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Construction of Mono- and Multimolecular Layers with Electron Transfer Mediation Function and Catalytic Activity for Hydrogen Evolution on a Hydrogen-Terminated Si(111) Surface via Si–C Bond

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Organic molecular layers with viologen moiety (i.e., electron acceptor) were constructed on a hydrogen-terminated Si(111) surface via a Si–C bond. Electrochemical characteristics after each synthetic process were measured, and electron mediation capability of the viologen moiety was demonstrated. Incorporation of platinum particles on the viologen-modified Si(111) surface was proved to enhance the hydrogen evolution reaction (HER) rate. Further improvement of the HER rate was achieved by the modification with viologen/Pt multilayers. Photoelectrochemical HER at the p-Si(111) electrode was also significantly accelerated by the modification with mono- and multiviologen/Pt layers.

Introduction

Construction of molecular layers on solid surfaces has attracted much attention not only because it is important from a fundamental science point of view but also because it is a key technique for a wide range of applications such as molecular and biomolecular electronic devices, catalysis, and sensors.

Although the most studied molecular layer system is self-assembled monolayers (SAMs) of alkanethiols on various metals, especially on gold,1–5 ordered molecular layers with various functionalities on semiconductor, particularly Si, surfaces should be more important for technological applications. For example, a monolayer with electron transfer function on Si is very important as far as the application for molecular devices,6 sensors,7 photoelectrochemistry,8–10 bioelectrochemistry,11 and electrocatalysis12–14 are concerned. Organic monolayer can be formed on Si surface via direct Si–C bond utilizing thermal photochemical,24,25 electrochemical,26–28 or catalytic reaction28,29 or reaction with radical initiators.18,27,31,32 We investigated the organic monolayer formation process on a hydrogen-terminated Si(111) by using attenuated total reflectance Fourier transform infrared (ATR FT-IR) and sum frequency generation spectroscopy31 and also found that organic monolayers formed on Si(111) surfaces are in a relatively high conformational order as alkanethiol SAMs on Au(111).32

Both theoretical and experimental understandings of photovoltaic reactions at semiconductor surfaces have been significantly progressed in the past 30 years because of the interest in solar energy conversion.33,34 Photo-induced water splitting at the semiconductor surface is the most important photovoltaic reaction.35,36 To construct a highly efficient and stable solar energy conversion/storage system,37,38 One of the most critical issues is that the semiconductor surface is usually not suitable for multielectron processes such as oxidation and reduction of water, and appropriate catalysts are required to drive these processes efficiently.

Although many groups reported that p-type semiconductor electrodes coated with thin noble metal layers efficiently generated hydrogen under illumination,36–38 modification of a semiconductor surface with a continuous metallic layer often resulted in a low efficiency because of the semiconductor/metal Schottky barrier formation.39,40 It was suggested that the modification with discontinuous metallic islands (i.e., nanoparticles) has an advantage for photoelectrochemical hydrogen evolution reaction (HER) because the barrier height of a semiconductor/metal junction can be controlled by the size and density of the metal nanoparticles.37,41–47 Unfortunately, however, this approach has several problems. Photoelectrochemical efficiency of the electrode was degraded because of lower coverage of the metal layer and, furthermore, the modification of semiconductor surface with discontinuous metal also sometimes leads to a significant loss of photoelectrochemical HER current because the metal acts as a recombination center.48,49 To provide a solution to these problems, various groups used polymer layers with electron mediator groups and catalytic metal particles to modify the semiconductor surfaces.50–59

Recently, we briefly demonstrated that an organic monolayer with viologen terminal group bonded on hydrogen-terminated n- and p-type Si(111) surfaces via a Si–C bond acted as electron transfer mediator and improved the electrochemical hydrogen evolution reaction rate in the dark and under illumination, respectively.50 Nakato and colleagues also showed that the stability of the Si photoelectrode for I− oxidation was improved by P/alkyl monolayer modification.13,14 Here, we investigated in detail the construction processes of organic monolayers with viologen moieties. In addition, we also studied with multilayer layers, on n- and p-type Si(111) electrodes and the electrochemical characteristics of the modified n- and p-Si(111) electrodes in the dark and under illumination, respectively. After each modification step, surfaces were characterized by XPS, ellipsometry, and ATR FT-IR, and electrochemical characteristics were measured.

