Selective Deposition of an Ultrathin Pt Layer on a Au-Nanoisland-Modified Si Photocathode for Hydrogen Generation

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ABSTRACT: Platinum, being the most efficient and stable catalyst, is used in photoelectrochemical (PEC) devices. However, a minimal amount of Pt with maximum catalytic activity is required to be used to minimize the cost of production. In this work, we use an environmentally friendly, cost-effective, and less Pt-consuming method to prepare PEC devices for the hydrogen evolution reaction (HER). The Pt monolayer catalyst is selectively deposited on a Au-nanoisland-supported boron-doped p-type Si (100) photocathode. The PEC device based on the Si photocathode with an ultralow loading of the Pt catalyst exhibits a comparable performance for the HER to that of devices with a thick Pt layer. In addition, we demonstrate that by using a thin TiO2 layer deposited by atomic layer deposition photo-oxidation of the Si photocathode can be blocked resulting in a stable PEC performance.

INTRODUCTION

Photoelectrochemical (PEC) water splitting technology effectively meets the challenge of producing inexpensive and greenhouse-gas-free energy. Recently, a tandem cell PEC device for direct water splitting achieved a record efficiency of 14%. The major requirement to obtain efficient and stable tandem-based PEC devices is to engineer different active parts (photoelectrodes, co-catalysts, and stabilizing layers) with an optimal contribution from each one.

Semiconducting materials such as silicon used as photoelectrodes in PEC devices have no or very little catalytic activity; as a result, they cannot directly convert photogenerated electrical energy into chemical energy. This issue is typically solved by covering the surface of the photocathode with a co-catalyst, which accelerates the oxygen and hydrogen evolution reactions (HER). However, surface structuring of Si is also used to enhance the photocatalytic activity of Si photoelectrodes. It is estimated that the catalyst will contribute 10% of the total production cost of a PEC device when noble metals are used as the catalytic material. To reduce the device fabrication costs an alternative, low-cost, and abundant material or a feasible procedure for catalyst deposition that consumes a reduced amount of the expensive catalyst needs to be designed. Different non-noble-metal-based catalysts, such as transition metal-based phosphides and sulfides as well as metal chalcogenides, have been developed for the HER. These materials need overpotentials of about 50 mV at a current density of 10 mA/cm2 for the HER. However, metal sulfides can work efficiently only in acidic media, whereas metal phosphides can be used in electrolytes, within a wide range of pHs. However, the low stability of these catalysts is still a major hindrance for their successful application in PEC devices. State-of-the-art catalysts, such as CoP and Ni3P, are not stable during long-term operation. The transition metal-based phosphides have a lower exchange current density than that of the traditional Pt HER catalyst and hence a higher amount of catalyst material on the photocathode is needed to obtain a lower overpotential. Conversely, the use of an excess amount of catalyst material can result in a decreased current density due to the parasitic absorption of illuminated light on it. Besides the material costs, the synthesis of metal sulfides and phosphides requires multiple steps and also involves the use of dangerous and poisonous gases (phosphine, sulfur). Multiple production steps also complicate the fabrication process of the PEC devices. To date, no single material has been developed that matches the performance (efficiency and stability) of the Pt catalyst for HER in different electrolyte media. Therefore, Pt is supposed to be the best choice for HER in PEC technology.

