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Photoelectrocatalytic hydrogen production using nitrogen containing water soluble wastes

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ABSTRACT

Hydrogen has been produced by photoelectrocatalytic degradation of model nitrogen-containing water soluble wastes urea, formamide and aqueous ammonia. Hydrogen production was monitored in a simple reactor using a “Photoelectrocatalytic Leaf” as functional component, i.e. an FTO electrode bearing both photocatalyst and electrocatalyst, which allows for a very simple but effective configuration. Nanoparticulate titania was used as photocatalyst while a combination of commercial carbon paste with dispersed Pt nanoparticles was used as electrocatalyst. Urea produced the largest quantity of hydrogen, which could be accelerated by application of an external electric bias. Current-voltage measurements provided an indication of current-doubling in the case of formamide.

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Introduction

Hydrogen production by photocatalytic and photoelectrocatalytic procedures has been one of the most popular subjects of research. Hydrogen can be produced in a photoelectrochemical cell by water splitting, however, hydrogen yield is higher when an organic or inorganic material is photo(electro)catalytically decomposed to yield hydrogen. If this sacrificial agent is a waste, then a double environmental benefit may be made by the production of a valuable solar fuel and the simultaneous decomposition of a harmful material. Most of the so far published works deal with the photo(electro)catalytic decomposition of ethanol, methanol, glycerol and other similar oxygenates [1–13]. The reason is that these substances can be obtained as products of biomass and they

offer the highest hydrogen yield of all studied materials. Another category of high hydrogen yield compounds is sulfide containing wastes [4,14–18]. There is still a third category of waste materials that can be used for hydrogen production: nitrogen, amide and carbamide-based compounds, which have been rather neglected. However, these compounds are typical animal wastes, they are found in large quantities in both urban and agricultural wastes and they make an interesting target for photo(electro)catalytic hydrogen production [19–23]. For this reason, in the present work, we are studying hydrogen production by photoelectrocatalytic degradation of the lowest molecular weight representatives of this category of wastes, namely, aqueous ammonia, formamide and urea.

The configuration of a hydrogen-producing photoelectrochemical cell comprises a photoanode electrode

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carrying a light absorbing oxidation photocatalyst, a cathode (counter) electrode carrying a reduction electrocatalyst, an electrolyte where the target substance is dissolved and possibly a reference electrode, which is useful for analytical studies. Typical photocatalyst, also used in the present work, is nanoparticulate titania (np-TiO₂). Typical electrocatalyst is a mixture of carbon nanoparticles dispersing platinum nanoparticles. In the present work, we have employed a new electrocatalyst made by dispersing Pt nanoparticles in a commercial carbon paste employed also in our recent works [2,24]. Finally, also typical is an alkaline electrolyte, which provides OH⁻ ions that interact with photogenerated holes giving highly reactive ·OH radicals. When photons are absorbed by the photocatalyst, electron–hole pairs are generated. Holes carry out oxidation reactions while electrons move through the external circuit towards the counter electrode, where by the help of the electrocatalyst they carry out reduction reactions. In the absence of O₂, hydrogen may be produced by such reduction reactions. Hydrogen production is accelerated by applying an external electric forward bias, which decreases electron–hole recombination and facilitates electron flow. It is, however, possible to produce hydrogen simply by short-circuiting photoanode and cathode electrode. Furthermore, if both photocatalyst and electrocatalyst are deposited on the same electrode, forming a “Photoelectrocatalytic Leaf” [24], losses are minimized, the system is greatly simplified and the photoelectrocatalytic hydrogen production may become very simple, easy and inexpensive [2,5,15,24,25]. In the present work, production of hydrogen has been studied both by using a Photoelectrocatalytic Leaf (cf. Fig. 1A and B) and by using a photoelectrochemical cell under electric bias (cf. Fig. 1C).