Electron mediation capability of “wired” viologen moieties was
demonstrated, and significant enhancement of the (photo)electrochemical hydrogen evolution reaction rate was achieved by incorporating Pt particles at the mono- and multiviologen layer modified Si(111) surface.

**Experimental Section**

**Materials.** Ultrapure nitrogen (99.9995%) and argon (99.999%) were purchased from Air-Water. Ultrapure-grade sulfuric acid and potassium chloride and reagent-grade sodium sulfate, hydrochloric acid, hydrofluoric acid, hydrogen peroxide, benzene, ethanol, potassium tetrachloroplatinate(II), 1-bromobutane and 1,4-dibromobutane, triethylamine (TEA), 4-vinylbenzylchloride (4VBC), 1-decene, and 4,4′-bipyridine from Aldrich, methyl iodide from Tokyo Kasei, ultrapure-grade methylene chloride (dichloromethane), dimethylformamide from Dojin laboratory, and special grade (for semiconductor industries) ammonium fluoride from Morita Chemical were used as received except for 4VBC, which was purified by vacuum distillation before use. Water was purified using a Milli-Q system (Yamato, WQ-500). Ag (99.99%) and Pt wires (99.99%) were purchased from Nilaco.

Double-side polished Si(111) single-crystal wafers of 100 mm in diameter, 480 µm in thickness, and resistivity of 1–10 Ω cm (n-type; phosphorus-doped, p-type; boron-doped) were donated by Shin-Etsu Semiconductor. The silicon wafers were treated as follows immediately before using. Si wafers were cleaned with acetone and then with Milli-Q water several times in an ultrasonic bath for 5 min each time. Silicon substrates for the electrochemical and the X-ray photoelectron spectroscopic measurements were square (10 × 10 mm²). Parallelogram ATR prisms (28 × 35 × 0.48 mm³) were prepared by cutting and polishing with 45° bevies.

The Si(111) substrate was cleaned by sequential immersion of the sample in freshly prepared sulfuric acid and hydrogen peroxide (2:1 by volume) at 60 °C for 5 min in an aqueous solution of 0.5% hydrofluoric acid at room temperature (RT) for 5 min and in freshly prepared RCA solution (water/hydrogen peroxide/hydrochloric acid, 4:1:1 by volume) at 80 °C for 20 min. After these treatments, the sample was immersed in deaerated aqueous solution of 40% ammonium fluoride for 5 min to obtain a monohydride-terminated surface, H−Si(111).61,62

**Synthesis.** 1-Methyl-4-(4′-pyridyl)-pyridinium iodide (MQ) was synthesized by refluxing 4,4′-bipyridine and methyl iodide in benzene under Ar atmosphere overnight. An orange solid was precipitated from solution after cooling. The solution was filtered to collect the orange solid, followed by washing with benzene and hexane. The solid was dissolved in acetonitrile and filtered to remove any insoluble product. Acetonitrile was removed by evaporation to yield the desired product. Structure and purity of the product were confirmed by nuclear magnetic resonance.

**Formation of Molecular Layers.** Monoviologen-layer formation was performed as shown in Scheme 1.60 A freshly prepared H−Si(111) substrate was illuminated with 254-nm light (∼1 mW cm⁻²) for 24 h in deaerated 4VBC in the Ar-filled glovebox to yield a 4-ethylbenzylchloride (EBC)-modified Si(111) surface (Scheme 1, step i). The substrate was then rinsed with deaerated dichloromethane followed by sonication in dichloromethane for 10 min twice. EBC-Si(111) substrate was kept in MQ-saturated DMF solution at 100 °C under Ar atmosphere for 20 h to yield a viologen-modified (V²⁺-Si(111)) surface (Scheme 1, step ii). TEA, which is an electroinactive species, was also attached to the EBC-Si(111) surface as shown in Scheme 2. The EBC-Si(111) substrate was refluxed in TEA under Ar atmosphere for 20 h to yield a (4-ethylbenzyl)triethylammonium chloride-modified (EBTEA-Si(111)) surface (Scheme 1, step ii). 1-Decene was reacted with H−Si(111) in neat 1-decene at reflux temperature for 50 h to yield a decyl-modified Si(111) surface (C₁₀-Si(111)).