For effective PEC water splitting, the amount of Pt catalyst needed for PEC devices is supposed to be around 180 tons/year. However, the abundance of Pt on earth does not allow the use of such a large amount. Nonetheless, a similar HER activity (HER overpotential of around 50 mV) can be achieved by using thin films or nanoparticles of other catalytic materials, such as metal phosphides and sulfides. However, these kinds of catalyst are not stable compared with bulk noble catalyst Pt; therefore, to realize a stable and efficient catalyst, it is necessary to use a minimal amount of this precious catalyst to achieve an...
equivalent catalytic effect compared to that of the bulk Pt. Among the various approaches, atomic layer deposition (ALD) is the most promising process to get ultralow loadings of Pt nanoparticles on the photodecote. A Pt monolayer can also be deposited by the galvanic exchange method on Au islands supported for PEC water splitting. In this work, we demonstrate a fluorine-free method to produce a Pt monolayer on Au-nanosized (Au-NI)-supported Si photoelectrodes for the HER. The Au-NI template is prepared by an inexpensive physical vapor deposition technique and thermal quenching, which avoids the use of typically chosen fluorine-based electrolytes or expensive lithography-based processes for the template of Au nanostructures on Si. Furthermore, our approach can change the nanostructure by varying the parameters of film deposition and quenching. The Pt monolayer is then deposited on Au-NI by a galvanostatic exchange process. We found that the same catalytic activity shown by Si PEC devices with a thin Pt layer can be achieved when using only a Pt monolayer in the Pt/Au-NI/Si PEC device. Moreover, the Pt monolayer does not show any parasitic effect, which could contribute to the higher photocurrent density of the Si photocathodes. Conclusively, the Pt monolayer can be achieved when using only a Pt monolayer in the Pt/Au-NI/Si PEC device. Moreover, the Pt monolayer does not show any parasitic effect, which could contribute to the higher photocurrent density of the Si photocathodes.

RESULTS AND DISCUSSION

The maximum performance of Pt with minimal loading can be obtained by its nanostructuring, and this can be done by depositing an ultrathin layer of Pt on nanostructured non-noble metals on photoelectrodes. Therefore, in the present study we fabricated Au-NI on boron-doped p-type Si, which was subsequently used as a template for Pt layer deposition. The Au-NI template for the deposition of the Pt monolayer prepared by thermal Au evaporation and subsequent thermal quenching was investigated by atomic force microscopy (AFM) and scanning electron microscopy (SEM) (Figure 1). The surface morphology measurements of the as-deposited Au film on Si in Figure 1a,c show that the Au layer is compact, with certain pinholes. The Au layer surface has an average roughness of around 6 nm (Figure 1a), and the reason for this smooth film could be the deposition of Au under high vacuum conditions. The Au-NI formation after the thermal quenching is confirmed in Figure 1b. Layers by quenching are around 70 nm in diameter, with an average distance of 150 nm between the islands and an average height of the islands of around 15 nm; these dimensions are in agreement with the literature values.

Annealing at high temperature may result in the formation of gold silicide at the Au/Si interface, which affects the photoelectric properties of the Si photodecote. The formation of the Au/Si interface was studied by X-ray photoelectron spectroscopy (XPS) on the Au/Si and Au-NI/Si systems (Figure 2a,b). The Au 4f/2 and Au 4f/2 peaks are located at binding energies of ~84.1 and ~87.9 eV, with full width at half-maximum (FWHM) values of 1.1 and 1.2 eV, respectively (Figure 2a), confirming that the deposited Au film is indeed metallic. The peak position of the Au 4f/2 level is shifted by only 70 meV to a higher binding energy after the heat treatment and formation of Au-NI on Si. This small shift indicates that there is no formation of gold silicide at the Au/Si interface otherwise the shift would be expected to be around 1.1 eV due to the sd hybridization between Au and Si by charge transformation from the Au d orbital to the Si s orbital.

Both Au 4f peaks of the Au-NI data show an increase in the FWHM of ~80 meV compared to that of the as-deposited Au/Si (Figure 2a). However, this slight increase is within measurement accuracy. We suppose that the formation of gold silicide is hindered due to the presence of native SiO2 between the Si and Au layers. The presence of an intermediate SiO2 layer is evident from the core-level Si 2p XPS spectra in Figure 2b at a binding energy ~103 eV, which corresponds to SiO2 states.

Figure 2b shows the normalized Si 2p core-level XPS spectra before and after quenching of the Au/Si stack. The Si 2p peak (SiO2) intensity of Au/Si is lower than that of Au-NI/Si due to the attenuation of the Si 2p core electron in the Au film on Si, as shown in the inset (Figure 2b). After thermal quenching (i.e., Au-NI/Si), the intensity of the Si 2p peak increased because of the formation of well-separated Au-NI on Si accompanied by reduced signal attenuation compared to that of the Au film on the Au/Si stack. Hence, the formation of Au-NI on Si without gold silicide formation is confirmed from the morphology and spectroscopic analyses shown in Figures 1 and 2. A schematic diagram of the Au film deposition and subsequent formation of Au-NI on Si upon quenching is shown in Figure 2c.

