A metal-free polymeric photocatalyst for hydrogen production from water under visible light

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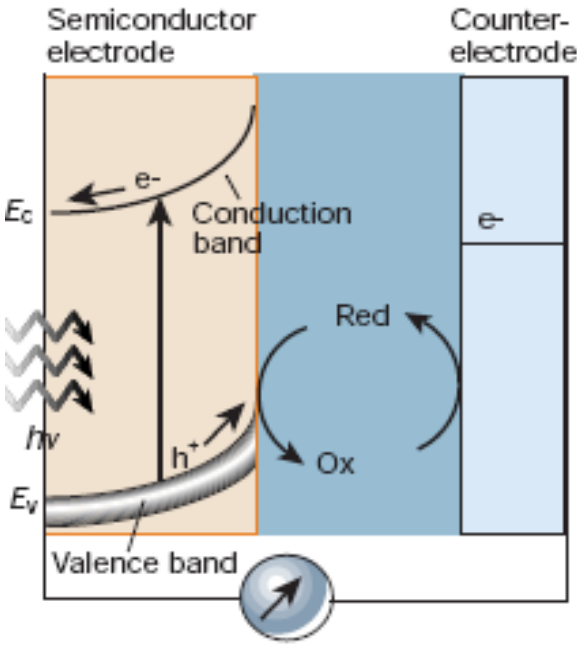
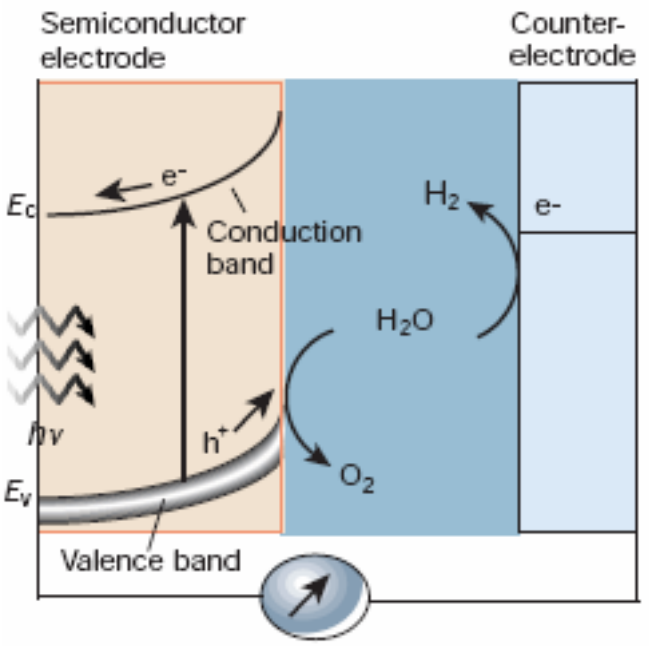
Introduction to Photoelectrochemical Cells

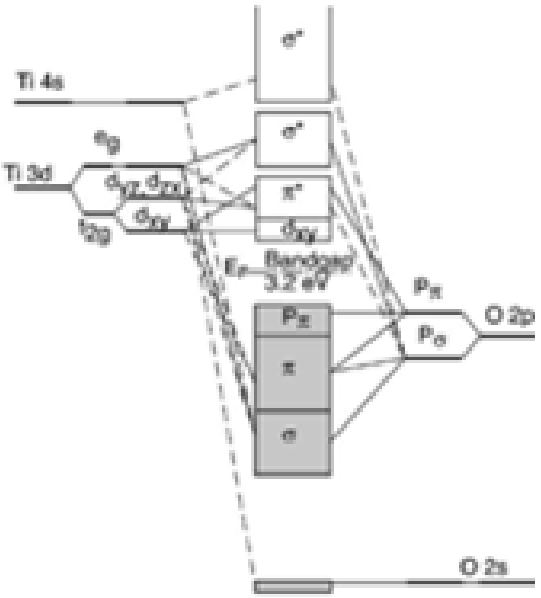
- **Photoelectrochemical cells are solar cells which generate electrical energy from light, including visible light. Each cell consists of a semiconducting photoanode and a metal cathode immersed in an electrolyte.**