Multiviologen-layer was formed as shown in Scheme 3. The EBC-Si(111) substrate was kept in a 4,4′-bipyridine-saturated benzene solution at reflux temperature under Ar atmosphere for 12 h (Scheme 3, step i).
SCHEME 3: Steps for Construction of a Multiviologen Layer on H–Si(111) (V$_{2}^{2+}$–Si(111)) and Deposition of Pt (Pt–V$_{2}^{2+}$–Si(111))

1. The substrate was placed in H$_2$-saturated water for 20 min. Because there is a possibility that V$_{2}^{2+}$ aqueous solution of 0.1 M HCl for 30 s to reoxidize V$^{•+}$. The Si(111) substrates after each modification step were rinsed with water, ethanol, and dichloromethane.

2. The V$_{2}^{2+}$ substrate was immersed in an 10 mM K$_2$PtCl$_4$ aqueous solution for 20 min to ion exchange the halide ions of the viologen groups (Scheme 1, step iii) or EBTEA–Si(111) surface (Scheme 2, step iii) by keeping the substrate in a H$_2$-saturated water for 20 min. Because there is a possibility that V$_{2}^{2+}$ was reduced to V$^{•+}$ during the reduction of PtCl$_4^{2-}$, the Pt–V$_{2}^{2+}$–Si(111) substrate was immersed in an aqueous solution of 0.1 M HCl for 30 s to reoxidize V$^{•+}$ to V$_{2}^{2+}$.

3. The 3L or 5L–V$_{2}^{2+}$–Si(111) substrate was immersed in an aqueous solution of 10 mM K$_2$PtCl$_4$ for 20 min to ion exchange the halide ions of the viologen groups by PtCl$_4^{2-}$ (Scheme 3, step iii) or EBTEA–Si(111) surface (Scheme 2, step iii) by keeping the substrate in a H$_2$-saturated water for 20 min so that PtCl$_4^{2-}$ was reduced to Pt to yield a 3L- or 5L–V$_{2}^{2+}$–Si(111) surface (Scheme 3, step iv). The Si(111) substrates after each modification step were rinsed with water, ethanol, and dichloromethane.

4. The substrate was placed in 1-bromobutane under Ar atmosphere at 100 °C for 12 h (Scheme 3, step ii) then in 4,4′-bipyridine-saturated benzene solution at reflux temperature for 12 h (Scheme 3, step iii). After repeating the modification steps ii and iii alternately for 2 or 4 times so that the monolayer was terminated with bipyridine group, the modification steps ii and iii alternately for 2 or 4 times so that the monolayer was terminated with bipyridine group, the substrate was kept in 1-bromobutane under Ar atmosphere at 100 °C for 12 h to yield a 3L- or 5L–V$_{2}^{2+}$–Si(111) surface (Scheme 3, step v). The Si(111) substrates after each modification step were rinsed with water, ethanol, and dichloromethane.

5. The 3L or 5L–V$_{2}^{2+}$–Si(111) substrate was placed in a H$_2$-saturated water for 20 min. After repeating the modification steps ii and iii alternately for 2 or 4 times so that the monolayer was terminated with bipyridine group, the substrate was kept in 1-bromobutane under Ar atmosphere at 100 °C for 12 h to yield a 3L- or 5L–V$_{2}^{2+}$–Si(111) surface (Scheme 3, step vi). The Si(111) substrates after each modification step were rinsed with water, ethanol, and dichloromethane.

6. The substrate was placed in 4,4′-bipyridine-saturated benzene solution at reflux temperature for 12 h (Scheme 3, step iii). After repeating the modification steps ii and iii alternately for 2 or 4 times so that the monolayer was terminated with bipyridine group, the substrate was kept in 1-bromobutane under Ar atmosphere at 100 °C for 12 h to yield a 3L- or 5L–V$_{2}^{2+}$–Si(111) surface (Scheme 3, step iv). The Si(111) substrates after each modification step were rinsed with water, ethanol, and dichloromethane.
Results and Discussion

Formation and Characterization of Molecular Layers. Figures 1 and 2 show XP spectra of wide scan and narrow scan in Si 2p region, respectively, of (a) H–Si(111), (b) EBC–Si(111), (c) V^{2+}–Si(111), and (d) Pt–V^{2+}–Si(111) surfaces.