Finally, the Pt monolayer is deposited on Au-NI/Si by a combination of the Cu underpotential deposition (UPD) and galvanic exchange deposition methods. The Cu2+ from the electrolyte is deposited as Cu0 on Au at an applied potential of 0.2 V (Ag/AgCl). The deposition of Cu using UPD on Au-NI/Si can be confirmed from XPS analysis of the Cu/Au/NI/Si system. The Cu 2p core-level XPS spectra (Figure 3a) of the Cu deposited by the UPD method on Au-NI/Si have a low intensity, where the signal-to-noise ratio is very low due to the deposition of only a very little amount of Cu. The Cu 2p/2 peak position at ~932.2 eV and the absence of a shake-up satellite peak at around ~942.0 eV show that the Cu is metallic after its UPD on Au-NI/Si. After the galvanic exchange of Cu by Pt, the Pt 4f XPS core levels were recorded (Figure 3b). The Pt 4f XPS spectrum possesses coincidence with the binding energy range of Au 5p1/2 (~74 eV) along with contributions from Cu 4f shake-off satellites (labeled as Au 4f8/3, 4f7/2, 4f5/2, 4f3/2, and 4f1/2).
increasing the complexity of its analysis. However, after the deposition of Pt, the Pt 4f\(_{7/2}\) peak intensity at −72.6 eV increases distinctly, which can be understood as the substitution of Cu by Pt, resulting in the transition from the Cu/Au-NI/Si system to the Pt/Au-NI/Si system. The Pt peak position at −72.6 eV further suggests that the Pt monolayer exhibits Pt\(^{2+}\) states. This finding is confirmed by the Pt 4d\(_{5/2}\) level at −316.4 eV (inset in Figure 3). The weaker signal of Pt 4f in the XPS data indicates that the thickness of the Pt overlayer on Au-NI/Si is around 1 nm.

The deposition of metal nanoislands on Si may also change the reflectance of the surface or increase the light absorption of the incident light; as a result, the PEC performance of the Si photocathode may deteriorate. Therefore, we studied the surface reflectance of these samples using ultraviolet–visible (UV–vis) spectroscopy (Figure 4). Bare Si has a reflectance of about 40% in the visible wavelength (450–800 nm), whereas for the as-deposited Au/Si, a reflectance of 60% is observed in this region. In contrast, Au-NI/Si and Pt/Au-NI/Si exhibit a relatively comparable reflectance with respect to that of bare Si.

To prove the concept of using a thin Pt monolayer on Au-NI/Si for the HER, different photocathode architectures, such as Si, Au/Si, Au-NI/Si, Pt/Au-NI/Si, and Pt/Si, were tested and compared, as shown in Figure 5. First, the influence of the Au layer on the Si photocathode performance is investigated (Figure 5a). The bare Si photocathode has an onset potential of around −620 mV (Figure 5a, gray line). The higher cathodic onset potential is due to the generation of a lower open circuit potential, which is governed by the band edge position of Si with respect to the redox potential; the noncatalytic property of Si photoelectrodes is also responsible for this higher cathodic potential. The Au film deposition on Si does not improve the PEC performance.
the photocatalytic properties, as Au is catalytically inactive for the HER. Rather, the Au film on Si decreases the photocurrent density (Figure 5a, black line) due to the higher light reflectance, as shown in Figure 4 (compare the gray with black line therein). Moreover, the interface between Au and Si can contribute to the lower current density than that of the bare Si.

However, the formation of nanoislands by thermal treatment of the Au film on Si (Au-NI/Si) results in similar reflectance to that of bare Si (Figure 4, red and gray lines). This fact might be partially supported by the similar LSV data in Figure 5a (red line), even though more parameters, such as interface properties and co-catalyst, affect the LSV characteristic. In comparison to those of the bare Si electrode, the Au-NI/Si photocathode shows a similar current density and has an onset potential shift toward the anodic direction of ∼100 mV.

