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Highly efficient hydrogen production using p-Si wire arrays and NiMoZn heterojunction photocathodes

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ABSTRACT

Highly efficient photoelectrochemical (PEC) hydrogen production is achieved using p-Si wire arrays loaded with NiMoZn particles in aqueous sulfuric acid under simulated sunlight (AM 1.5 G; 100 mW cm^{-2}). Vertically-aligned wire arrays are grown on planar Si wafers via a quick electroless etching process within 5 min, leading to short Si wires of ~4 μm and diameters of ~0.2 μm. Despite the short length of the wires, the reflectance of the arrays is < 5% over the wavelength range of 400–800 nm (the reflectance of planar Si is ~40%) and the photocurrent density (I_{ph}) is enhanced by ~ 30% relative to planar Si. To further improve the PEC performance, ~ 100 nm NiMoZn particles are photoelectrochemically deposited onto the wires. The wire arrays with evenly distributed NiMoZn particles show a photocurrent onset potential (E_{on}) of ~ + 0.27 V vs. RHE and produce an I_{ph} of ~1.45 mA cm^{-2} at 0 V vs. RHE with a Faradaic efficiency of ~ 100% for H_2 evolution. This I_{ph} value is ~10-fold greater than that with the planar Si/NiMoZn samples. The excellent performance of the wire arrays and NiMoZn heterojunction is attributed to enhanced light absorption (decreased reflectance), facilitated charge transfer (radial-directional electron transfer), and NiMoZn-catalyzed hydrogen production.

1. Introduction

Sunlight-driven production of molecular hydrogen (H_2) from water has received growing attention as an alternative to conventional carbon-footprint H_2 production processes (e.g., steam-methane reforming) [1–3]. There are several technical pathways for solar hydrogen production; yet photoelectrochemical (PEC) systems are likely the most viable in terms of synthesis and material modification, system installation, evolved gas separation (e.g., H_2 and O_2), and hybridization with conventional photovoltaics. Despite this great potential, PEC devices suffer from low efficiency, stability, and durability, as well as high costs of the electrode materials [4–7]. Particularly, low efficiency often results from the slow kinetics of charge carriers at the electrode/electrolyte interface [8–11].

p-Type silicon (Si) is widely used as the photocathode in PEC devices because of its narrow bandgap (E_g ~1.2 eV) and suitable band level for the hydrogen evolution reaction (HER) [12,13]. However, the mirror-like planar surface of Si reflects a significant fraction of incident photons. In addition, the small absorption coefficient of Si requires a thick film in order to absorb more photons; however, the short diffusion length of the minority carriers causes significant bulk recombination [14,15]. A wire-array geometry of Si has been demonstrated to possess superior antireflection property capable of absorbing ~96% of the solar photons over a wide range of incident angles [16]. In addition, the photogenerated minority carriers in the bulk can be radial-directionally transported to the electrolyte [14]. Furthermore, wire geometries with a high surface roughness can provide a better environment to tailor the particle size of the loaded catalysts [17].

Despite these morphological effects, the catalytic property (i.e., the interfacial electron injection efficiency) remains mostly unchanged, and HER catalysts are required for prompt electron injection. In contrast to traditional platinum group metals, transition metal alloys (Ni-Mo [18] and Ni-Zr [19]), sulfides (MoS_2 [20] and NiS_2 [21]), phosphides (Ni_2P [22] and CoP [23]), and nitrides (WN and TiN [24]) have been developed as earth-abundant element-based catalysts. The interstitial metal alloys can tune the proton binding energy (ΔG_H) to the metal surface by adjusting the electronic structure of the metal, leading to an optimal ΔG_H and a reduction in the HER overpotential [19,25]. For instance, the intro-

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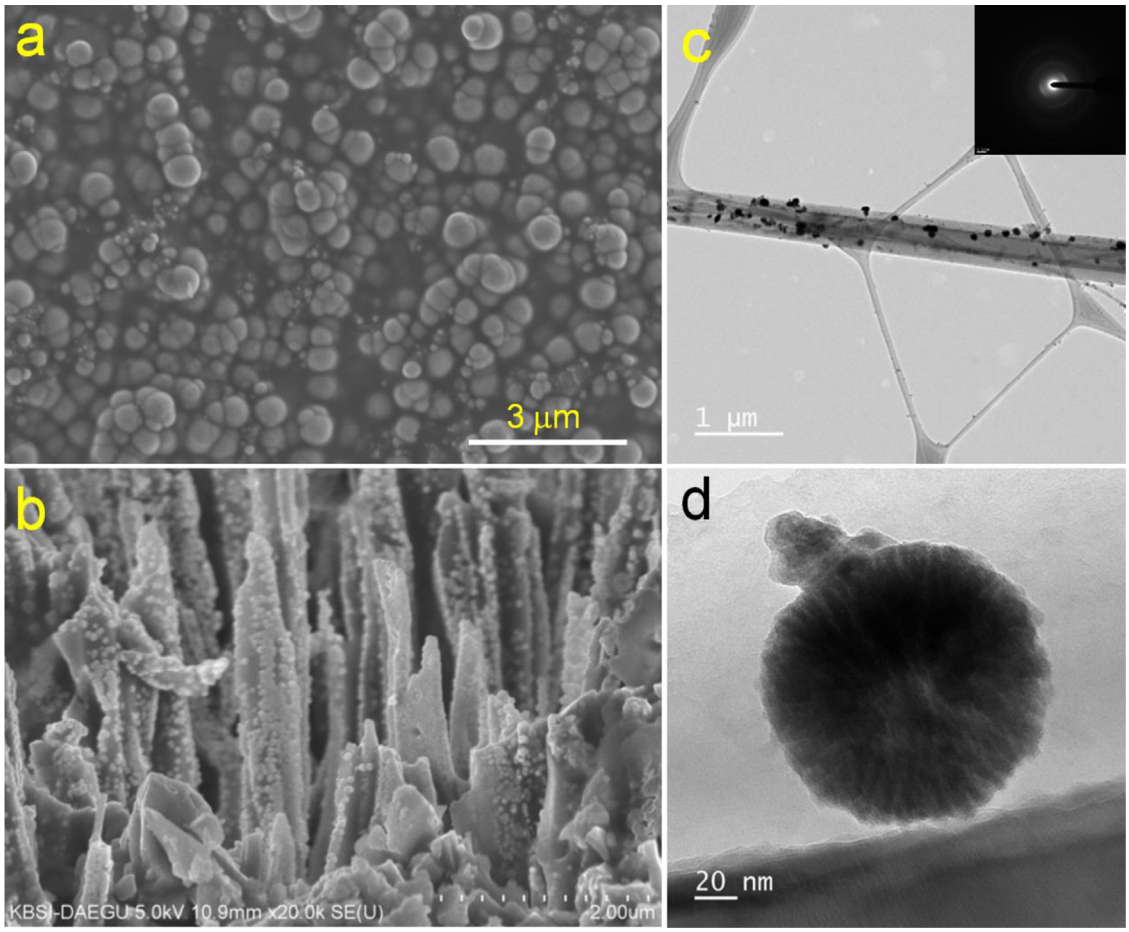