Regenerative cells



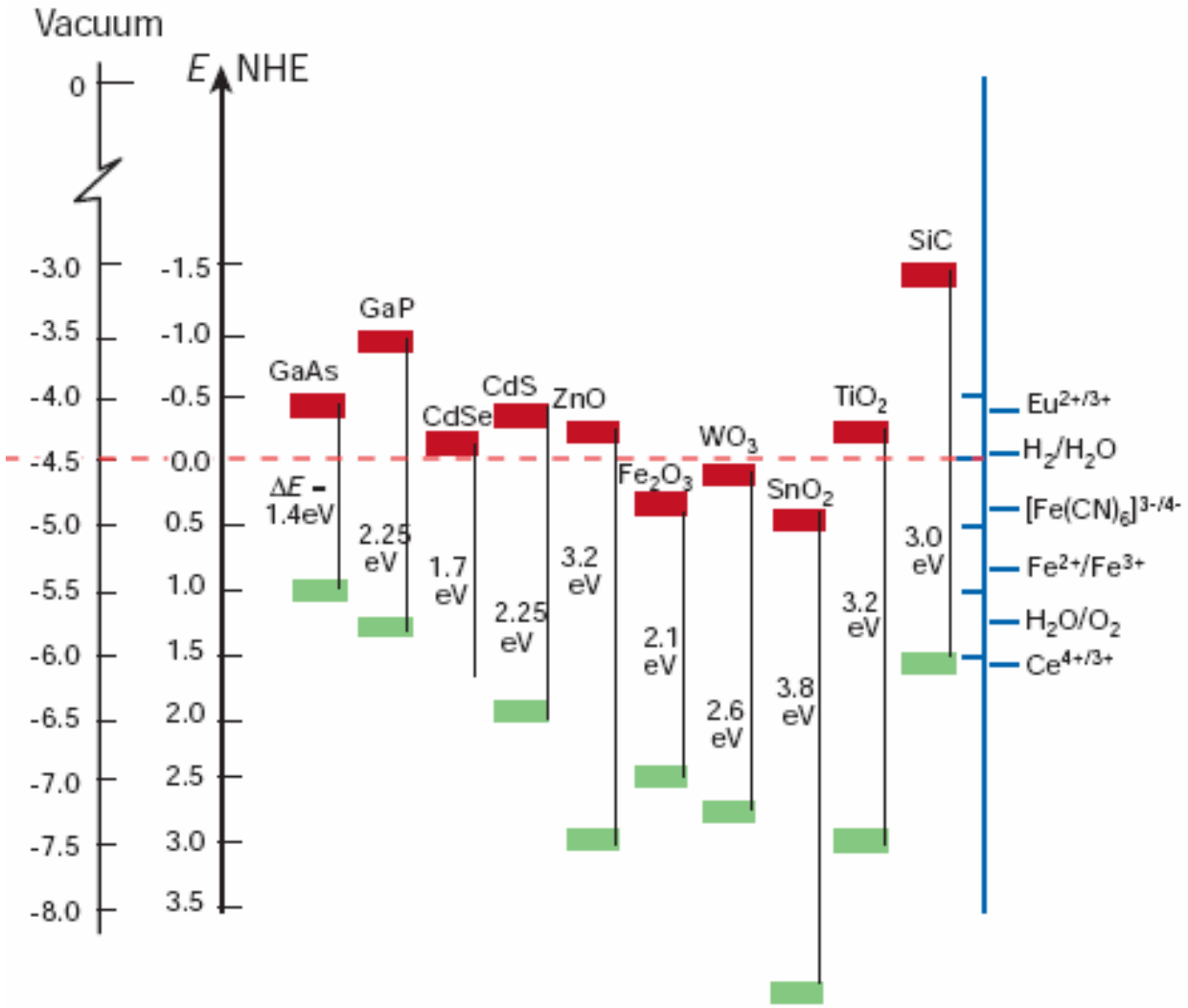
Photosynthetic cells



MO diagram for TiO_2 (Anatase)

M. Gratzel, Photoelectrochemical Cells, Nature, 2001, 414, 338
http://students.chem.tue.nl/ifp20/pages/Chapter 5/ch5par1.html

Introduction to Photoelectrochemical Cells



Band positions of several semiconductors in contact with aqueous electrolyte at pH 1

M. Gratzel, Photoelectrochemical Cells, Nature, 2001, 414, 338

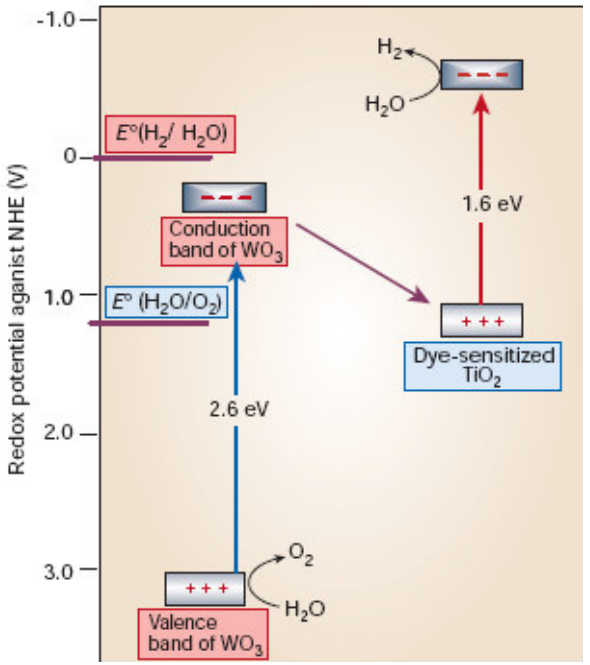
Important features of Photoelectrochemical Cells