The LSV of bare Si and Pt-decorated Si are compared in Figure 5b. After the deposition of the Pt nanolayer on Cu/Au-NI/Si by the galvanic exchange method, the Pt/Au-NI/Si photocathode (Figure 5b, green line) shows a large shift of the onset potential of around 500 mV toward the anodic direction in comparison to that of the bare Si electrode (Figure 5b, gray line). At a current density of −10 mA/cm², the overpotential of Pt/Au-NI/Si for the HER decreased by 700 mV with respect to that of the bare Si photocathode. This decrease shows that Pt delivers an effective catalytic enhancement even with very low loading on the nanoislands. Although Pt/Au-NI/Si shows a slightly higher reflectance (Figure 4, green line) than that of bare Si (Figure 4, gray line), the photocurrent densities of these structures are comparable. It should be noted that the reflectance cannot be directly related to the current density as the catalytic effect of the co-catalyst and the charge separation at the photoelectrode-electrolyte interface play important roles in the photocurrent density as well. Therefore, the resulting current density could be due to the catalytic effect of the Pt overlayer on the nanoislands, but also other factors may contribute. Here, we would like to mention that although the XPS shows Pt is in the 2+ oxidation state the LSV shows an even stronger catalytic effect. The catalytic effect of Pt²⁺ could be due to the coupling of the catalyst on the photocathode. Also, Pt²⁺ suppresses the back reaction in the electrochemical medium to block the oxidation of the H⁺ ion, which results in a higher HER activity. Hence, a further check of the Pt oxidation states after the HER with XPS is required to clarify this point. However, in this article, the minimal use of Pt was the main focus and no additional analytical study of the Pt oxidation state was done. The performance of reference photocathodes prepared by Pt nanoparticle deposition on Si by the electrochemical method (thin-EC-Pt/Si and thick-EC-Pt/Si) is also included in Figure 5b, and it was found that thin-EC-Pt/Si and Pt/Au-NI/Si have similar photocatalytic activities. This comparison of two different kinds of samples shows that with a significantly smaller amount of Pt co-catalyst on the nanoislands the same catalytic activity can be obtained on Si photocathodes. Consequently, this fact confirms that consumption of a minimized amount of Pt facilitates maximal performance. Moreover, an excess amount of Pt on Si can also reduce the current density due to the absorption of incident light by the Pt overlayer on Si. This can be observed in the data on the thick-EC-Pt/Si reference sample (Figure 5b, navy blue line), for which the photocurrent density is reduced due to the absorption of light by the Pt overlayer on Si. This is avoided in the Pt/Au-NI/Si photocathode. At this point, it should be emphasized that for an efficient Pt co-catalyst coated Si photocathode the optimization of size and coverage of Pt particles is still necessary, as both influence the photocatalytic activity of the Pt/Si photocathode.

Figure 4. UV−vis spectroscopy of bare Si (gray line), Au/Si (black line), Au-NI/Si (red line), and Pt/Au-NI/Si (green line), showing the surface reflectance of these photocathodes.

Figure 5. LSV in 0.1 M H₂SO₄ under illumination (solid lines) and in the dark (dotted lines) is performed on Si (gray line), Au/Si (black line), and Au-NI/Si (red line) (a), and Si (gray line), Pt/Au-NI/Si (green line), thin-EC-Pt/Si (Pt deposited by the electrochemical method for a shorter time, navy blue line), and thick-EC-Pt/Si (Pt deposited by the electrochemical method for a longer time, orange line) (b).
The long-term stability of the produced photocathodes under operating conditions was examined using the chronoamperometry test with visible light illumination. Figure 6 shows the corresponding results of Si, Pt/Au-NI/Si, Pt/Au-NI/Al2O3-Si, and Pt/Au-NI/TiO2-Si at an applied potential of −1.2 V (RHE) for 10 h. In the upper panel of Figure 6, the Si and Pt/Au-NI/Si photocathodes show an almost constant photocurrent density up to 3.5 h of illumination, followed by a decrease from −20 to −15 mA/cm² within the next 6.5 h of testing. The decrease in photocurrent density could be due to the surface oxidation of Si by the evolved O2 or photocorrosion. For PEC stability of Si photoelectrodes, their surfaces must be protected against any kind of photocorrosion or oxidation. Si photoelectrodes can be protected against PEC degradation by coating them with metal oxide ALD layers. Therefore, we use either Al2O3 or TiO2 ALD layers for the protection of the Si photoabsorber against PEC degradation. The lower panel in Figure 6 shows that the thin metal oxide ALD layer indeed results in stable photocurrent density during 10 h of experiments. The thickness of the ALD layer is normally restricted to ∼4 nm to ensure the flow of the photogenerated charge carriers through the protecting layer. An even longer stability of the photocathode can be achieved by the use of a "leaky" thicker TiO2 protection layer, whereas for Al2O3, the applicable thickness is limited to the aforementioned value due to the increasing insulating behavior with increasing thickness.

