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Silicon nanowires' based photoanode for hydrogen evolution

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ABSTRACT

The solar driven photo-electrolysis of water for hydrogen and nanoparticles formation from electrolyte with corresponding metal salts was investigated. The photoanode consisted of a thin layer of silicon nanowires deposited on molybdenum and a platinum wire as the cathode was used. The prepared photo-anodes were stable up to 0.3 V against the saturated Ag/AgCl electrode without any signs of gaseous oxygen evolution. This photo-electrochemical system enhanced the nanoparticle formation during the illumination phase accompanied with lowering the external potential needed. The present results show that hydrogen *in statu nascendi* is formed during illumination of photoanode, which causes the formation of nanoparticles by reduction of metal salts. During the photo drive electrolysis, hydrogen is stored in/on forming nanoparticles. The size of nanoparticles can be determined by time and an external bias value inserted between the working and platinum electrodes in a classical three electrode system. It was confirmed that the formation of nanoparticles was limited by diffusional processes of hydrogen *in statu nascendi* in electrolyte, which is in agreement with literature.

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Introduction

Energy and environmental issues at a global level belong to the most important topics. It is indispensable to construct clean energy systems in order to solve the issues. Hydrogen will play an important role in such systems due to the fact that it is the ultimate clean energy and it can be used in fuel cells. The use of solar energy for electricity generation and the use of this electricity for hydrogen production by alkaline water electrolysis promises to be a truly sustainable scheme for hydrogen economy [1–3].

There are several ways of solar hydrogen production and storage [4–7]. One of them is the photocatalytic water splitting

process, in which the photon energy is converted into chemical energy accompanied with a largely positive change in the Gibbs free energy through water splitting [8–10]. This reaction is similar to photosynthesis used by green plants because these are uphill reactions. Therefore, photocatalytic water splitting is regarded as an artificial photosynthesis and is an attractive and challenging theme in chemistry.

During the past 40 years, various photocatalyst materials have been developed to split water into H₂ and O₂ under UV and visible light illumination. However, efficient materials for water splitting under visible light irradiation have not been found yet. Nevertheless, new photocatalyst materials for water splitting have recently been discovered one after another. One of the perspective material is the

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nanocrystalline silicon, which is a surface-nanostructured Si with an extremely efficient light absorption capability [11,12] and, regrettably, with intense charge recombination and low electrochemical stability. Nevertheless, the photocatalytic water splitting is still a challenging reaction even though the research history is long. Moreover, hydrogen produced by this process can be either stored in metal hydride or carbon nanotubes, polymers and chemical complexes for subsequent utilization [13–15].

For that reason, this work was focused on evolution of hydrogen in a newly designed (photo)electrochemical cell in which two photovoltaic panels served as the source of electric energy for long-term experiments. Specially prepared Si nanowires on molybdenum were employed as one of electrodes [16]. Subsequently, utilization of evolving hydrogen for preparation of nanoparticle catalysts together with its storage in Palladium were also tested. This method is unique since the preparation of nanoparticles can be carried out continuously without an addition of further reducing agents.

Experimental part

Preparation of Si nanowires

Si nanowires were grown on molybdenum (0.5 mm, 99.9 w/w %, Aldrich) and iron substrates (0.5 mm, 99.9w/w%, Aldrich) in a quartz tube placed in an oven. Prior to the deposition, 2 nm thick gold layers were sputtered on the substrate. First of all, the tube was evacuated using a turbo station unit (TC110 Pfeiffer Vacuum) to reach pressure lower than $5.0 \cdot 10^{-4}$ Pa. Subsequently, the temperature in the oven was increased up to 500 °C and after reaching that value, silane SiH₄ was allowed to enter the tube to be decomposed over the substrates. The pressure in the tube was controlled by a needle valve integrated between the tube and the rotary pump. After the 60-min run, the silane flow was stopped and the temperature dropped to room temperature. Consequently, the samples were analysed by a Scanning Electron Microscopy (SEM) setup (Vega 3 Tescan Indusem) equipped with an EDX module (Bruker XFlash Detector 5010) for detecting the elemental composition. Raman spectra were performed by a dispersive Raman Nicolet Almega XR with excitation wavelength of 473 nm, power of 10 mW and resolution of 2 cm⁻¹. Transmission electron microscopy (TEM) was performed on a Philips CM 120 (LaB₆, 120 kV) equipped with NanoMEGAS precession unit DigiStar, an Olympus SIS CCD camera Veleta (2048 × 2048 px), and an EDAX windowless EDS detector Apollo XLTW. The samples were prepared on holey-carbon coated Cu grids by brushing a grid against the substrate containing nanowires.

