Polymer Semiconductors for Artificial Photosynthesis: Hydrogen Evolution by Mesoporous Graphitic Carbon Nitride with Visible Light

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Due to energy and environmental issues, a key target of modern chemistry is to mimic natural photosynthesis to generate energy storage molecules from water using sunlight, in the simplest case hydrogen. The creation of efficient, simple, and sustainable materials as photocatalysts working with visible light represents a central challenge of the field. Spectacular advances have been made using inorganic nanomaterials.[1] Polymer or supermolecular systems, which would be much closer to nature, have been rarely explored, although they are known from "plastic optoelectronics".[2] The first polymer semiconductor reported to allow hydrogen evolution was poly(p-phenylene), but with ultraviolet light only and rapid decomposition under irradiation.[3]

A polymeric or solid state semiconductor of great potential might be represented by covalent carbon nitrides. They have attracted much attention since the theoretical prediction of their remarkable mechanical and electronic properties of some phases.[4] Carbon nitrides are obviously also "sustainable", as they are composed of carbon and nitrogen only, and melem-based carbon nitrides with various textures can be made from simple liquid precursors or monomers[5] for the price of a typical mass polymer. In the past few years, we analyzed for instance the metal-free catalysis mediated by graphitic carbon nitride (g-C_3N_4), regarded as the most stable phase of C_3N_4 at ambient conditions. Polymeric C_3N_4 can function as metal-free organocatalysts for Friedel–Crafts reactions[5a,6] and the chemical binding and reduction of CO_2.[7] An infinite g-C_3N_4 sheet is calculated to feature an electronic band structure with band edges straddling H_2O redox potentials,[8] and thus it is thermodynamically enabled to photosplit water. Considering the high stability of g-C_3N_4 in aqueous solution, we recently proved that bulk g-C_3N_4 is indeed a new kind of visible-light photocatalyst to split water.[8] However, the quantum yield of the system (0.1% at 420–460 nm) has yet to be improved.

Mesoporous materials are especially attractive as heterogeneous catalysts due to an accessible porous framework with a large surface area but were restricted mostly to inorganic insulators with amorphous/semicrystalline walls[9] which limit their application in optoelectronics. Mesoporous g-C_3N_4 (mpg-C_3N_4) feathers unique semiconductor properties along with an open crystalline pore wall and a large surface area facilitating mass transfer. The structure can in principle enhance the light harvesting ability of the material due to its large surface and multiple scattering effects (see Figure 1A), but one might also expect the photochemical properties to differ from the bulk ones. Indeed, the effect of optimizing nanostructure in dye-sensitized mesoporous TiO_2 solar cell has been

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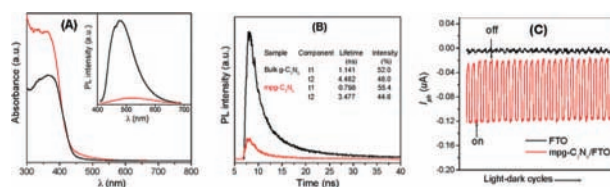§ The University of Tokyo.

Figure 1. (A) Diffuse reflectance absorption spectrum and photoluminescence (PL) spectrum (inset) under 420 nm excitation, and (B) time-resolved PL spectrum monitored at 525 nm under 420 nm excitation at 298 K for bulk g-C_3N_4 (black) and mpg-C_3N_4 (red). (C) Periodic on/off photocurrent I_{ph} response of mpg-C_3N_4 electrode in 0.5 M Na_2SO_4 under zero bias in a standard two electrode photoelectrochemical cell.

found to improve the cell performance by $10^3 – 10^4$ times as compared with a cell based on a bulk TiO_2 electrode.[10] Similarly, we believe that a metal-free mpg-C_3N_4 catalyst, when appropriately modified, holds the greatest promise for visible light photocatalysis. Here, we advance g-C_3N_4 catalysts by generating nanopore structures into the polymeric matrix to improve their structural and electronic functions for solar energy conversion.

First we tested for this new polymer semiconductor the optical and photoelectrochemical properties of g-C_3N_4. Time-resolved PL experiments characterizing the photoinduced charge separation of recombining species (Figure 1B) showed a lifetime of ~5 ns even at 298 K, which provides circumstantial evidence supporting our previous photocatalytic results. The PL signal of mpg-C_3N_4 is greatly suppressed. This is an indication of electron relocation on surface terminal sites, which is believed to promote the catalytic redox functions, e.g., of graphitic structures.[7] Visible light illumination ($\lambda > 420$ nm) of mpg-C_3N_4 layers coated on fluoride-tin oxide (FTO) glass plates revealed a short circuit photocurrent (Figure 1C), which is however still rather low, presumably due to the poor contact between the substrate and the organic powder featuring grain boundaries. A comprehensive study on optimizing electrode-fabrication conditions and electrolyte compositions is currently underway.

