A Solution-Processable Polymer Photocatalyst for Hydrogen Evolution from Water

Duncan J. Woods, Reiner Sebastian Sprick, Charlotte L. Smith, Alexander J. Cowan, and Andrew I. Cooper*

Direct photocatalytic water splitting is an attractive strategy for clean energy production, but multicomponent nanostructured systems that mimic natural photosynthesis can be difficult to fabricate because of the insolubility of most photocatalysts. Here, a solution-processable organic polymer is reported that is a good photocatalyst for hydrogen evolution from water, either as a powder or as a thin film, suggesting future applications for soluble conjugated organic polymers in multicomponent photocatalysts for overall water splitting.

The direct production of hydrogen from water using solar energy could be an important technology to meet future energy demands. Sunlight is an abundant energy source that can be stored in dihydrogen molecules, which have a high gravimetric energy density. Semiconductors with an appropriate bandgap are required to harvest solar energy, and to facilitate hydrogen evolution from water. Such materials can either be used as part of photoelectrochemical (PEC) cells[1–3] or as direct photocatalysts in aqueous suspensions.[4] Direct photocatalysis has the advantage of being technologically simple and having a lower projected cost.[5]

A large number of inorganic photocatalysts have been studied for hydrogen evolution.[6–9] By contrast, organic photocatalysts are much less explored, despite possible advantages such as tunable bandgaps, synthetic control over structure, good processability, and preparation from earth-abundant materials.[10,11] The most widely studied organic-derived photocatalysts for hydrogen evolution are the family of materials known as “graphitic carbon nitrides” (g-C₃N₄). Graphitic carbon nitrides were shown to exhibit photocatalytic hydrogen evolution in 2009,[12] and many advances have been made since then.[13,14] After the potential of g-C₃N₄ was first observed, while focusing on the hydrogen evolution half-reaction, interest has begun to shift to achieving overall water splitting using these materials.[15,16] However, the exact structure of most g-C₃N₄ materials is unknown and the synthesis usually involves high temperature processing, which offers limited scope for fine-tuning structure and properties.

Rather few organic photocatalysts have been studied for hydrogen evolution other than g-C₃N₄. Recently, nitrogen-containing poly(azomethine) networks and covalent triazine-based frameworks (CTFs) were shown to have photocatalytic activity with the addition of platinum cocatalysts.[18,19] We have shown that a series of conjugated microporous polymers (CMPs) could facilitate hydrogen evolution from water in the presence of a sacrificial electron donor, without any additional heavy metal cocatalyst.[20,21] Other CMPs have since been studied for photocatalysis[22,23] and recent studies have demonstrated that linear conjugated polymers can have high photocatalytic activities.[24,25] However, as with g-C₃N₄, none of these organic materials are soluble in common organic solvents. This insolvibility makes it more challenging to process these materials into functional composites. Moreover, photocatalysts are typically kept in suspension by stirring to prevent sedimentation, which results in loss of photocatalytic activity.[26] The loss of activity of insoluble catalysts can be prevented with the use of support substrates,[27] however, using solution processability allows the use of simpler supports and easier development of photoelectrodes.

Soluble oligo(phenylene)s have been previously reported as photocatalysts, however, they displayed low activity, were only active under UV light, required a Ru cocatalyst and were only poorly soluble in organic solvents limiting processability.[28] More recently soluble metal-chelating polymers have been prepared although the photocatalytic activity of these polymers also appear to be very low with apparent quantum yields (AQY) below 3 × 10⁻⁶.[29] The solubility of some alkylated conjugated polymers has also facilitated the preparation of polymer nanoparticles (PDots).[30,31] The preparation of these PDots enabled significant enhancements in rate over the pristine polymer although scalability and long-term stability of this approach has yet to be shown.
We report here a well-defined soluble organic polymer that photocatalyzes the evolution of hydrogen from water in the presence of a sacrificial electron donor with no added metal cocatalyst. We demonstrate that despite the low molecular weight of the soluble fraction of the polymer, high rates of hydrogen evolution are maintained relative to the higher molecular weight insoluble fraction. We hypothesize that this solubility could open up a range of opportunities that are not available with insoluble photocatalyst materials, such as the use of solution processing for the scalable preparation of nanocomposites (e.g., an organic hydrogen-evolving polymer film with an embedded inorganic oxygen-evolving catalyst). Also, soluble polymers might be cast as films and used as part of a PEC cell or in an “artificial leaf” architecture.\\(^{12}\)