- Stability against photo-corrosion: Wider band gap implies higher stability
- Separating optical absorption and charge-generating functions: Inter-penetrating and individually continuous network
- Large absorption cross-section and wavelength window promotes absorption of larger % of incident light
- Use of nanostructured materials: Prevention of depletion layer, minimal junction voltage drop, increased chemisorption surface area
- Following Z-scheme for complementary absorption of solar spectrum

Table 1 Performance of photovoltaic and photoelectrochemical solar cells

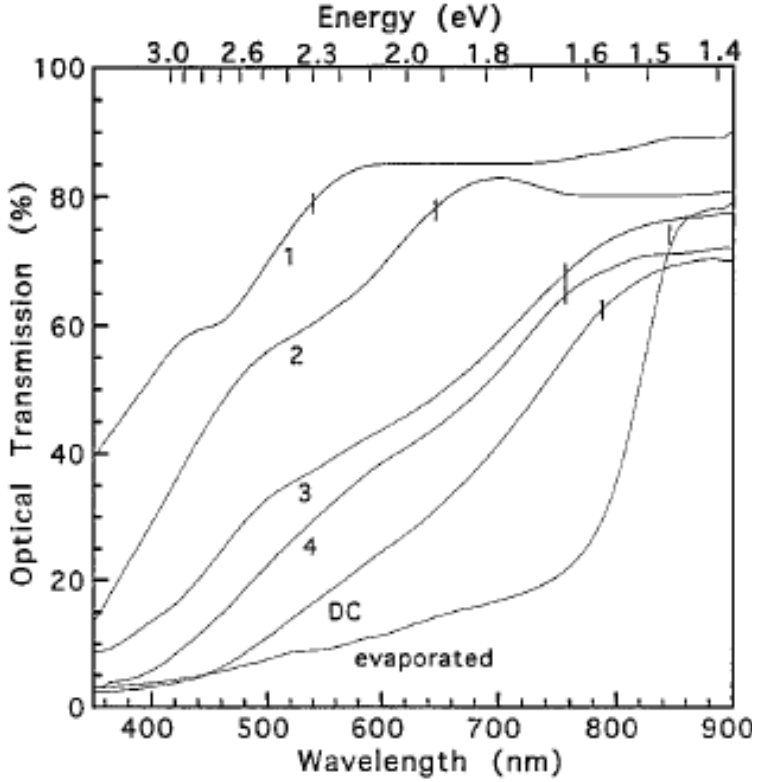
Type of cell	Efficiency (%)* Cell	Module	Research and technology needs
Crystalline silicon	24	10–15	Higher production yields, lowering of cost and energy content
Multicrystalline silicon	18	9–12	Lower manufacturing cost and complexity
Amorphous silicon	13	7	Lower production costs, increase production volume and stability
$CuInSe_2$	19	12	Replace indium (too expensive and limited supply), replace CdS window layer, scale up production
Dye-sensitized nanostructured materials	10–11	7	Improve efficiency and high-temperature stability, scale up production
Bipolar AlGaAs/Si photoelectrochemical cells	19–20	—	Reduce materials cost, scale up
Organic solar cells	2–3	—	Improve stability and efficiency

*Efficiency defined as conversion efficiency from solar to electrical power.



Relevance to our work: Size-quantization effects

Size-quantization effect: Chemistry of nanomaterials increasingly becomes chemistry of electrons/atoms/molecules. This brings new dimension to the chemical properties of relevance.



1: 4 nm, E_g = 2.3 eV

2: 5 nm, E_g = 1.92 eV

3: 6.5 nm, E_g = 1.64 eV

4: 7 nm, E_g = 1.64 eV

Optical transmission spectra (corrected for specular reflectance) of the four films from Figure 1, a constant potential (dc)-plated film (ca. 100 nm thick) and an evaporated CdTe film (ca. 200 nm thick; nonquantized as a comparison). Estimated values of E_g are shown.

Size Quantization in Electrodeposited CdTe Nanocrystalline Films, Y. Mastai, G. Hodes, J. Phys. Chem. B 1997, 101, 2685

Commercial activity in photoelectrochemical cells

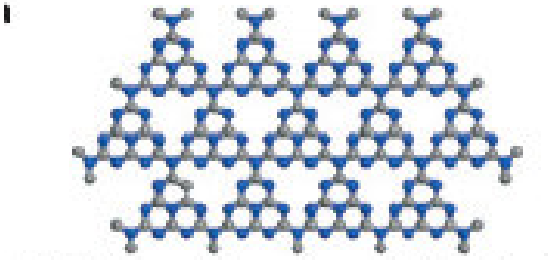
Early "Google" age for alternative energy sources

