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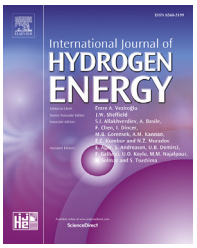

Photocatalytic degradation of cationic and anionic dyes in water using hydrogen-terminated silicon nanowires as catalyst

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ABSTRACT

The photocatalytic degradation of cationic (methylene blue (MB)) and anionic (methyl orange (MO)) dyes was investigated using hydrogen-terminated silicon nanowires (H-SiNWs) as photocatalysts. Several silicon nanowires samples with different morphologies were elaborated and the morphology was changed by acting on the silicon nanowires formation parameters such as substrate type, doping level, crystallographic orientation, silver deposition time and etching time. It was shown that the photocatalytic activity strongly depends on the morphology of SiNWs arrays. Indeed, it was found that n-type H-SiNWs elaborated on highly doped Si (100) substrates exhibit the highest photocatalytic activity for the degradation of MB. In addition, it was demonstrated that H-SiNWs are more efficient for the photodegradation of MO than MB in the solutions with pH values higher than the pH of zero charge point of silica (pH_{pzc}).

Introduction

The textile industry is a large consumer of water, much of which is used in the dyeing process. Thus a large quantity of dye effluents is discharged in the environment [1]. The treatment of these waters remains a major challenge especially for developing countries that did not have all the opportunities to integrate sustainable development concepts. Conventional treatments (activated carbon adsorption, membrane processes, coagulation-flocculation, chemical oxidation, etc.) have the disadvantage of transferring pollution from an aqueous phase to a new phase, and lead mostly to the formation of concentrated sludge. This creates a problem of secondary waste which needs very expensive treatment processes [1,2]. Advanced Oxidation Processes (AOPs) are promising alternative techniques of destruction of dyes and many other organics in wastewater and effluents [3]. Indeed, they have the advantage to be less expensive and allow to a complete mineralization of organic pollutants.

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Semiconductor photocatalysis is a newly developed AOP, which can be used for the degradation of dye pollutants. A lot of studies were reported on the photocatalytic degradation of refractory organics. TiO_2 was the most used in photocatalysis because of its exceptional stability towards chemical and photochemical corrosion [4–8]. However, it possesses low photocatalytic efficiency under visible-light irradiation because of its intrinsic large band gap [9]. Silicon is a low cost and environmental friendly semiconductor, which prevails in integrated microelectronics. However, it is not used in pollution control because its valence band is not positive enough to oxidize pollutant species [10]. Nevertheless; the nanostructured silicon has recently attracted a great deal of attention because of their high specific surface. It is expected to have potential applications in the development of new catalysts [11]. Indeed, it was reported by Yoneyama et al. that platinized n-type crystalline silicon and silicon powder are good photocatalysts for formic acid decomposition [12]. Also, Chen et al. used one dimensional hydrogen-terminated silicon nanowires (SiNWs) prepared by oxide-assisted- growth, under ultrasonic agitation for the degradation of methyl red [13]. Shao et al. investigated the performance of hydrogen-terminated SiNWs substrates prepared by the VLS method for the degradation of Rhodamine B under visible light irradiation. It was found that hydrogen-terminated SiNWs exhibited a high efficiency which was attributed to an electron deficiency of H atoms in $Si-H_x$ terminating the surface [14]. In addition, Pan et al. found that Cu-modified silicon nanowires show enhanced catalytic activity for the coupling reaction of benzene halides (iodobenzene, bromobenzene, and chlorobenzene) and aniline [15]. Also, Tsang and al. show that Au– and Cu-modified Si nanowires (SiNWs) are superior catalysts for selective oxidation of hydrocarbons [16]. The aim of the present work is to investigate the photocatalytic properties of H-SiNWs elaborated by an Ag-assisted electroless etching process for the degradation of textile dyes in water under UV irradiation. The dyes used in this work were Methylene Blue and Methyl Orange. The effects of the morphology of H-SiNWs arrays and the molecular structure of the dyes on the photocatalytic process were studied.

Experimental

Materials

Silicon wafers were purchased from Siltronix. All cleaning and etching reagents used in this study such as hydrogen fluoride (50%), oxygen peroxide (30%), nitrates of silver (≥99.8%), acetone (98%), ethanol (≥99.8%), sulfuric acid (98%) and nitric acid (65%) were obtained from SIGMA- Aldrich. Methylene blue (≥95%, FLUKA Analytical) and Methyl Orange (SIGMA-ALDRICH, ACS reagent, dye content 85%) powders were used without further purifications. Deionized water (18 MΩ) was used for all the experiments.

Samples preparation

Nanowires samples were prepared by the Ag– assisted chemical etching method from n- and p-type Si (100) with resistivities of 0.02 Ω cm, 5–10 Ω cm and 100 Ω cm. n- and p-type silicon substrates with the crystallographic orientations (100), (111) and (110) were also used. The Si wafers were cut to samples having a size of $0.7 \times 1.5\ cm^2$ and were first cleaned by ultra-sonication in acetone, ethanol and deionized water (5 min each). The cleaned samples were then immersed into a beaker containing a piranha solution for 20 min at room temperature, followed by a dip in 10% HF aqueous solution for 1 min at room temperature to remove the native oxide. Ag electroless chemical deposition was carried out in a solution containing 0.005 M $AgNO_3$ and 4.8 M HF for 1 min at room temperature [17]. The Si samples with deposited silver were rinsed with deionized water and then immediately immersed into an etching bath containing 4.8 M HF and 0.4 M H_2O_2 at room temperature [17,18]. After etching, the silver metal was removed from the nanowires by immersing the samples in the concentrated nitric acid for 5 min. The resulting interface was rinsed with water and dried under a gentle stream of nitrogen.

Photocatalytic testing

The methylene blue (MB) and methyl orange (MO) were used in this work as the representative dyes pollutants to evaluate the photocatalytic activity of H-SiNWs samples. The MB and MO solutions with the initial concentrations of 10^{-6} M were prepared by dissolving methylene blue and methyl orange powders in deionized water under a magnetic stirring at room temperature for 10 min. An UV spot light source (Hamamatsu LC8 series) was used for the dye solutions irradiation. The photocatalytic degradation reactions were carried out at room temperature by immersing the sample into 4 mL aqueous solutions and were irradiated for 200 min. The photocatalytic performance was measured by the decay of the absorption every 20 min.

Characterization

The morphology of the samples was examined by a PHILIPS XL30 Scanning Electron Microscope (SEM). The absorption spectra of the methylene blue and methyl orange solutions in quartz cuvettes with an optical path of 10 mm were recorded using a CARY 500 "VARIAN" UV–Vis spectrophotometer.

Results and discussion

Morphology

Effect of the crystallographic orientation

n-and p-type Cz-silicon substrates with a resistivity of about 0.02 Ω cm and different crystallographic orientations were subjected to Ag-assisted electroless etching for 60 min at room temperature. When silicon samples of orientation (100) were used, SiNWs were uniformly formed on the surfaces (Fig. 1a and c). The cross section SEM images show that the SiNWs are vertically aligned to the surface and the interface between nanowires and substrate is clearly distinguished thus indicating that the etching was uniform (Fig. 1b and d). In addition, it can be observed that the nanowires tips aggregate to form bundles which are caused by van der Waals forces (Fig. 1a, b, c

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