H–Si(111) Surface. The wide-scan XP spectra (Figure 1a) showed peaks corresponding to Si2p, Si2s, Cl1s, and O1s around 100, 150, 285, and 530 eV, respectively, and no other peaks corresponding to elements such as fluorine at the H–Si(111) surface. The C1s and O1s peaks should be due to the surface contamination. Only a peak corresponding to Si0 at 99.4 eV was observed in the wide-scan XP spectrum of the EBC–Si(111) surface (Figure 1c), implying the formation of a thin Si oxide layer at this modification step. In the ATR FT-IR spectrum of the EBC–Si(111) surface (Figure 3b), intensity of the broad band due to the C–H stretching vibration of the symmetric methyl group, respectively, and a broad band between 3000 and 3100 cm\(^{-1}\) corresponding to the C–H stretching vibration of benzene ring were observed. These results support the formation of the EBC layer on the Si(111) surface via Si–C covalent bond without any Si oxide layer. Ellipsometric thickness of the EBC layer was determined to be 1.1 nm, which is in good agreement with the molecular length of 4-ethylbenzylchloride.

Attachment of a Viologen Group to the EBC–Si(111) Surface and Formation of a Multiviologen Layer. After the modification step ii of Scheme 1 (i.e., V^{2+}–Si(111)), a wide-scan XP spectrum (Figure 1c) shows the significant decrease of Si2s and Si2p peaks and a new peak around 103 eV was absent in the XP spectra in the Si 2p region (Figure 2b). In the ATR FT-IR spectrum of the EBC–Si(111) surface (Figure 3b), the Si–H peak disappeared and two bands at 2852 and 2923 cm\(^{-1}\) corresponding to the C–H stretching vibration of the symmetric and asymmetric methylene group, respectively, and a broad band between 3000 and 3100 cm\(^{-1}\) corresponding to the C–H stretching vibration of benzene ring were observed. These results confirm the attachment of viologen to the EBC layer on the Si(111) surface via Si–C covalent bond without any Si oxide layer. Ellipsometric thickness of the EBC layer was determined to be 1.1 nm, which is in good agreement with the molecular length of 4-ethylbenzylchloride.

Attachment of the Triethylamine Group to the EBC–Si(111) Surface. There is no remarkable difference in features of the wide-scan XP spectrum of the EBTEA–Si(111) surface (after

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\text{H--Si(111)_Surface. The wide-scan XP spectra (Figure 1a) showed peaks corresponding to Si2p, Si2s, Cl1s, and O1s around 100, 150, 285, and 530 eV, respectively, and no other peaks corresponding to elements such as fluorine at the H--Si(111) surface. The C1s and O1s peaks should be due to the surface contamination. Only a peak corresponding to Si0 at 99.4 eV was observed in the wide-scan XP spectrum of the EBTEA--Si(111) surface (Figure 1c), implying the formation of a thin Si oxide layer at this modification step. In the ATR FT-IR spectrum of the EBTEA--Si(111) surface (Figure 3b), intensity of the broad band due to the C--H stretching vibration of the asymmetric methylene group was increased and a new band at 2983 cm\(^{-1}\) corresponding to the C--H stretching vibration of the asymmetric methyl group was observed. These results confirm the attachment of viologen to the EBC layer on the Si(111) surface via Si--C covalent bond without any Si oxide layer. Ellipsometric thickness of the EBC layer was determined to be 1.1 nm, which is in good agreement with the molecular length of 4-ethylbenzylchloride.}

\(\text{Attachment of a Viologen Group to the EBC--Si(111)_Surface and Formation of a Multiviologen Layer. After the modification step ii of Scheme 1 (i.e., V^{2+}--Si(111)), a wide-scan XP spectrum (Figure 1c) shows the significant decrease of Si2s and Si2p peaks and a new peak around 103 eV corresponding to N1s. A small Si^{2+} peak was observed in the Si 2p region (Figure 2c), implying the formation of a thin Si oxide layer at this modification step. In the ATR FT-IR spectrum of the V^{2+}--Si(111) surface (Figure 3c), intensity of the broad band due to the C--H stretching vibration of the benzene ring increased and a new band at 2983 cm\(^{-1}\) corresponding to the C--H stretching vibration of the asymmetric methyl group was observed. These results confirm the attachment of viologen to the EBC layer on the Si(111) surface via Si--C covalent bond without any Si oxide layer. Ellipsometric thickness of the V^{2+}--Si(111) surface was determined to be 2.8, 5.6, and 8.6 nm, respectively, as shown by filled circles in Figure 7(b). These values are in good agreement with those evaluated from the sums of lengths of molecules in the respective molecular layers. }