A detailed description of our silica-templated self-polymerization route for mpg-C_3N_4 was reported elsewhere.[5b] We optimized the preparation conditions for mpg-C_3N_4 for hydrogen evolution from water under visible light irradiation. Textural characterization results (Figure 2a, Figure S2 and Table 1) show that all mpg-C_3N_4 feature a mesoporous, nanocrystalline structure with a controlled surface area (68–373 m^2/g) and a three-dimensionally (3D) interconnected framework with a semiconductor band gap of 2.7 eV, as estimated from the UV/vis spectrum.

mpg-C_3N_4 is insoluble in aqueous solutions (pH = 0–14), allowing for the wide adjustment of reaction conditions for water
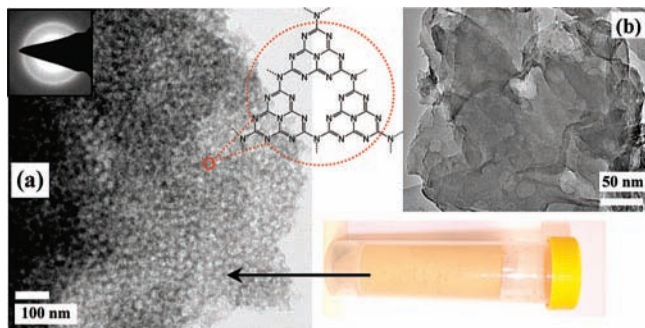
Figure 2. (a) TEM image of mpg-C_3N_4, showing a 3D porous framework constructed from tri(s)triazine units. The stacking distance of 0.332 nm is evident by the intense electron diffraction ring (inset), proving high partial crystallinity of the wall. (b) TEM image of bulk g-C_3N_4.

Table 1. Textural Properties and Photocatalytic Activity of Pt/mpg-C_3N_4 for the Hydrogen Evolution Reaction with Visible Light[a]

entry	catalyst	surface area (m^2/g)	H_2 evolution rate (μmol/h)	TOF[b] $\times$ 100 (h^{-1})
1	mpg-$C_3N_{4/0.2}$	67	149	27
2	mpg-$C_3N_{4/0.5}$	126	142	26
3	mpg-$C_3N_{4/1.0}$	235	124	23
4	mpg-$C_3N_{4/1.5}$	373	69	13
5	g-C_3N_4	8	18	3
6[c]	g-C_3N_4	10	19	3

[a] For reaction conditions, see Supporting Information. [b] Turnover frequency: n (H_2) per n (melem units) per hour. [c] Subjected to the same NH_4HF_2 treatment as for the synthesis of mpg-C_3N_4.

splitting reaction. Photocatalytic results showed that 0.2 μmol/h of hydrogen gas could be generated without any modification in the presence of triethanolamine as a sacrificial reagent (Figure S4); however, the activity was improved by a factor of ~750 after adding a small amount (3 wt. %) of Pt cocatalyst promoting charge transfer[11] and creating hydrogen desorption sites (data in Table 1).

Indeed, mpg-C_3N_4 samples show a remarkable improvement in H_2 evolution activity over bulk g-C_3N_4. As a reference, bulk g-C_3N_4 treated with NH_4HF_2 (which was used for removing SiO_2 from mpg-C_3N_4) was used under the same conditions and was found to be by a factor of 8 less active. It is however not that the activity simply increases with the surface area, as an excess of surface area (373m^2/g) appears to be detrimental, presumably due to the change of semiconductor properties and the increase of defects with the wall thickness shrinking to the lower nanorange. Further variations of the recipe let us additionally identify an optimal condensation temperature of 823 K, making less condensed, polymeric C_3N_4 the most active species (Table S1).

A 25 h experiment with intermittent evacuation every 5 h under visible light (>420 nm) was performed to examine the stability of the polymeric catalyst (Figure 3, inset). The system produced a total amount of 3.5 mmol of hydrogen gas (78.4 mL) during the course of the 25 h irradiation without noticeable catalyst deactivation. No N_2 evolution was observed, indicating the strong binding of N within the covalent structure, even in the mesoporous environment. The turnover number in terms of total amount of H_2 gas evolved to catalyst exceeded 6.5 after 25 h of reaction, indicating that the reaction indeed proceeds catalytically. No reaction occurred when the system was illuminated in the absence of mpg-C_3N_4. To confirm that the reaction is indeed driven by light absorption on the catalyst, wavelength dependence of the photocatalytic H_2 evolution by mpg-C_3N_4 was examined using different long pass optical filters. As depicted in Figure 3, the H_2 evolution
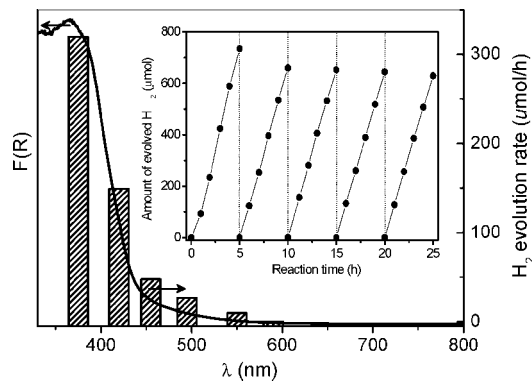

Figure 3. Wavelength dependence of H_2 evolution rate on Pt/mpg-C_3N_4. The inset is the stability test for Pt/mpg-C_3N_4 under visible light irradiation (>420 nm). For reaction conditions, see Supporting Information.

rates agree well with the diffuse reflectance spectra. Activity being proportional to absorption indeed was found up to the 590 nm wavelength, which makes us very positive about potential sensitization experiments to increase the absorbance of the material. Photochemical activity of up to 590 nm would indeed cover the main peak of the solar spectrum on the Earth's surface.

In summary, we have shown the semiconductor characteristics for g-C_3N_4 and that the efficiency of hydrogen production from the photochemical reduction of water can be improved by ~1 order of magnitude via introducing mesoporosity into polymeric C_3N_4. We anticipate a wide rang of potential applications of g-C_3N_4 as energy transducers for artificial photosynthesis in general, especially with a 3D continuous nanoarchitecture. Moreover, the results of finding photoactivity for carbon nitrides can enrich the discussion on prebiotic chemistry of the Earth, where HCN polymeric clusters have long been considered as the most-readily formed and most stable organic macromolecules.[12]

Supporting Information Available: Experimental details and more characterization and reaction results. This material is available free of charge via the Internet at http://pubs.acs.org.

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