Alkyl side chains are commonly used to make solution-processable conjugated polymers for organic photovoltaic devices.\\(^{33}\) We selected the insoluble polymer (poly[(9H-carbazole-2,7-diyl)-1,4-phenylene]) (P4) as a starting point because we showed previously that P4 has good photocatalytic activity.\\(^{24}\) Also, the carbazole nitrogen in P4 offers scope for alkylation to produce soluble analogs. Addition of the 2-ethylhexyl side chain yielded the polymer P8 (Figure 1a). We used this side chain because branched alkyl chains give rise to greater solubility enhancements compared to equivalent linear chains.\\(^{33}\)

Polymer P8 was synthesized via Suzuki–Miyaura polycondensation of 1,4-benzenediboronic acid bis(pinacol) ester and 2,7-dibromo-9-(2-ethylhexyl)-9H-carbazole in toluene with Na₂CO₃ (0.2 m), Aliquat 336, and [Pd(PPh₃)₄] in toluene at 80 °C.\\(^{14}\) After 48 h, the reaction mixture was extracted with toluene and the organic products were further purified using Soxhlet extraction in methanol, acetone, and ethyl acetate. The chloroform-soluble fraction of the 2-ethylhexyl-substituted polymer, P8-s, was recovered and reprecipitated into methanol. A higher molecular weight chloroform-insoluble fraction of the polymer, P8-i, was also obtained.\\(^{13}\) All other fractions contained only trace amounts of product and were therefore discarded.

Fourier-transform infrared spectroscopy (FT-IR) demonstrated the presence of the expected alkyl C–H functionalities (2800–3000 cm⁻¹) and absence of any unsubstituted carbazole N–H (3400–3500 cm⁻¹) for both P8-i and P8-s (Figure S2, Supporting Information). In fact, the FT-IR spectra of P8-i and P8-s appear to be essentially identical, suggesting that they have analogous structures and differ only in terms of molecular weight. The solubility of P8-s allowed us to characterize it by ¹H NMR spectroscopy (Figure S4, Supporting Information). This spectrum shows the aliphatic protons of the 2-ethylhexyl side chain (1.4–1.7 ppm) as well as the aromatic signals (7.7–8.1 ppm) in the expected ratio. The molecular weight of P8-s was determined to be Mₙ = 2100 g mol⁻¹ (Mₙ = 1500 g mol⁻¹; D = 1.4) by gel permeation chromatography analysis calibrated against polystyrene standards.

UV–Visible and photoluminescence (PL) spectroscopy were used to probe the optoelectronic properties of these materials. Figure 1c,d shows the UV–vis and PL spectra of P8-s as a powder, as a chloroform solution, and as a cast film. The absorption spectra of the P8-s film and powder are similar,
as expected, with optical gaps of 2.79 eV for the film and 2.71 eV for the powder. However, a significant blue shift is observed for the polymer in solution, probably due to the loss of π–π stacking between chains.[36] The PL spectra for the film (430 nm) and powder (455 nm) are red shifted compared to the solution maximum (407 nm). Powder samples of the insoluble P8-i fraction displayed similar absorption and emission profiles to powdered P8-s (Figures S6 and S7, Supporting Information). Powder X-ray diffraction (PXRD) patterns of P8-s and P8-i both show limited degrees of crystallinity (Figure S16, Supporting Information). Thermogravimetric analysis shows that both P8-s and P8-i were stable up to temperatures of around 300 °C in air (Figure S18, Supporting Information).

The photocatalytic activity of the materials for hydrogen evolution from water in the presence of triethylamine (TEA) as a sacrificial electron donor was studied. In addition, methanol was used in the aqueous mixture to enhance miscibility of TEA with water, and to improve wettability of the hydrophobic polymer.[24] When acetonitrile was used instead of methanol as a cosolvent in the TEA/water mixture, a comparable hydrogen evolution rate was observed (P8-i, Figure S22, Supporting Information). Negligible hydrogen evolution was observed when methanol alone was used as a sacrificial electron donor, and no hydrogen evolution was observed for pure water (P8-i, Figure S23, Supporting Information). P8-i powder evolves hydrogen from the water/methanol/TEA mixture with a rate of 21.5 μmol h⁻¹ (860 μmol g⁻¹ h⁻¹) under λ > 295 nm irradiation, while powdered P8-s produced 13.6 μmol h⁻¹ (544 μmol g⁻¹ h⁻¹) under the same conditions in suspension (see Table 1).