\(\text{Attachment of the Triethylamine Group to the EBC--Si(111)_Surface. There is no remarkable difference in features of the wide-scan XP spectrum of the EBTEA--Si(111) surface (after}
(74.3 eV) peaks observed for bulk metallic platinum are metallic Pt, Pt 4f peaks of the Pt marked by solid lines. Although the positions of Pt 4f peaks of the XP spectrum in the Si 2p region of the EBTEA for shapes of those in the N 1s region. While a narrow-scan at the V2+ and (b) V2+–Si(111) surfaces. Figure 4. XP spectra in the Pt 4f region of the (a) Pt–EBTEA–Si(111) and (b) Pt–V2+–Si(111) surfaces.

Figure 5. XP spectra in the Pt 4f region of the (a) Pt–EBTEA–Si(111) and (b) Pt–V2+–Si(111) surfaces.

Incorporation of Pt. Pt 4f peak was observed around 70 eV of Pt–EBTEA–Si(111) surface except for shapes of those in the N 1s region. While a narrow-scan XP spectrum in the Si 2p region of the EBTEA–Si(111) surface (not shown) is similar to that of the V2+–Si(111) surface, XP spectra in the N 1s region of the (a) EBTEA– and (b) V2+–Si(111) surfaces are somewhat different, as shown in Figure 4. Although a single peak at 402.2 eV corresponding to nitrogen of benzyltriethylammonium chloride was observed at the EBTEA–Si(111) surface (Figure 4a), two peaks around 400.2 and 402.0 eV corresponding to nitrogen species of pyridinium iodide and chloride, respectively, were observed at the V2+–Si(111) surface (Figure 4b).

Electrochemical Characteristics of Viologen Moeities of the V2+–, 3L-V2+–, and 5L-V2+–Si(111) Electrodes. Figure 7a shows the CVs of the EBC, V2+–, 3L-V2+–, and 5L-V2+–n-type Si(111) electrodes measured in a 0.1 M Na2SO4 aqueous solution at a scan rate of 50 mV s−1. Two cathodic peaks were observed around –0.50 and –0.85 V corresponding to V2+/V+ and V+/V+, respectively, at the V2+–, 3L-V2+–, and 5L-V2+–Si(111) electrodes, whereas no peak was observed at the EBC–Si(111) electrode. Anodic peaks of viologen moieties are somewhat smaller than the corresponding cathodic peaks, reflecting the fact that the majority carrier is electron and the anodic process is inhibited at an n-type semiconductor electrode.

Surface concentrations of electroactive viologen moieties at the V2+–, 3L-V2+–, and 5L-V2+–Si(111) electrodes were estimated from the charge obtained by integrating the cathodic peak (open circles) of the first CV to be 3.1 × 10−10, 8.9 × 10−10, and 1.4 × 10−9 mol cm−2, respectively, and linearly increased with number of viologen layers by ca. 2.8 × 10−10 mol cm−2 per layer as shown in Figure 7b. Ellipsometric thick of the molecular layer at the EBC–, V2+–, 3L-V2+–, and 5L-V2+–Si(111) surfaces also linearly increased with the number of layers, as shown in Figure 7b. These results show that the formation of the multiviologen layer proceeded in layer-by-layer fashion with almost 100% yield and all viologen groups in the molecular layers are electroactive. The amount of viologen moiety per layer is a little smaller than the maximum coverage estimated from the surface-projected size of the perpendicular oriented bipyridyl group, 3.7 × 10−10 mol cm−2.