CONCLUSIONS

Our study has shown that the cost-effective, hazard-free, and nontoxic preparation method based on the combination of UPD and galvanic exchange using a Au-NI template on the Si photocathode results in an effective reduction of the catalyst loading while retaining the PEC performance for the HER achieved with a highly Pt-consuming method. Au-NI is used here as a template to deposit Pt in the form of a nanostructure. Furthermore, by changing the Au-NI size, the Pt island size can be changed to optimize the PEC performance of Pt/Au-NI/Si. The dimension of the Au-NI template can be further changed by varying the thickness of the Au intermediate layer and by thermal quenching. Moreover, the Au template is prepared here without the help of a masking process or the fluorine-based electroless deposition process. Hence, these results may strikingly contribute to the use of a minimized amount of Pt and variability of the Pt decoration on Si in the final PEC tandem device fabrication on the one hand and to the prolongation of the availability of the Pt material on the other hand. Moreover, we demonstrated that an ALD interlayer can be used to stabilize the photoelectrodes decorated with Pt/Au-NI against PEC degradation.

EXPERIMENTAL METHODS

The Pt monolayer was deposited on p-type Si combining UPD and galvanic exchange methods. For UPD, the Si was first coated with Au-NI. Prior to the deposition of Au, the boron-doped Si wafer (resistivity of 10–20 Ω cm) was diced into 1.5 × 1.5 cm² pieces and cleaned with isopropanol, acetone, and deionized water under constant sonication for 5 min each to remove surface contaminants. The p-type Si pieces always contained native SiO2 layers.

The Au deposition was carried out in high vacuum at 10⁻⁷ mbar using a Knudsen cell for evaporation. Au with a film thickness of about 8 nm was deposited on Si. Au-NI on Si (Au-NI/Si) was fabricated by applying thermal shock (thermal quenching) to the Au/Si stack, where the sample was subjected to heat treatment of 500 °C for 2 min at 10⁻⁵ mbar and then cooled to room temperature (RT).

The Au-NIs were used as the template for Pt monolayer deposition. Here, in the first step the Au-NI/Si stack was covered with a monolayer of Cu using UPD. The Cu UPD was carried out in a solution of 50 mL of 1 mM CuSO4 and 50 mM H2SO4 electrolyte at a potential of 0.2 V (Ag/AgCl) for 60 s. In the next step, the Pt monolayer was deposited on Au-NI/Si by simultaneous deposition of Pt onto and removal of Cu from the Au-NI surface. The Pt deposition was carried out by a galvanic exchange process at the open circuit potential for 3 min in a 30 mL solution of 10 mM K2PtCl4 and 0.1 M HClO4 electrolyte.

For comparison, Pt layers were deposited on Si and Au-NI/Si by an electrochemical route. A cathodic potential of −200 mV was applied to deposit Pt on Si and Au-NI/Si using a solution of 0.1 M K3PtCl4 and 0.5 M NaCl. The thin and thick layers of Pt were deposited by varying the time of deposition, and the thickness of the film was dependent on the electrodeposition time. For the thin film (i.e., thin-EC-Pt), the deposition was performed for 180 s, whereas the thick layer (i.e., thick-EC-Pt) was deposited by increasing the deposition time to 600 s. After 600 s, an optically visible thick layer of Pt was formed.