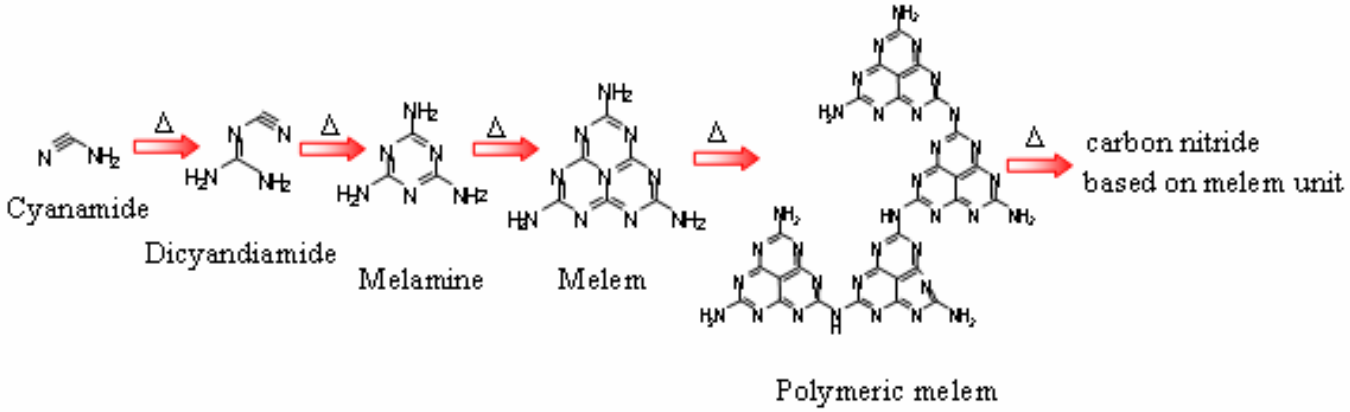
- **FirstSolar Inc.:** Commercialized solar cells based on CdTe
- **Solyndra Inc., Würth Solar AG, NanoSolar Inc., Heliovolt Inc.:** Commercialized thin film solar cells based on copper-indium-gallium selenide
- **SunPower Inc., Q-Cells Inc., Evergreen Solar Inc., SpectraWatt Inc., Bharat Electronics Ltd, BHEL, Moser Baer PV:** Commercialized silicon photovoltaic cell
- **Konarka Technologies Inc.:** Polymer-based, organic photovoltaic cells

Empty space left for new and innovative companies who can get in this market

Preparation of polymeric carbon nitride

- Carbon nitride is a promising candidate to complement carbon in the materials applications.
- At ambient conditions a graphitic-C_3N_4 allotrope (g-C_3N_4) is the most stable form.
- The first synthesis of a polymeric carbon nitride, melon, was reported by Berzelius and Liebig in 1834



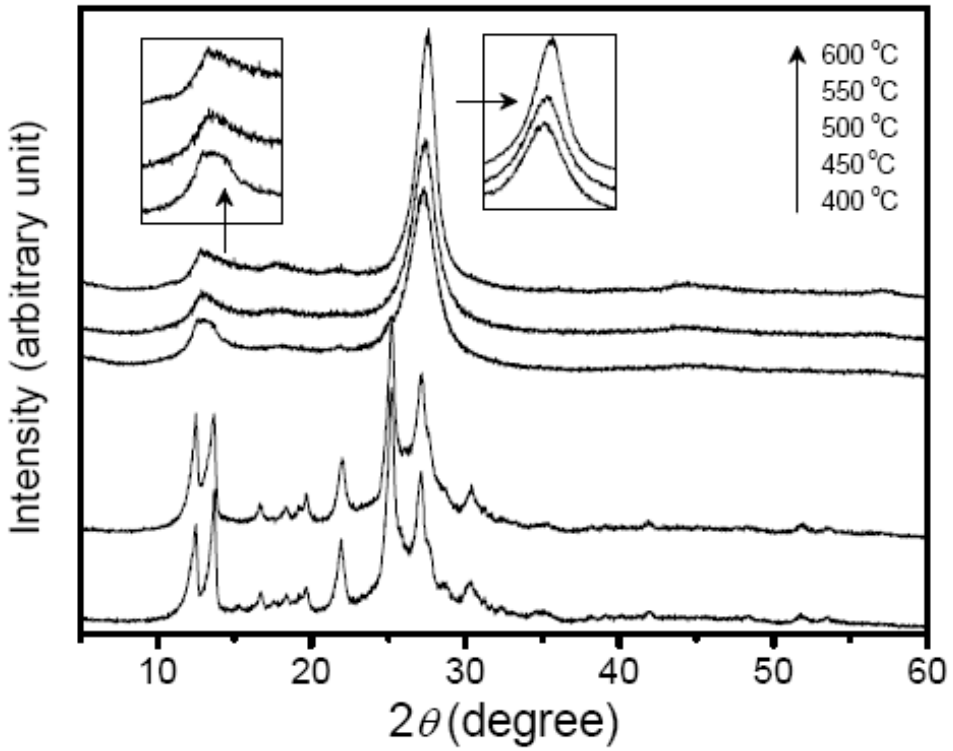


Temp	Process
47 ˚C	Cyanamide (MP)
137 ˚C	Dicyanamide formation
203 ˚C	Dicyanamide (MP)
234 ˚C	Melamine formation
335 ˚C	Melamine (SP)
389 ˚C	Polymeric melem formation
525 ˚C	Carbon nitride network