Fig. 1. SEM images of (a) the top view of planar Si and (b) the cross-sectional view of the Si wire arrays deposited with NiMoZn particles for 5 min. TEM images of (c) a Si wire deposited with NiMoZn (Inset: SAED pattern of NiMoZn) and (d) a magnified view of a NiMoZn particle.

duction of Mo into Ni has been shown to modify the electron density states of the *d* orbitals, thereby changing the ΔG_H on the metal surface [26,27]. Further, the addition of trace Zn to NiMo optimized the physicochemical properties, leading to a dramatic improvement in the HER [28].

With this in mind, we synthesized the p-Si wire arrays deposited with NiMoZn particles and examined the PEC hydrogen production in an aqueous sulfuric acid solution under AM 1.5 G light (100 mW cm^{-2}). Vertically aligned, free-standing p-Si wire arrays grew quickly on p-Si wafers via an electroless chemical etching process. In contrast to previous studies with 15–140 μm long wires, short wires (~4 μm) were synthesized because of their superior anti-reflectivity (< 5% in the wavelength range of 400–800 nm). NiMoZn particles were then deposited onto the wire arrays under a constant current for 5 min while irradiating with simulated sunlight. Despite the short synthetic process, the loading of NiMoZn significantly improved the photocurrent density of bare p-Si wire arrays by ~10 times at 0 V vs. RHE while achieving ~100% Faradaic efficiency for the HER. The as-synthesized wire arrays coupled with NiMoZn were characterized with various analytical tools and the NiMoZn-catalyzed HER was discussed in detail.

2. Experimental section

2.1. Synthesis of p-Si wire arrays and NiMoZn heterojunction

Unless otherwise specified, all chemicals and reagents were purchased from Sigma-Aldrich and used without any pretreatment. The Si wire arrays were prepared using an Ag-catalyzed electroless chemical etching method with *p*-type Si (100) wafers (WaferKorea, Inc.; B-doped at 10^{14}–10^{16} cm^{-3} based on its resistivity of 1–30 Ω cm according to the manufacturer's information). The Si wafer was washed with acetone, 2-propanol, and then ultrapure deionized water (>18 MΩ cm, Human Corporation). The back side of the Si wafer was sealed with Teflon tape to block contact with the Ag particles. The native Si surface oxides were removed by sequential cleansing with a piranha solution (i.e., 95% H_2SO_4/30% H_2O_2, 3:1 (v/v)) and a 5% HF solution. Ag seed particles were deposited on the Si wafer using aqueous solutions of $AgNO_3$ (10 mM, 99.8%, Duksan) and HF (5 M) for 3 min, which was then rinsed with deionized water. After the Ag particle deposition step, electroless chemical etching was performed in an aqueous mixed solution of H_2O_2 (0.27 M) and HF (5 M) for 5 min to grow the wire arrays. Then, the as-synthesized samples were soaked in 65% HNO_3 to remove the residual Ag particles, rinsed with deionized water, and dried in an N_2 stream.

The wire-arrayed Si wafers were cut into pieces onto which a silver paste (Cans, Inc.) was painted to create an ohmic contact with the back side. Following drying at 80 °C, the Si wafers were masked with epoxy (Loctite 1C Hysol) over an area of 0.2 cm^2 exposed to the electrolyte. NiMoZn particles were photoelectrochemically deposited from a mixed solution of $NiCl_2{\cdot}6H_2O$ (10 mM, 98%), Na_2MoO_4 $2H_2O$ (5 mM, 99%), $ZnCl_2$ (0.1 mM, 97%), $Na_4P_2O_7$ (30 mM, 99%), $NaHCO_3$ (200 mM, 99%), and hydrazine hydrate (1 mL/L, 98%). The Si samples were immersed in the plating solution and biased at a negative current of 5 mA cm^{-2}, typically for 5 min under AM 1.5 G irradiation at 100 mW cm^{-2} (150 W Xe-arc lamp, ABET Technologies).