It appears that the introduction of the 2-ethylhexyl side chain in P8-i and P8-s does not affect the hydrogen evolution rate greatly with respect to our previous insoluble polymer;[26] P4 – indeed, the catalytic activity for P8-i is somewhat higher than for P4 under λ > 295 nm irradiation. An analogous polymer, P9, with the longer, unbranched hexadecyl side chain was found to be significantly lower than that of P8 for both soluble and insoluble fractions (Figures S24 and S25, Supporting Information).

Table 1. Summary of solubility in chloroform, hydrogen evolution rates, and optical gap of P8-s and P8-i in comparison to P4 and commercially available g-C3N4[46] and TiO2.

| Photocatalyst | Solubility in CHCl3 | HER(>420 nm) [μmol h⁻¹] | HER(>295 nm) [μmol h⁻¹] | Optical gap [eV] |
|--------------|---------------------|--------------------------|--------------------------|-----------------|
| P4           | Insoluble           | 5.6 (±0.2)               | 13.8 (±0.2)              | 2.72            |
| P8-s         | Soluble             | 1.8 (±0.03)             | 13.6 (±0.2)             | 2.71            |
| P8-i         | Insoluble           | 3.1 (±0.02)             | 21.5 (±0.1)             | 2.77            |
| P9-s         | Soluble             | 0.5 (±0.01)             | 2.0 (±0.05)             | 2.49            |
| P9-i         | Insoluble           | 0.9 (±0.04)             | 3.2 (±0.04)             | 2.94            |
| g-C3N4       | Insoluble           | 2.7 (±0.1)              | 11.2 (±0.6)             | 2.70            |
| TiO2         | Insoluble           | 0.1 (±0.003)            | 37.3 (±1.3)             | 3.13            |

|^Reaction conditions (i) Polymers: 25 mg of photocatalyst (P8-s, P8-i or P4) suspended in water/methanol/TEA solution, irradiated using 300 W Xe lamp for 5 h using the stated band pass filter (no additional Pt added). (ii) 2% g-C3N4 (commercial grade): 25 mg photocatalyst suspended in 10 vol% triethanolamine in water loaded with 3 wt% Pt. (iii) TiO2: 25 mg photocatalyst suspended in water/methanol/TEA solution with photodeposition of 1 wt% Pt; (iv) Calculated from the onset of the absorption spectrum, see the Supporting Information. |

A strong dependency on the illumination wavelength was found for hydrogen evolution experiments of P8-s and the AQY was estimated for P8-s to be 0.56% at λ = 420 nm (Figure S37, Supporting Information). Analysis of palladium content by inductively coupled plasma optical emission spectrometry shows the palladium content of P8-s to be 0.02% compared to 0.50% for P8-i. Residual palladium has been suggested to act as cocatalysts in photocatalytic hydrogen evolution in covalent triazine-based frameworks,[37] and in conjugation with g-C3N4.[38] Low thresholds for the effect of residual palladium on the photocatalytic performance has been reported in conjugated microporous polymers,[39] and for Au loaded onto La-doped NaTaO3.[39] It is unclear whether the amount of residual palladium, difference in molecular weight, crystallinity, hydrophobicity or a combination of all of these factors affect the photocatalytic performance in comparison to P8-i.

Extended hydrogen evolution runs were performed for P8-s under λ > 420 and 295 nm irradiation and using a solar simulator (Figures S27–S29, Supporting Information). After 92.5 h under λ > 295 nm irradiation and with intermittent degassing, P8-s evolved 328 μmol of H2. The polymer showed good stability according to FT-IR, 1H NMR, UV–vis, and PL spectroscopy (Figures S31–S33, Supporting Information).

The soluble and insoluble fractions of P8, P8-s, and P8-i, have slightly different photocatalytic performances. P8-i showed superior performance under irradiation at both λ > 295 nm and λ > 420 nm, possibly because of its higher molecular weight. This is interesting in the context of other recent findings: for example, branched phenyl triazine oligomers were shown to have higher photocatalytic activities than the equivalent extended covalent triazine-based framework (CTF-1).[40] By contrast, increased molecular weights in linear semiconducting polymers have been shown to give higher charge carrier mobilities.[41] The relationship between the degree of polymerization and photocatalytic performance appears, therefore, to be system-dependent. However, the fact that P8-s still evolves hydrogen at a comparable rate to P8-i with such a low molecular weight suggests that only limited effective conjugation lengths are required for photocatalysis.