Experimental

Materials

Unless otherwise indicated, reagents were obtained from Aldrich and were used as received. Commercial nanocrystalline titania Degussa P25 (specific surface area 50 m²/g) was used in all cell constructions and Millipore water (18.2 MΩ cm at room temperature) was used in all experiments. SnO₂:F transparent conductive electrodes (FTO, Resistance 8 Ω/

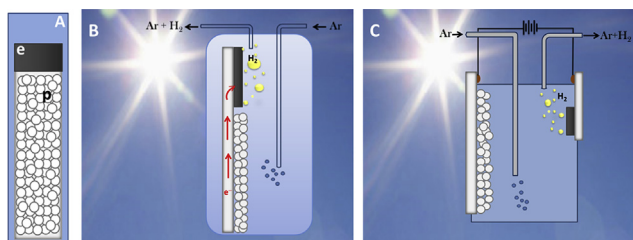


Fig. 1 – Illustration of a “Photoelectrocatalytic Leaf” (A) showing an area covered by the nanoparticulate photocatalyst (p) and an area covered by the electrocatalyst (e); a reactor producing hydrogen by employing a Photocatalytic Leaf (B); and a reactor producing hydrogen under external electric bias (C).

square) were purchased from Pilkington, USA and carbon paste Elcocarb C/SP from Solaronix, Switzerland.

Preparation of np-TiO₂ films

Nanoparticulate titania (np-TiO₂) films were deposited on FTO transparent electrodes by the following procedure. An FTO glass was cut in the appropriate dimensions and was carefully cleaned first with soap and then by sonication in isopropanol, water and acetone. A thin layer of compact titania was first sprayed over a patterned area by using 0.2 mol L⁻¹ diisopropoxytitanium bis(acetylacetonate) solution in ethanol and was calcined at 500 °C. Deposition of this bottom compact layer is a common practice with nanocrystalline titania photoanodes, since it enhances attachment of the top thick film, prevents short circuits and facilitates electron flow towards the electrode. On the top of this compact film, we applied a titania paste made of P25 nanoparticles by doctor blading. The film was calcined up to 550 °C at a rate of 20 °C/min. The final thickness of the film, as measured by SEM, was approximately 10 μm. The geometrical area of the film was 15 cm² (6 cm × 2.5 cm) when it was used for hydrogen production but was reduced to 1 cm² (1 cm × 1 cm) when it was used for tracing current–voltage curves.

Deposition of the electrocatalyst

The electrocatalyst was deposited on FTO by using the following procedure: Commercial carbon paste named Elcocarb C/SP (Solaronix) was applied on FTO by doctor blading and was annealed at 450 °C. This paste forms a uniform and very stable film. Its quantity was 0.67 mg/cm². Elcocarb was mixed with a solution of Diamminedinitroplatinum(II) in ethanol prior to deposition. The quantity of Pt contained in Elcocarb was 2 wt % (0.0134 mg/cm²). This quantity was optimized by several control experiments [24] and it is much smaller than used in other applications [2,26]. The electrocatalyst was in one case applied on the same FTO slide next to the photocatalyst occupying an area of 2.5 cm² (2.5 cm × 1 cm). Thus the FTO glass was partly covered by the photocatalyst while the rest was covered by the electrocatalyst, as illustrated in Fig. 1A (Photoelectrocatalytic Leaf [24]). In this way, the electrons could be directly transferred from the photocatalyst to the electrocatalyst through the FTO layer without wiring, thus minimizing losses. The ratio of the two areas (6:1) was optimized in a previous publication [24]. In a second case, photocatalyst and electrocatalyst were deposited on separate FTO electrodes providing the same 6:1 surface ratio and connected by external wires. In that case, hydrogen production rate could be enhanced by applying an external electric bias.

Device (reactor) construction

In the case of the Photoelectrocatalytic Leaf, Fig. 1A and B, the reactor was a pyrex cylinder containing 90 ml of an aqueous solution of 0.5 mol L⁻¹ NaOH where the sacrificial agent was added at various concentrations. The electrode was completely immersed in the electrolyte and was placed in an upright position, as in Fig. 1B. The cylinder was equipped with fittings allowing Ar gas flow through the electrolyte. The latter

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