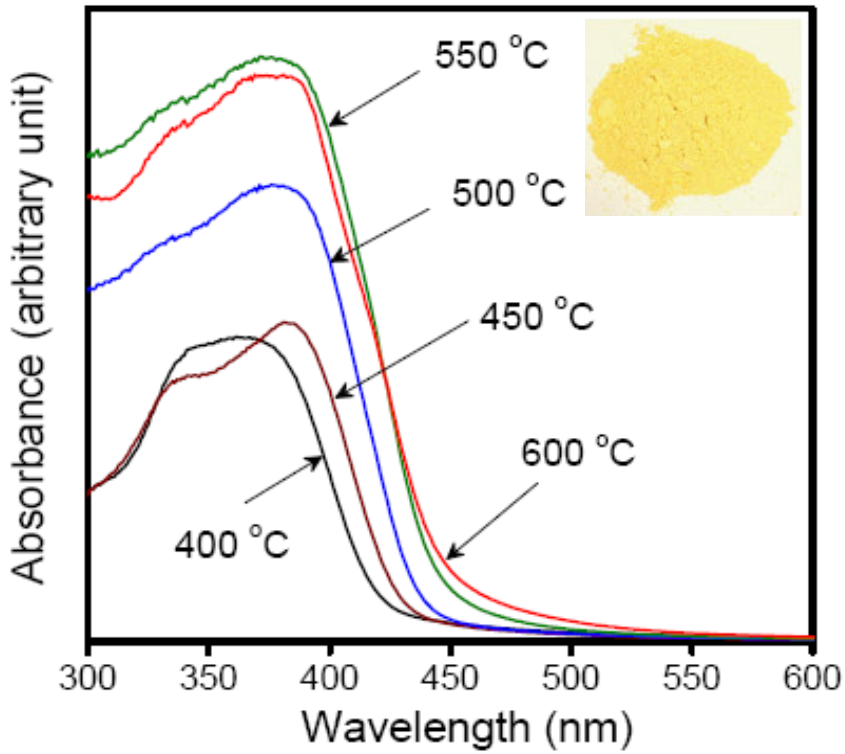
Chemical Synthesis of Mesoporous Carbon Nitrides Using Hard Templates and Their Use as a Metal-Free Catalyst for Friedel–Crafts Reaction of Benzene, F. Goettmann et. al., Angew. Chemie. Int. Ed., 2006, 45, 4467

Synthesis of g-C3N4 nanoparticles in mesoporous silica host matrices, M. Groenewolt et. al., Adv. Mater., 2005, 17, 1789

Characterization of polymeric carbon nitride

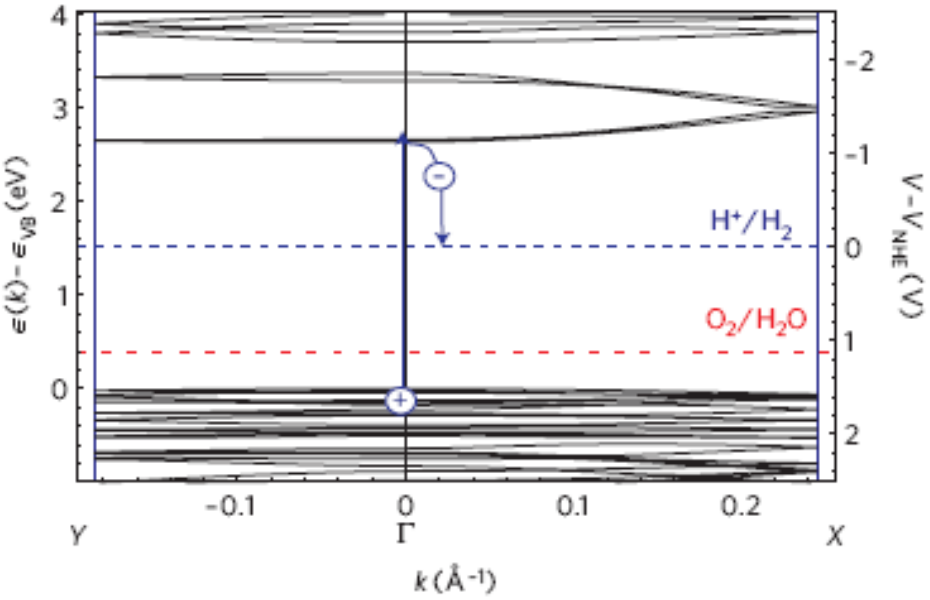


XRD patterns of carbon nitrides synthesized at different temperature.