An advantage of soluble, linear polymers over branched phenyl-triazine oligomers[40] or oligo(phenylene)[42] is that they can form coherent films with reasonable mechanical strength. Initially, we prepared a film of P8-s by drop casting from chloroform solution onto a glass slide. However, when this slide was immersed in the water/methanol/TEA mixture, partial delamination of the film occurred.

This problem was circumvented when P8-s (0.34 mg) was drop cast from chloroform onto mesoporous SnO2. This gave a more stable film with better adherence to the slide. Irradiation of the film immersed in the water-splitting medium (λ > 295 nm...
filter) resulted in the evolution of 0.66 µmol of hydrogen after 5 h (hydrogen evolution rate of 450 µmol g⁻¹ h⁻¹, Figure S30, Supporting Information). The slide was removed and the degassed solution was irradiated once more (λ > 295 nm filter) to determine if any delamination of the polymer had taken place during the irradiation. The rate of hydrogen evolution was reduced by almost a factor of ten, confirming that the polymer film on the slide was chiefly responsible for hydrogen evolution and only a small amount of delamination had occurred. No hydrogen evolution was observed from the uncoated SnO₂ slide under the same irradiation conditions. Clearly, further work is needed to optimize the film preparation and to prepare a completely stable film. Nevertheless, this is the first example, to the best of our knowledge, of direct photocatalytic hydrogen evolution from water using a solution-processed organic polymer film.

Transient absorption (TA) spectroscopic measurements could also be performed on films of P8-s as a result of their minimal scattering. TA spectroscopy can provide useful insight into lifetimes of excited states, quenching, and the role of solvents in the reaction mixture. Figure 2 shows TA spectra of P8-s films on glass following 365 nm excitation. In water, photoinduced absorptions (PIAs) are observed immediately after excitation at 524, 564, 648 nm, with a broad feature at 740 nm also being present on the approximate timescale of the instrument response (∼0.6 ps, Figure 2a). The TA spectral features initially decay rapidly with t₅₀% (∼1 ps to decay by 50%) being ∼2 ps, leaving a small (∼10% of the original) PIA that persists beyond the maximum timescale observable (3.1 ns) in this experiment (Figure 2a,c). Experiments in water and methanol (1:1) (Figure S38, Supporting Information) show similar behavior, with only a slight increase in excited state lifetime (t₅₀% ∼ 4 ps), confirming that the primary role of the methanol is not as sacrificial electron donor. This is in line with the hydrogen evolution experiments, which required TEA to yield significant levels of H₂ (vide supra). In contrast, in the presence of both methanol and TEA (Figure 2b), a more pronounced rapid decay of the initially formed PIAs at 524, 564, and 648 nm occurs. Simultaneously, a long-lived, very broad absorption (t₅₀% ∼ 50 ps, Figure 2c) grows in with a maximum at ∼700 nm with a shoulder at 570 nm (Figure S39, Supporting Information), which persists beyond 3.1 ns (Figure S40, Supporting Information). The long lifetime of this spectral feature in the presence of the sacrificial electron donor, coupled to its dissimilarity to previously reported spectra of positive polarons of related poly(carbazole)s[43] leads us to tentatively assign it to an electron polaron state, formed by the rapid (<2 ps) quenching of the excitonic state in the presence of the sacrificial electron donor, TEA (Figure 2d).

In summary, we have prepared a polymeric conjugated photocatalyst that can be processed in solution to form photocatalytically active thin films. This material also demonstrates good photocatalytic performance and photostability in suspension. TA spectroscopy studies give insights into excited state dynamics and their timescales, allowing for understanding of
the roles played by each component of the system. Furthermore, we have evidence for electron transfer from the amine scavenger onto the photolytically formed exciton state forming an electron polaron state.

