

Towards the activation of small molecules for the electrochemical production of solar fuels and ammonia: catalytic electrodes and cell design

Francesco Tavella¹, Chiara Genovese¹, Shiming Chen¹, Claudio Ampelli^{1*}, Siglinda Perathoner¹, Dangsheng Su², Gabriele Centi¹

1 Departments of MIFT and ChiBioFarAM (Industrial Chemistry) -, University of Messina, ERIC aisbl and INSTM/CASPE - V.le F. Stagno D'Alcontres 31, 98166 Messina, Italy;

2 Dalian Institute of Chemical Physics, Chinese Academy of Sciences, 457 Zhongshan Road, Dalian 116023, China

**Corresponding author: ampellic@unime.it*

Highlights

- The design of novel catalytic electrodes and (photo)electrochemical devices is discussed
- The involved reactions are water photo-electrolysis and electro-reduction of CO₂ and N₂
- The influence of the electrode properties on the overall catalytic efficiency is reported
- The nature of the active sites and the possible reaction mechanism are investigated

1. Introduction

The use of renewable sources rather than fossil fuels for the chemical production is one of the main points of solar-driven chemistry. In this vision, the primary feedstocks will be water, nitrogen and carbon dioxide, which can be converted to hydrogen (by water photo-electrolysis) [1], into a series of carbon-based chemical compounds (by CO₂ electro-reduction) [2], and to ammonia (through the simultaneous electro-reduction of N₂ and H₂O) [3]. However, the activation of small molecules, such as N₂ and CO₂, is still challenging, requiring the development of novel catalytic materials, as well as a proper design of the electrochemical systems. A multidisciplinary approach, ranging from catalysis to chemical reaction engineering, is of fundamental importance to reach the long-term goal of this vision, but that can shortly generate new knowledge and benefits to society and industry [4].

In this context, we discuss here on the main aspects to take into account in designing novel electrodic nanostructured materials and related lab-scale photo-electrocatalytic (PEC) set-ups, designed on purpose to maximize their performances. The research activities refer to the study of 1) the photoanode, for the production of H₂ by water splitting, and 2) of the electro-cathode, for the processes of CO₂ and N₂ reduction. In particular, we focus on the investigation of the following aspects: i) light harvesting and band gap structure of the photo-catalyst, ii) charge separation efficiency, iii) good collection of the charges iv) catalytic activity and selectivity of the redox half-reactions and v) Faradaic efficiency, overall yield and productivity. The preparation of 3D nanostructured electrodes can highly favour all these factors, by increasing the active area and limiting the overpotential phenomena.

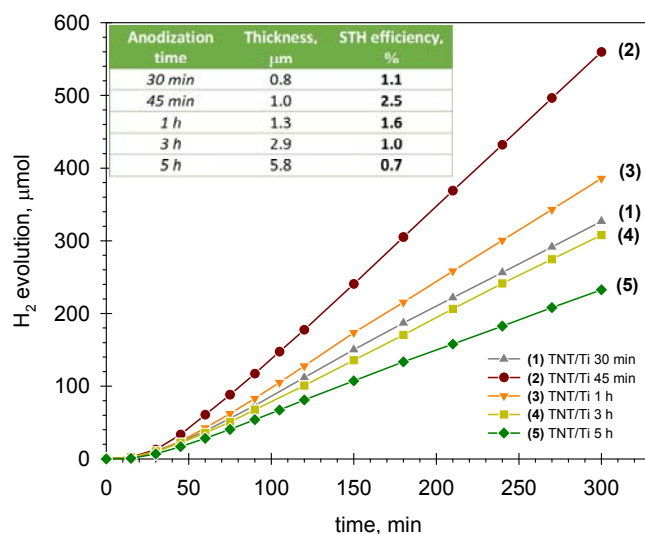
2. Methods

For the preparation of the photoanode, highly ordered TiO₂ or Ta-oxy-N nanotube arrays were synthesized by controlled anodic oxidation under the application of a constant voltage in the presence of fluoride-based electrolytes. Gold or copper nanoparticles (NPs) were deposited by adopting different techniques (wet impregnation, photo-reduction and electrodeposition) in order to improve the visible light absorption properties of the photo-catalyst. The electro-cathode synthesis consists of the early preparation of functionalized carbon nanotubes (CNTs) and deposition of platinum, iron or copper NPs by incipient wetness impregnation, and then assembling the as-prepared catalytic sample between a gas diffusion layer and a proton conductive membrane. The electrodic materials were finally tested using compact (photo-) electrochemical reactors, designed on purpose to maximize the overall efficiency. These homemade set-ups take advantage of fuel cell technology and can work both in gas and liquid phase.