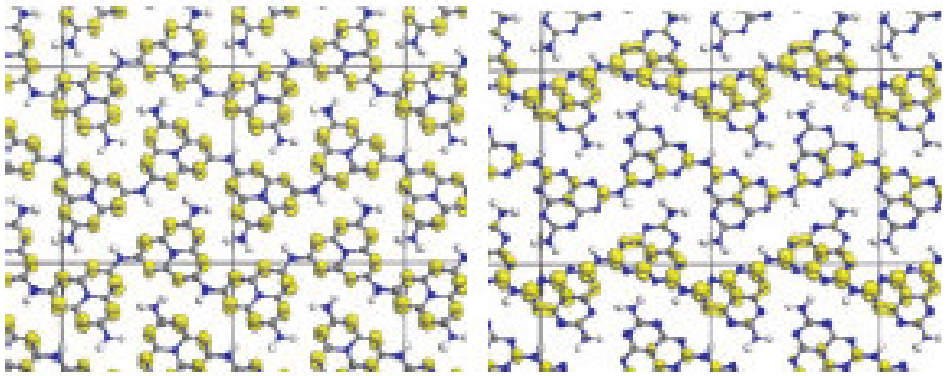


UV diffuse reflectance spectrum of carbon nitrides prepared at different temperature.

Explanation of the structure and band gap

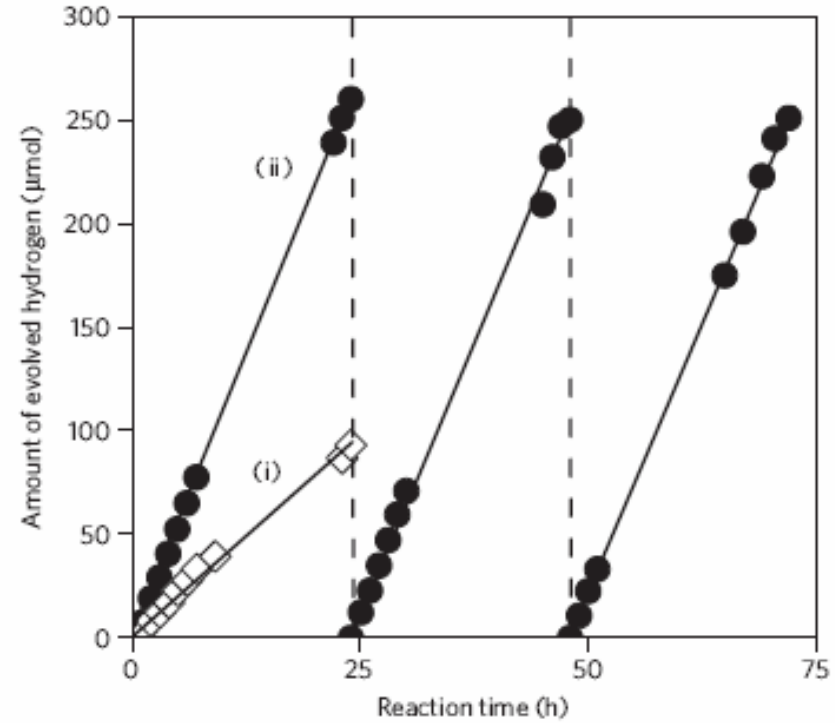


Density-functional-theory band structure for polymeric melon calculated along the chain (0–X direction) and perpendicular to the chain (Y–0 direction).

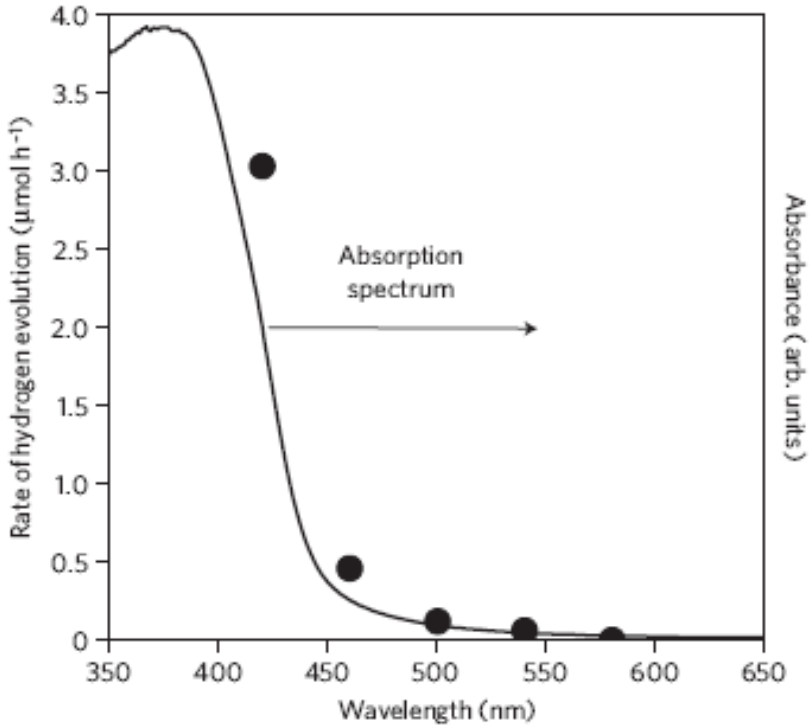


The Kohn–Sham orbitals for the valence band of polymeric melon. The corresponding conduction band. The carbon atoms are grey, nitrogen atoms are blue and the hydrogen atoms are white. The isodensity surfaces are drawn for a charge density of 0:01qe Å3.