Electrochemical cell

The evolution of hydrogen in combination with nanoparticles of metals was performed in a newly designed (photo)electrochemical cell. As the source of electric energy for long-term experiments, two photovoltaic panels (2 × 5 W (peak), 12 V, 0.4 A) were used. These panels were connected to a Li-polymer battery with a control unit connected to the electrochemical

cell. A potentiostat (NuVant EZstat Pro with IES) was used for the determination of electrochemical response of layers on incident light during Cyclic Voltammetry and Amperometry for Hydrogen Evolution Reaction (HER) on Pt contra-electrode, whereas the anode was made of studied materials deposited on Molybdenum. The Solar simulator at 100 W AM1.5G served as a source of incident light. The design of the cell is shown in Fig. 1a. The pH value for all experiments was lower than 7 (5.2–6.4).

Photoinduced electrochemical properties of Si nanowires on Mo electrodes in solution of metal salts (K₂PdCl₄: 0.5023 g + 100 mL deionised water, AgNO₃: 2.34 g + 200 mL deionised water) (unbuffered, not stirred, no gas purging) as electrolyte were investigated in a three-electrode arrangement [16,17] (Fig. 1b). The pH value of the electrolyte solution was constant during the experiments. The prepared Si/Mo layer was always used as the working electrode and the area was fixed at 1 cm². It was irradiated in a Pyrex cell with a light beam of AM1.5G of the intensity of 50 Suns. The temperature was kept at 23 °C during the whole measurement. Open Circuit Potential (OCP) measurements were performed (30 s dark, 60 s illumination, 60 s dark). The cyclic voltammetry was measured between –0.3 and 0.3 V (50 mV s⁻¹) against a standard saturated Ag/AgCl electrode. The HER was studied in 0.15 Na₂SO₄ using Cyclic Voltammetry (–0.6 to 0.6 V against the standard saturated Ag/AgCl electrode and amperometry at 0.0–0.6 V against the standard saturated Ag/AgCl electrode with 0.1 V step. The final evolution of nanoparticles was performed during the amperometry at 0.3–0.4 V for 2 h against the Ag/AgCl electrode for all samples.

Results and discussion

Layers preparation

The deposition of silane on molybdenum, which yielded thick brown films, was applied for the electrode preparation based on Si nanowires on Mo substrate with 2 nm thick gold layers. The used preparation system provided the growth of Si nanowires with a uniform thickness profile. EDX analysis (not shown) revealed that nanowires are composed of silicon. According to the Scanning Electron Microscopy (SEM) photographs (Fig. 2a), a large part of prepared nanowires possessed the length of more than 20 μm. Raman analysis revealed a sharp peak whose position and form was dependent on the actual excitation laser power, density of grown SiNWs and the focusing laser spot inside SiNWs. The peak position varied from 503 to 527 cm⁻¹, which is close to the value for bulk silicon [18]. In Fig. 3, several examples of Raman spectra measured for a single SiNW film are presented. Such a peak shift and form demonstrates a heating effect of the Raman excitation laser [19]. No quantum effects were expected because SiNW thickness was far above 20 nm [19–22].

Moreover, Transmission Electron Microscopy (TEM) analysis of these samples showed a uniform type of SiNWs. Only a small SiNW fraction was kinked and/or suffered from tapering. Prepared SiNWs possessed the length of several microns with the width of about 100 nm (Fig. 2b and c). SiNWs were composed of a core and a mantle. The crystalline core

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