Solution processing opens several directions that are more challenging with insoluble catalysts. For example, fabrication of large-scale photocatalytic devices on flexible supports by established printing techniques, e.g., inkjet or roll-to-roll printing.[44] Moreover, the solubility of P8-s should also enable the facile preparation of nanoparticles. Nanoparticles of \( \pi \)-conjugated polymers have generated a great deal of interest in recent years as a result of their excellent fluorescent properties.[45,46] By greatly decreasing the particle size of these soluble materials, we might be able to achieve better optical penetration of light (i.e., reduced scattering) and enhanced hydrogen evolution rates, as has recently been achieved with other soluble polymer photocatalysts.[30] More generally, overall water splitting without any sacrificial hole or electron scavengers may require more than one photocatalyst, and we anticipate that solution processability might open up routes to new composite photocatalysts in the future.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

The authors thank the Engineering and Physical Sciences Research Council (EPSRC) for financial support under Grants EP/N004884/1 and EP/K006851/1. The Laser Loan Pool of the Central Laser Facility (CLF), part of the UK Science and Technology Facilities Council (STFC), is thanked for the loan of equipment through EP/G03088X/1. The authors also thank J. Lee and F. Jäckel for assistance with TA experiments, R. Clowes for performing SEM, Prof. K. Durose for access to the profilometer, and Dr. K. Doherty for performing contact angle measurements.

Conflict of Interest

The authors declare no conflict of interest.

Keywords

conjugated polymers, organic, photocatalysis, soluble, solution processable

Received: February 22, 2017
Revised: June 30, 2017
Published online: September 1, 2017

[1] E. Lanzarini, M. R. Antognazza, M. Biso, A. Ansaldo, L. Laudato, P. Bruno, P. Metrangolo, G. Resnati, D. Ricci, G. Lanzani, J. Phys. Chem. C 2012, 116, 10944.

[2] F. Fumagalli, S. Bellani, M. Schreier, S. Leonardi, H. Comas-Rojas, A. Ghardirzadeh, G. Tullii, A. Savoini, G. Marra, L. Meda, M. Grätzel, G. Lanzani, M. T. Mayer, M. R. Antognazza and F. Di Fonzo, J. Mater. Chem. A 2015, 4, 2178.
[33] J. Mei, Z. Bao, Chem. Mater. 2014, 26, 604.
[34] F. Dierschke, A. C. Grimsdale, K. Müllen, Synthesis 2003, 16, 2470.
[35] B. A. Miller-Chou, J. L. Koenig, Prog. Polym. Sci. 2003, 28, 1223.
[36] A. B. Koren, M. D. Curtis, A. H. Francis, J. W. Kampf, J. Am. Chem. Soc. 2003, 125, 5040.
[37] C. B. Meier, R. S. Sprick, A. Monti, P. Guiglion, J.-S. M. Lee, M. A. Zwijnenburg, A. I. Cooper, Polymer 2017; https://doi.org/10.1016/j.polymer.2017.04.017.
[38] K. Maeda, K. Domen, J. Phys. Chem. Lett. 2010, 1, 2655.
[39] A. Iwase, H. Kato, A. Kudo, Appl. Catal., B 2013, 136–137, 89.
[40] K. Schwinghammer, S. Hug, M. B. Mesch, J. Senker, B. V. Lotsch, Energy Environ. Sci. 2015, 8, 3345.
[41] M. Tong, S. Cho, J. T. Rogers, K. Schmidt, B. B. Y. Hsu, D. Moses, R. C. Coffin, E. J. Kramer, G. C. Bazan, A. J. Heeger, Adv. Funct. Mater. 2010, 20, 1959.
[42] S. Matsuoka, H. Fujii, T. Yamada, C. Pac, A. Ishida, S. Takamuku, M. Kusaba, N. Nakashima, S. Yanagida, J. Phys. Chem. 1991, 95, 5802.
[43] C. Huang, M. M. Sartin, M. Cozzuol, N. Siegel, S. Barlow, J. W. Perry, S. R. Marder, J. Phys. Chem. A 2012, 116, 4305.
[44] R. Søndergaard, M. Hösel, D. Angmo, T. T. Larsen-Olsen, F. C. Krebs, Mater. Today 2012, 15, 36.
[45] C. Wu, C. Szymanski, J. McNeill, Langmuir 2006, 22, 2956.
[46] E. J. Park, T. Erdem, V. Ibrahimova, S. Nizamoglu, H. V. Demir, D. Tuncel, ACS Nano 2011, 5, 2483.