environment by inelastic neutron scattering in order to resolve possible coupling between host and guest. We are undertaking molecular dynamics simulation on this class of materials and the inelastic neutron scattering measurements will be accompanied by density functional theory calculations.

ACS APPLIED POLYMER MATERIALS

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Impact of Chemical Structure on the Dynamics of Mass Transfer of Water in Conjugated Microporous Polymers: A Neutron Spectroscopy Study

Anne A. Y. Guilbert,* Yang Bai, Catherine M. Aitchison, Reiner Sebastian Sprick, and Mohamed Zbiri*

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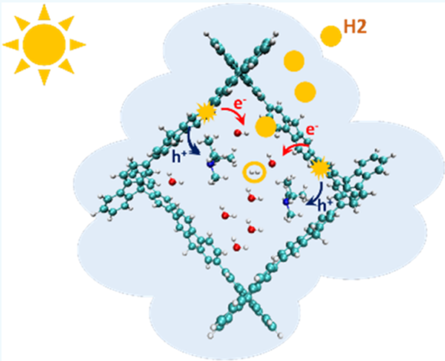

ABSTRACT: Hydrogen fuel can contribute as a masterpiece in conceiving a robust carbon-free economic puzzle if cleaner methods to produce hydrogen become technically efficient and economically viable. Organic photocatalytic materials such as conjugated microporous materials (CMPs) are potential attractive candidates for water splitting as their energy levels and optical band gap as well as porosity are tunable through chemical synthesis. The performances of CMPs depend also on the mass transfer of reactants, intermediates, and products. Here, we study the mass transfer of water (H_2O and D_2O) and of triethylamine, which is used as a hole scavenger for hydrogen evolution, by means of neutron spectroscopy. We find that the stiffness of the nodes of the CMPs is correlated with an increase in trapped water, reflected by motions too slow to be quantified by quasi-elastic neutron scattering (QENS). Our study highlights that the addition of the polar sulfone group results in additional interactions between water and the CMP, as evidenced by inelastic neutron scattering (INS), leading to changes in the translational diffusion of water, as determined from the QENS measurements. No changes in triethylamine motions could be observed within the CMPs from the present investigations.

KEYWORDS: *water diffusion, conjugated microporous polymers, neutron spectroscopy, water splitting, photocatalysis*

■ INTRODUCTION

The need for a renewable energy carrier has resulted in intense research over the last decades on the generation of hydrogen from water via water splitting. Solar energy can be utilized to facilitate the water splitting process using a photocatalyst. Most of the photocatalysts studied are inorganic,[1,2] but, since the first report on carbon nitrides as potential photocatalyst in 2009,[3] organic polymer photocatalysts have also been studied intensively.[4−6] Initially, carbon nitrides[3,7] were the main focus, but in recent years, conjugated microporous polymer networks (CMPs),[8−10] linear conjugated polymers,[11−17] triazine-based frameworks,[18−21] covalent organic frameworks (COFs),[22−24] and molecular compounds[25,26] have also been proposed for sacrificial proton reduction half-reaction. Activities that rival those obtained with inorganic systems have been achieved in some cases.[27−29] The interest in organic photocatalysts arises from the ease of synthesis of polymer photocatalysts via low-temperature routes that allow for precise control over the polymer sequence, hence allowing for tailoring of their functionalities.[5,30]

Over the years, these studies have led to an understanding of the importance of several factors that result in high activity in polymer photocatalysts, such as light absorption,[8,31,32] driving force for proton reduction and scavenger oxidation,[31] exciton separation,[16,33] and crystallinity.[34−36] Due to the hydrophobic nature of most polymeric photocatalyst surface, wetting seems to be particularly important.[37−39] Several studies have shown that the introduction of polar groups results in materials with higher photocatalytic activities.[12,39−41] Large surface area to maximize the exposed surface to water can also be beneficial. Therefore, porous photocatalysts with high Brunauer−Emmett−Teller surface areas (SA_{BET}), namely, COFs and CMPs,[42−44] have been developed for photocatalysis.[10,34,45−47] In a previous paper, we studied CMPs and their linear polymer analogues and found that the porous materials do not always outperform their non-porous analogues.[45]

