

Photocatalytic Hydrogen production using recovered Silicon from End of Life (EoL) photovoltaic panels

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Introduction

Over the past decades the use of photovoltaic panels (PVPs) to harness solar energy has been widely expanded. As installed PVPs reach the end of their lifespan, recycling, reuse and safe disposal of PVP waste are becoming a critical and global challenge. Ways to recover valuable materials like silver and semiconductors are studied, as well as potential ways to reuse semiconductors. First generation photovoltaic panels utilize crystalline silicon as semiconductor. In several studies commercial crystalline silicon is modified into photocatalyst through techniques like metal assisted chemical etching, deep reactive ion etching or vapor-liquid-solid synthesis (Liu D. et al, 2017). Modified silicon and its structures (i.e. silicon nanowires) are then used in photocatalytic processes such as pollutant degradation and photocatalytic hydrogen production (Puga A.V., 2016).

The scope of this work is to evaluate the potential of 1st generation photovoltaic panels' semiconductors (crystalline silicon) to be modified and used as photocatalyst in photocatalytic hydrogen production in aquatic methanol solution under UV and solar irradiation.

Materials and methods

Polycrystalline Si End-of-Life (EoL) PVPs were provided by POLYECO S.A. The PVPs was cut into pieces and placed in a furnace in porcelain crucibles at 550 °C for 30 min in order to remove polymer sheets, ethylene vinyl acetate (EVA). The resulting mixture of Si flakes, soda lime glass, electrodes and ash was separated in a trommel screen.

The fraction containing Si flakes was washed with deionized water and acetone to remove ash and residues, followed by 4N HNO₃ treatment, shaken at 200 rpm for 24h. The samples were also treated with 10% w/w HF aquatic solution for 3h to remove the Anti-Reflective Coating, Al coating and oxides from their surface. Finally, the flakes were dried and ground to powder.

The first step is a Ag-assisted chemical etching, which aims to create high surface area Nanowire structures on Si. This is schematically described in Figure 1. Si powder was immersed into a 4.6 M HF aquatic solution containing 0.035M AgNO₃ 30 min at 55°C. After etching, Si oxides were removed from the sample's surface using 10% w/w HF aqueous solution for 1 min. Finally, the samples were rinsed with deionized water and dried at 105 °C for 24h (Fellahi et al, 2016).

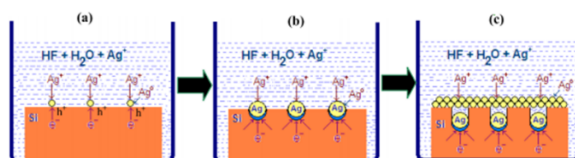


Figure 1: Single step Ag assisted chemical etching (Srivastava et al., 2014)

The second step employed is a simple deposition of Cu on the etched Si surface that aims to create a Schottky barrier that acts as an electron trap. This barrier inhibits the recombination of photo-generated electron-hole pairs assisting the photocatalytic process. It was carried out in 1.4M HF aquatic solution containing 0.035M CuSO₄·5H₂O for 2 min at room temperature

An aquatic methanol solution with initial concentration of 26 g/L was prepared. The photocatalytic hydrogen production was carried out by suspending the catalyst powder into 600mL of the aqueous solution under stirring with a 275mL headspace, at pH values of 3, 7 and 10. The solution was then irradiated with simulated solar light from a 150W Xe arc lamp or a UV 150W Hg arc lamp immersed in the reactor (Figure 2) using an immersion tube for 450 min. The concentration of methanol was measured using high performance liquid

chromatography and the generated hydrogen with gas chromatography. The performance of the Si photocatalyst is comparable to that of TiO₂ and control experiments.

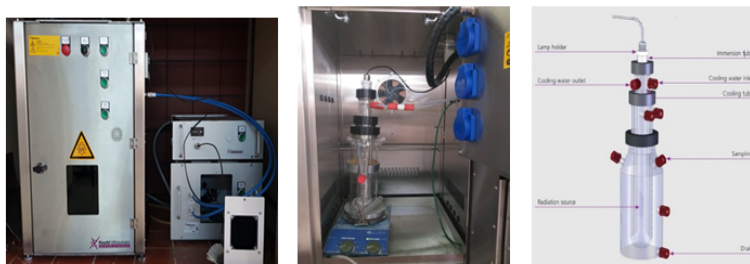


Figure 2: Photoreactor set up by Peshl Ultraviolet GmbH, Mainz -Germany

Results and Discussion

Evolution of hydrogen in the reactor headspace is measured and recorded alongside with the reduction of methanol in the solution to evaluate the yield of the process. Preliminary results indicate that at low pH values (3) under UV irradiation, hydrogen production is achieved using the silicon photocatalyst prepared from EoL PVPs (Figure 3).

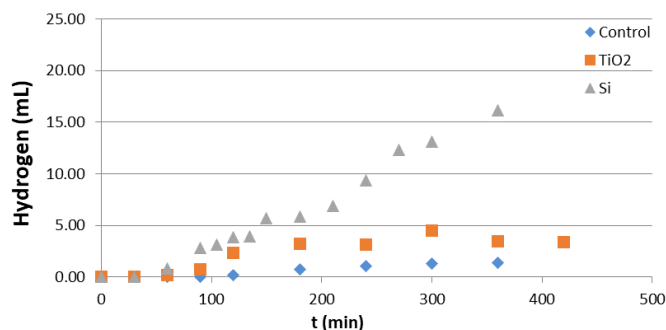


Figure 3: Photocatalytic hydrogen production under UV irradiation in pH 3 with Si, TiO₂ photocatalysts and control experiment.

Conclusions

Si recovered from End-of-Life 1st generation photovoltaic panels may be etched and doped through simple, electroless, chemical methods for the preparation of a catalyst. The resulting material may be used for heterogeneous photocatalytic hydrogen production in methanol solution under simulated solar light and UV irradiation. Preliminary results showed that the process is feasible, as up to 16mL of hydrogen gas were produced under UV irradiation in pH 3 so far. Further experiments to optimize the process are underway.

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