Demonstration of photocatalytic property

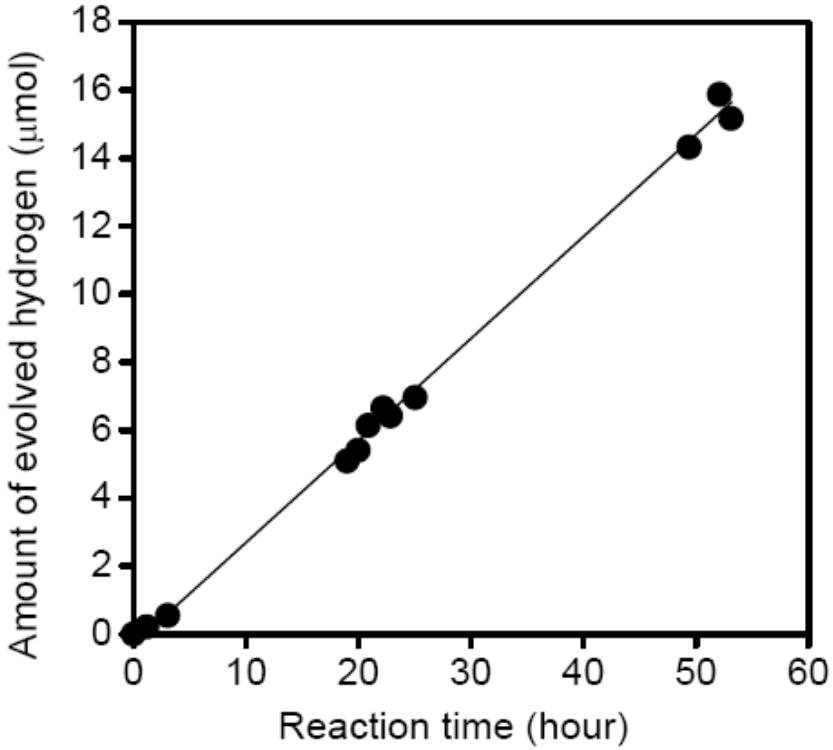


Stable hydrogen evolution from water by g-C_3N_4. A typical time course of H2 production from water containing 10 vol% triethanolamine as an electron donor under visible light (of wavelength longer than 420 nm) by (i) unmodified g-C_3N_4 and (ii) 3.0 wt% Pt-deposited g-C_3N_4 photocatalyst. The reaction was continued for 72 h, with evacuation every 24 h (dashed line).

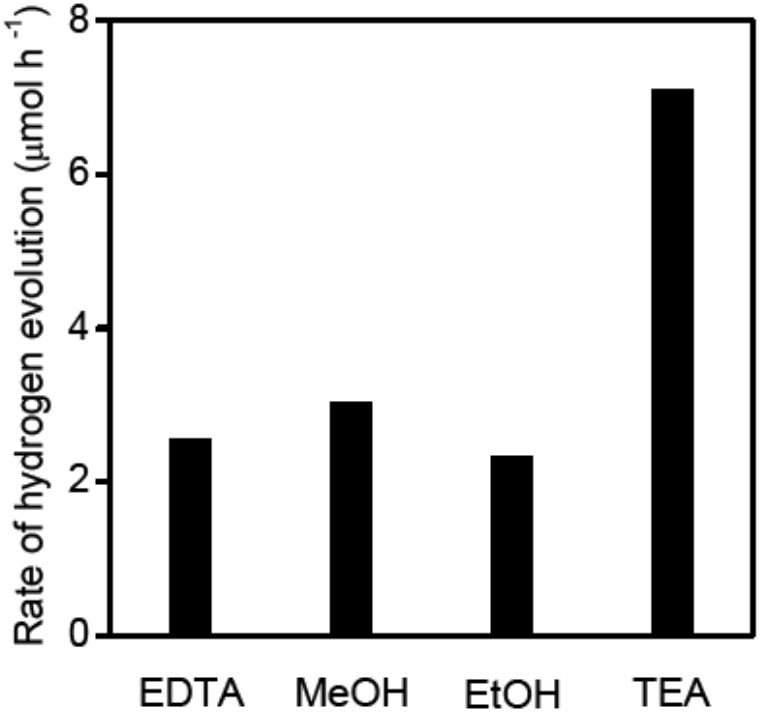


Wavelength-dependent hydrogen evolution from water by g-C_3N_4. Steady rate of H_2 production from water containing 10 vol% methanol as an electron donor by 0.5 wt% Pt-deposited g-C_3N_4 photocatalyst as a function of wavelength of the incident light. Ultraviolet–visible absorption spectrum of the g-C_3N_4 catalyst is also shown for comparison.