For porous materials, the interaction between the surface of the photocatalyst and water, which can be tuned by modifying the polarity of the photocatalyst,[34,45] as well as the size of the pores will impact the dynamics of water on the surface and within the material. If the water dynamics is particularly slow in comparison to the kinetics of the photocatalytic reaction, the increased surface area will not improve significantly the overall activity. However, very few studies have explored transport of

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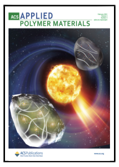

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Article

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Photocatalytic Hydrogen Evolution from Water Using Fluorene and Dibenzothiophene Sulfone-Conjugated Microporous and Linear Polymers

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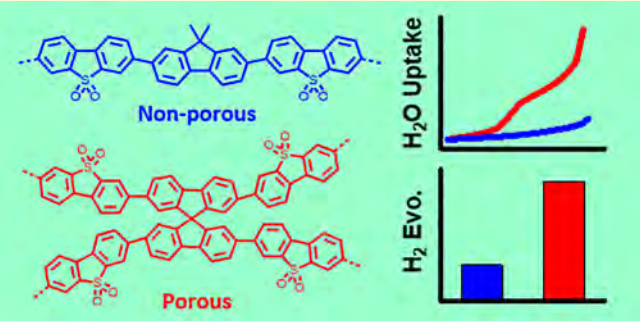
Supporting Information



ABSTRACT: Three series of conjugated microporous polymers (CMPs) were studied as photocatalysts for hydrogen production from water using a sacrificial hole scavenger. In all cases, dibenzo[*b*,*d*]thiophene sulfone polymers outperformed their fluorene analogues. A porous network, S-CMP3, showed the highest hydrogen evolution rates of 6076 μmol h^{-1} g^{-1} ($\lambda > 295$ nm) and 3106 μmol h^{-1} g^{-1} ($\lambda > 420$ nm), with an external quantum efficiency of 13.2% at 420 nm. S-CMP3 outperforms its linear structural analogue, P35, whereas in other cases, nonporous linear polymers are superior to equivalent porous networks. This suggests that microporosity might be beneficial for sacrificial photocatalytic hydrogen evolution, if suitable linkers are used that do not limit charge transport and the material can be wetted by water as studied here by water sorption and quasi-elastic neutron scattering.

INTRODUCTION

The use of hydrogen as an energy carrier has the potential to radically reduce greenhouse gas emissions from hydrocarbon combustion but, at the moment, most hydrogen is produced by methane steam reforming. Photocatalytic water splitting has the potential to produce hydrogen from water with oxygen as the only side product. Inorganic oxide materials such as TiO_2, WO_3, and $SrTiO_3$ have been studied for hydrogen and oxygen production via oxidative or reductive half reactions; based on these half reactions, overall water splitting has been achieved,[1] for example, via Z-schemes[2,3] and heterojunctions.[4] To be scalable, photocatalysts should be based on earth-abundant and nontoxic elements. Recently, organic photocatalysts have become the subject of much research, prompted in large part by a study on carbon nitride published in 2009.[5−8] Other organic material classes such as conjugated polymers,[9−16] conjugated microporous polymers (CMPs),[17−25] covalent triazine-based frameworks (CTFs),[26−34] and covalent organic frameworks[35−39] have also been explored. Copolymerization with a range of comonomers[9,12,40−45] and reducing the size of photocatalyst particles have been found to enhance the activity,[46−48] giving promising results, especially for the hydrogen-evolving half reaction. However, the large structural diversity that is available makes it challenging to formulate simple structure−property relationships.

In particular, we do not yet understand the complex interplay between optical gap, charge mobility, excited state lifetime, and other properties such as particle size, porosity, and surface hydrophilicity. This is compounded by the fact that there are relatively few mechanistic studies for these materials, and it is often unclear whether these polymers act as light absorbers, as catalysts, or as both. Previously, we[12] and others[22−24] have reported nonporous linear polymers with sacrificial hydrogen evolution rates (HERs) that exceed those that we reported for porous CMPs. This suggested that microporosity may not be essential for good photocatalytic activity—or perhaps even that porosity and linkers that are used might introduce limitations, perhaps by reducing charge carrier mobilities. Here, we test this by comparing a range of porous network polymers and nonporous linear polymers based on either fluorene or dibenzo[*b*,*d*]thiophene units copolymerized with one of six different linkers. We investigate

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