Topography measurements were performed at RT by atomic force microscopy using a Veeco CP-II AFM system in a contact mode.

SEM images were recorded with a FEI Quanta 250 FEG high-resolution scanning electron microscope operated at 20 kV.

The depositions of Au, Cu, and Pt were checked by elemental analysis using XPS in ultrahigh vacuum (3 × 10⁻⁹ mbar). A Specslab analyzer and Mg Kα X-ray source with a photon energy of 1253.6 eV were used. The spectral data were collected at a step width of 0.1 eV and a pass energy of 20 eV.

Figure 6. Stability tests of photocathodes by the chronoamperometry method. The chronoamperometry test is carried out at an applied potential of −1.2 eV (RHE) in 0.1 M H2SO4 under visible light illumination. The upper panel shows the current density vs time curve for Si and Au-NI/Si, whereas the lower panel shows the current density vs time curve of TiO2- and Al2O3-protected Pt/Au-NI/Si photocathodes.
The total reflectance spectra were recorded in the wavelength range from 200 to 900 nm using a Varian Cary 4000 spectrophotometer with a diffuse reflectance accessory; an incident beam was directed at 3°20' angle with respect to the sample normal.

The electrochemical and PEC experiments were carried out in a three-electrode bottom-cell system. A VERSTAT4 potentiostat was used to perform the electrochemical measurements, whereas Pt (wire), Ag/AgCl, and Si were used as the counter, reference, and working electrodes, respectively. For the characterization of the photoelectrodes, a light lamp from Euromex Illuminator EK1, with a light intensity of 40 mW cm⁻² at the wavelength of 580 nm, was used. The current–voltage measurements were performed using LSV, with a sweeping speed of 50 mV s⁻¹ in 0.1 M H₂SO₄ electrolyte.

To enhance the stability of the photoelectrodes, ALD layers of TiO₂ and Al₂O₃ were deposited in a home-built shower-head-type ALD reactor. Both TiO₂ and Al₂O₃ were deposited by a thermal ALD process, and the thicknesses of these layers were around 4 nm.

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**Notes**

The authors declare no competing financial interest.