Demonstration of photocatalytic property

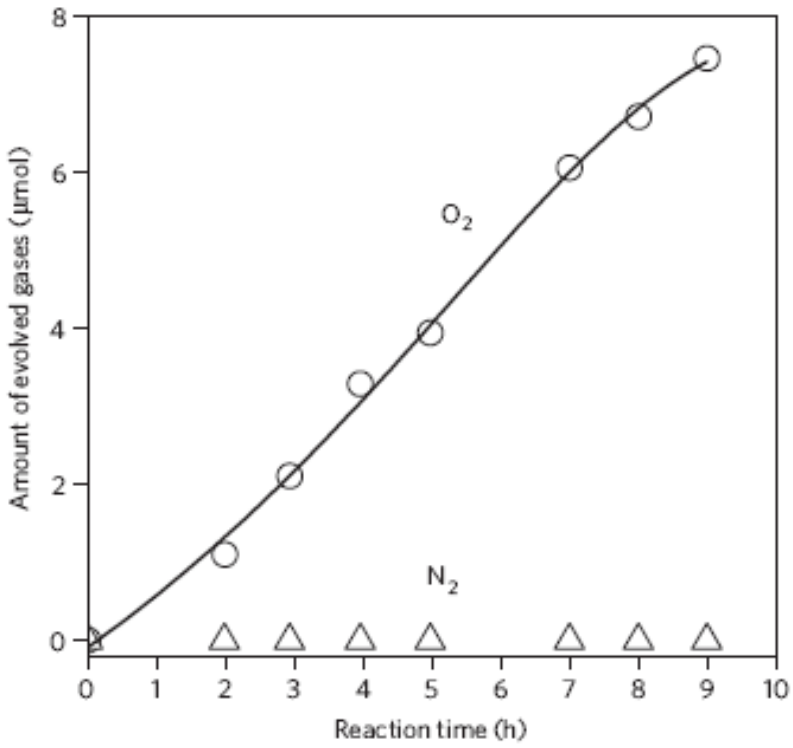


Time courses of H_2 production from water containing 10 vol.% methanol as an electron donor by bare g-C_3N_4 under visible light irradiation (of wavelength larger than 420 nm).

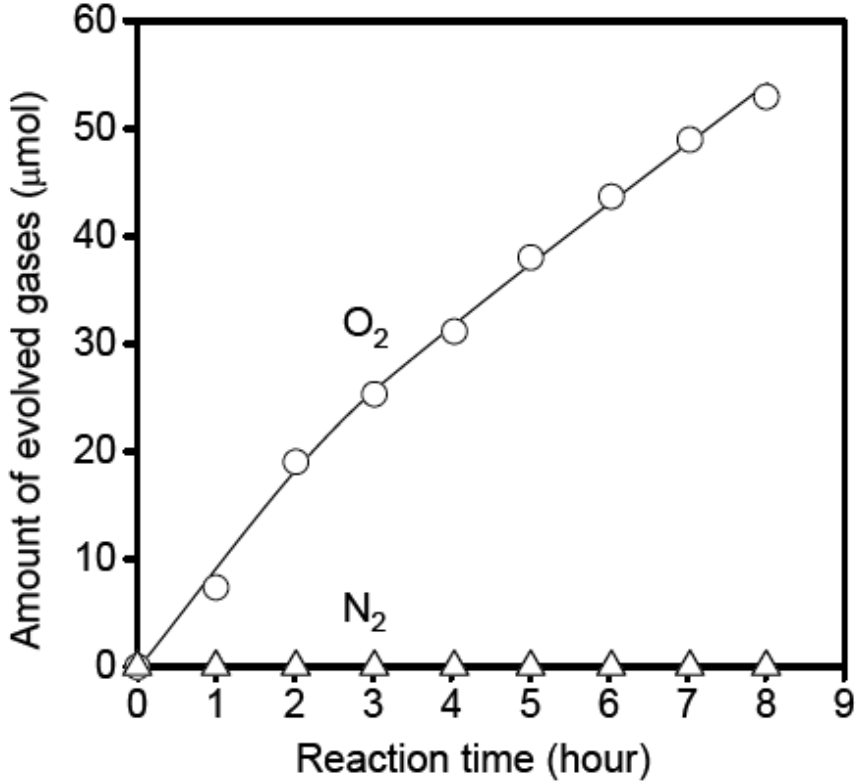


Steady rate of H_2 production from water containing various electron donors under visible light (of wavelength longer than 420 nm) by 0.5 wt% Pt-loaded g-C_3N_4. EDTA (10 mM); MeOH (10 vol.%); EtOH (10 vol.%); TEA (10 vol.%).

Demonstration of photocatalytic property



Oxygen evolution from water by g-C_3N_4. Time courses of O_2 production from water containing 10 mM silver nitrate as an electron acceptor under visible light (of wavelength longer than 420 nm) by 3.0 wt% RuO_2-loaded g-C3N_4. La_2O_3 (0.2 g) was used as a buffer (pH 8–9).



Time course of O_2 production from water containing 10 mM silver nitrate as an electron accepter under ultraviolet light (of wavelength longer than 300 nm) by 3.0 wt% RuO_2-loaded g-C_3N_4. La_2O_3 (0.2 g) was used as a buffer (pH 8–9).

Thank you!