3. Results and discussion

The effects of the size and distribution of the metal NPs, the nano-architecture of the electrodes, the thickness of the catalytic layers, the proton mass diffusion, the electron transport, the kind of the electrolyte, the separation of the two half-reactions, the reaction phase (gas vs. liquid) are fully analysed and discussed.

As an example, Figure 1 shows the H₂ formation and solar-to-hydrogen (*STH*) efficiency for non-doped TiO₂-based nanostructured electrodes prepared at different anodization times, evidencing a maximum *STH* efficiency of 2.5% for a 1 μm-thick catalytic layer. This value is among the best ever reported insofar as PEC cells use undoped TiO₂ photoanodes and in absence of external bias or sacrificial agents [1].



$$STH = \frac{R_{H_2} * \Delta G^0}{P_{tot} * A}$$

R_{H_2} = hydrogen production rate ($mol\ s^{-1}$)

ΔG^0 = standard Gibbs energy at standard conditions
($2.372 \times 10^5\ J\ mol^{-1}$)

P_{tot} = light irradiance ($W\ cm^{-2}$)

A = irradiated area of the photocatalyst (cm^2).

Figure 1. Hydrogen evolution vs. time for TiO₂ nanotubes (TNT)/Ti electrodes prepared at different anodization times (with different thickness). Inset, a table showing the *STH* efficiency, calculated by the formula given on the right-hand side.

Iron oxide supported on CNTs (30 wt.%), instead, allowed obtaining good results in the electrochemical synthesis of ammonia starting from N₂ and H₂O, giving $1.89 \times 10^{-11}\ mol\ cm^{-2}\ s^{-1}$ ammonia formation rate at room temperature and atmospheric pressure under an applied potential of 2 V (vs. Ag/AgCl). The performances greatly depend on cell design, reaction conditions, type and concentration of the electrolyte, pH and applied voltage [3]. Similar types of electrocatalysts and active sites (Pt, Fe or Cu on CNTs) are active also in the electrocatalytic reduction of CO₂. Particularly, the reaction mechanism to acetic acid (a critical step involving C-C bond formation) was investigated by comparing the reactivity in tests with CO₂ and CO. The results indicated the importance of having a high local concentration of CO₂ on the electrode surface to form acetic acid, likely via the reaction of CO₂⁻ with surface adsorbed -CH₃ like species [2,4].

4. Conclusions

The use of novel electrocatalytic electrodes in highly challenging reactions (water photo-electrolysis to H₂, CO₂ electro-reduction to liquid fuels and direct electro-synthesis of ammonia from N₂ and H₂O) and the related photo-electrochemical (PEC) set-ups were discussed. The testing results are very promising for the commercial implementation of these electrochemical systems in a future solar-driven energy scenario.

References

- [1] C. Ampelli, F. Tavella, S. Perathoner, G. Centi, Chem. Eng. J. 320 (2017) 352–362.
- [2] C. Genovese, C. Ampelli, S. Perathoner, G. Centi, Green Chem. 19 (2017) 2406–2415.
- [3] S. Chen, S. Perathoner, C. Ampelli, C. Mebrahtu, D. Su, G. Centi, Angew. Chem. Int. Ed. 56 (2017) 2699–2703.
- [4] B.C. Marepally, C. Ampelli, C. Genovese, T. Saboo, S. Perathoner, F.M. Visser, L. Veyre, J. Canivet, E.A. Quadrelli, G. Centi, ChemSusChem (2017), DOI: 10.1002/cssc.201701506.

Keywords

Photo-electrocatalytic (PEC) cells; TiO₂ nanotubes; ammonia synthesis; Iron-doped carbon nanotubes (Fe-CNTs).