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**REFERENCES**

(1) May, M. M.; Lewerenz, H.-J.; Lackner, D.; Dimroth, F.; Hannappel, T. Efficient direct solar-to-hydrogen conversion by in situ interface transformation of a tandem structure. Nat. Commun. 2015, 6, No. 8286.
(2) Walter, M. G.; Warren, E. L.; McKeone, J. R.; Boettcher, S. W.; Mi, Q.; Santori, E. A.; Lewis, N. S. Solar Water Splitting Cells. Chem. Rev. 2010, 110, 6446–6473.
(3) Hu, s.; Lewis, N. S.; Ager, J. W.; Yang, J.; McKeone, J. R.; Strawnitz, N. C. Thin-Film Materials for the Protection of Semiconductor Photoelectrodes in Solar-Fuel Generators. J. Phys. Chem. C 2015, 119, 24201–24228.
(4) Maier, C. U.; Specht, M.; Bilger, G. Hydrogen evolution on platinum-coated p-silicon photocathodes. Int. J. Hydrogen Energy 1996, 21, 859–864.
(5) Oh, J.; Deutsch, T. G.; Yuan, H.-C.; Branz, H. M. Nanoporous Black Silicon Photocathode for H₂ Production by Photoelectrochemical Water Splitting. Energy Environ. Sci. 2011, 4, 1690–1694.
(6) Rodriguez, C. C.; Modestino, M. M. A.; Moser, C.; Psaltis, D. Design and cost considerations for practical solar-hydrogen generators. Energy Environ. Sci. 2014, 7, 3828–3835.
(7) Zou, X.; Zhang, Y. Noble metal-free hydrogen evolution catalysts for water splitting. Chem. Soc. Rev. 2015, 44, S148–S1580.
(8) Kempenain, E.; Bodin, A.; Sebok, B.; Pedersen, T.; Seger, B.; Mei, B.; Bae, D.; Vesborg, P. C. K.; Hâlme, J.; Hansen, O.; Lund, P. D.; Chorkendorff, I. Scalability and feasibility of photoelectrochemical H₂ evolution: the ultimate limit of Pt nanoparticle as an HER catalyst. Energy Environ. Sci. 2015, 8, 2991–2999.
(9) Vesborg, P. C. K.; Jaramillo, T. F. Addressing the terawatt challenge: scalability in the supply of chemical elements for renewable energy. RSC Adv. 2012, 2, 7933–7947.
(10) Dai, P.; Xie, J.; Mayer, M. T.; Yang, X.; Zhan, J.; Wang, D. Solar hydrogen generation by silicon nanowires modified with platinum nanoparticle catalysts by atomic layer deposition. Angew. Chem., Int. Ed. 2013, 52, 11119–11123.
(11) Dasgupta, N. P.; Lu, X.; Andrews, S.; Prinz, F. B.; Yang, P. Atomic layer deposition of platinum catalysts on nanowire surfaces for photoelectrochemical water reduction. J. Am. Chem. Soc. 2013, 135, 12932–12935.
(12) Kye, J.; Shin, M.; Lim, B.; Jang, J. W.; Oh, J.; Huang, S. Platinum Monolayer Electrocatalyst on Gold Nanostructures on Silicon for Photoelectrochemical Hydrogen Evolution. ACS Nano 2013, 7, 6017–6023.
(13) Fabre, B.; Hennous, L.; Girard, S. A.; Meriadeck, C. Electroless Patterned Assembly of Metal Nanoparticles on Hydrogen-Terminated Silicon Surfaces for Applications in Photoelectrolysis. ACS Appl. Mater. Interfaces 2013, 5, 338–343.
(14) Sui, M.; Li, M.-Y.; Kim, E.-S.; Lee, J. Annealing temperature effect on self-assembled Au droplets on Si (111). Nanoscale Res. Lett. 2013, 8, 525.
(15) Lee, J.; Pandey, P.; Sui, M.; Li, M.-Y.; Zhang, Q.; Kunwar, S. Evolution of Self-Assembled Au NPs by Controlling Annealing Temperature and Dwellling Time on Sapphire (0001). Nanoscale Res. Lett. 2015, 10, 494.
(16) Seah, M. P.; Smith, G. C.; Anthony, M. T. AES: Energy calibration of electron spectrometers. I—an absolute, traceable energy calibration and the provision of atomic reference line energies. Surf. Interface Anal. 1990, 15, 293–308.
(17) Lu, Z. H.; Sham, T. K.; Norton, P. R. Interaction of Au on Si(100) Studied by Core Level Binding Energy Shifts. Solid State Commun. 1993, 85, 957.
(18) Sohn, Y.; Pradhan, D.; Radi, A.; Leung, K. T. Interfacial Electronic Structure of Gold Nanoparticles on Si(100): Alloying versus Quantum Size Effects. Langmuir 2009, 25, 9557–9565.
(19) Schön, G. ESCA studies of Cu, CuO and CuO. Surf. Sci. 1973, 59, 96–108.
(20) Kim, S. H.; Jeong, H.; Kim, J.; Lee, I. S. Fabrication of Supported AuPt Alloy Nanocrystals with Enhanced Electrocatalytic Activity for Formic Acid Oxidation through Conversion Chemistry of Layer-Deposited Pt²⁺ on Au Nanocrystals. Small 2015, 11, 4884–4893.
(21) Prieto, M. J.; Filho, U. P. R.; Landersb, R.; Filho, G. T. The ethanol electrooxidation at Pt layers deposited on polycrystalline Au. Phys. Chem. Chem. Phys. 2012, 14, 599–606.
(22) Warren, E. L.; Boettcher, S. W.; Walter, M. G.; Atwater, H. A.; Lewis, N. S. pH-Independent, 520 mV Open-Circuit Voltages of Si/H₂ Production by Photoelectrochemical Water Splitting. Energy Environ. Sci. 2013, 6, 5994–5998.
(23) Hou, Y.; Abrams, B. L.; Vesborg, P. C.; Björkstun, M. E.; Herbst, K.; Bech, L.; Setti, A. M.; Damsgaard, C. D.; Pedersen, T.; Hansen, O.; Rossmeissl, J.; Dahl, S.; Norskov, J. K.; Chorkendorff, I. Bioinspired molecular co-catalysts bonded to a silicon photocathode for solar hydrogen evolution. Nat. Mater. 2011, 10, 434–8.
(24) Smiljanic, M.; Srejic, I.; Grugr, B.; Rakovec, Z.; Štrbac, S. Catalysis of Hydrogen Evolution on Au(111) Modified by Spontaneously Deposited Pd Nanoclustes. Electrocatalysis 2012, 3, 369–375.
(25) Li, Y. H.; Xing, J.; Chen, Z. J.; Li, Z.; Tian, F.; Zheng, L. R.; Wang, H. F.; Hu, P.; Zhao, H. J.; Yang, H. G. Unidirectional suppression of hydrogen oxidation on oxidized platinum clusters. Nat. Commun. 2013, 4, No. 2500.
(26) Xing, J.; Jiang, H. B.; Chen, J. F.; Li, Y. H.; Hu, L.; Yang, S.; Zheng, L. R.; Wang, H. F.; Hu, P.; Zhao, H. J.; Yang, H. G. Active sites on hydrogen evolution photocathode. J. Mater. Chem. A 2013, 1, 15258–15264.
(27) Lombardi, I.; Marchionna, S.; Zangari, G.; Pizzini, S. Effect of Pt Particle Size and Distribution on Photoelectrochemical Hydrogen Evolution by p-Si Photocathodes. Langmuir 2007, 23, 12413–12420.
(28) Choi, M. J.; Jung, J. Y.; Park, M. J.; Song, J. W.; Lee, J. H.; Bang, J. H. Long-term durable silicon photocathode protected by a thin Al2O3/SiOx layer for photoelectrochemical hydrogen evolution. J. Mater. Chem. A 2014, 2, 2928−2933.

(29) Scheuermann, A. G.; McIntyre, P. C. Atomic Layer Deposited Corrosion Protection: A Path to Stable and Efficient Photo-electrochemical Cells. J. Phys. Chem. Lett. 2016, 7, 2867−2878.

(30) Das, C.; Tallarida, M.; Schmeisser, D. Si microstructures laminated with a nanolayer of TiO2 as long-term stable and effective photocathodes in PEC devices. Nanoscale 2015, 7, 7726−7733.

(31) Hu, S.; Shaner, M. R.; Beardslee, J. A.; Lichterman, M.; Brunswig, B. S.; Lewis, N. S. Amorphous TiO2 coatings stabilize Si, GaAs, and GaP photoanodes for efficient water oxidation. Science 2014, 344, 1005−1009.

(32) Hachiya, T.; Honbo, H.; Itaya, V. Detailed underpotential deposition of copper on gold(III) in aqueous solutions. J. Electroanal. Chem. Interfacial Electrochem. 1991, 315, 275−291.

(33) Brankovic, S. R.; Wang, J. X.; Adžić, A. R. Metal monolayer deposition by replacement of metal adlayers on electrode surfaces. Surf. Sci. 2001, 474, L173−L179.

(34) Koda, R.; Fukami, K.; Sakka, T.; Ogata, Y. H. Electrodeposition of platinum and silver into chemically-modified microporous silicon electrodes. Nanoscale Res. Lett. 2012, 7, 330.

(35) Das, C.; Henkel, K.; Tallarida, M.; Schmeißer, D.; Gargouri, H.; Kärkkäinen, I.; Schneidewind, J.; Gruska, B.; Arens, M. Thermal and plasma enhanced atomic layer deposition of TiO2: Comparison of spectroscopic and electric properties. J. Vac. Sci. Technol., A 2015, 33, No. 01A144.

(36) Das, C.; Richter, M.; Tallarida, M.; Schmeißer, D. Electronic properties of atomic layer deposition films, anatase and rutile TiO2 studied by resonant photoemission spectroscopy. J. Phys. D: Appl. Phys. 2016, 49, No. 275304.