Although viologen multilayers have been previously constructed on gold52 and silicon58 substrates by using viologen molecules with two alkyl thiol and two alkyl trimethoxysilyl groups, respectively, at both ends, the present multilayer formation process is far better controlled than these cases where multilayers are formed via intermolecular disulfide formation or condensation of trimethoxysilyl groups, which takes place randomly at any molecule with free thiol or trimethoxysilyl groups both at the surface and in the solution. The strategy of layer-by-layer growth can be also used for other tailor-made multifunctional layers by choosing appropriate molecules as building blocks.

Electrochemical Hydrogen Evolution at Modified n-Si(111) Electrodes in the Dark. Figure 8 shows quasi-steady-state current–voltage (I–V) curves obtained in the dark with a very slow scan rate (1 mV s−1) in a 0.1 M Na2SO4 aqueous solution at a n-type Si(111) electrode after each modification step. At the H–Si(111) electrode, the cathodic current started to flow from around –0.6 V. Since steady current was observed,
the current should be due to HER. At the EBC–Si(111) electrode, the HER current started to flow at more negative potential than at the H–Si(111) electrode and the I–V curve shifted negatively by about 0.1 V, showing that the EBC layer acts as an electron transfer barrier. Although an additional layer was attached and thickness of the molecular layer increased by ca. 1.7 nm, the HER rate at the V\textsuperscript{2+}–Si(111) electrode was increased and the I–V curve shifted positively by 0.1 and 0.2 V from the ones at the H–Si(111) and EBC–Si(111) electrodes, respectively. On the other hand, the HER rate at the EBTEA–Si(111) electrode became significantly slower than the ones at the H–Si(111) and EBC–Si(111) electrodes, showing that the electroinactive EBTEA moiety acts as a more effective barrier. These results suggest that the electron transfer was mediated by the viologen moiety in the organic monolayer. A much smaller current was observed at the C\textsubscript{10}–Si(111) electrode because the barrier is thicker than the EBTEA–Si(111) and the alkyl chain is more insulating than the aromatic group.

Figure 9 shows quasi-steady-state I–V curves of the n-type EBTEA–, Pt–EBTEA–, V\textsuperscript{2+}–, Pt–V\textsuperscript{2+}–, 3L–Pt–V\textsuperscript{2+}–, and 5L–Pt–V\textsuperscript{2+}–Si(111) electrodes obtained in the dark with very slow scan rate (1 mV s\textsuperscript{-1}) in a 0.1 M Na\textsubscript{2}SO\textsubscript{4} aqueous solution. The I–V curve shifted in a positive direction by 0.2 and 0.5 V at the EBTEA– and V\textsuperscript{2+}–Si(111) electrode by platinum deposition on surfaces, proving that the Pt particles on the Si(111) surfaces served as a catalyst for HER. A potential shift by Pt deposition at the V\textsuperscript{2+}–Si(111) electrode larger than that at the EBTEA–Si(111) electrode also proved the electron transfer mediation capability of the viologen moiety. At the Pt–V\textsuperscript{2+}–Si(111) electrodes, electrons are used to reduce viologen moiety and reduced viologen was oxidized to viologen by H\textsuperscript{+} with Pt catalyst because the redox potential of V\textsuperscript{2+}/V\textsuperscript{+} is more negative than that of H\textsuperscript{+}/H\textsubscript{2}, resulting in the hydrogen evolution as shown by the following equations.

\begin{equation}
V\textsuperscript{2+} + e^- \rightarrow V^+ \quad (1)
\end{equation}

\begin{equation}
2V^{+} + 2H^+ \rightarrow H_2 \quad (2)
\end{equation}

Thus, the viologen moiety acts as an electron-transfer mediator for hydrogen evolution reaction at the Pt nanoparticles. On the other hand, electrons must tunnel through the electroinactive barrier layer at the Pt–EBTEA–Si(111) electrode to the Pt catalyst, resulting in the relatively slow HER rate. In addition, the extremely small size of the Pt nanoparticles formed at the Pt–V\textsuperscript{2+}–Si(111) electrode may play an important role in high catalytic activity for HER. Furthermore, the Pt–V\textsuperscript{2+}–Si(111) electrode was stable as the HER current at −0.9 V remained constant even after the potential was scanned between −0.9 and −0.1 V five times. One reason for this stability should be because the Pt nanoparticles were present within the molecular layer with low mobility.

The I–V curve shifted positively (i.e., HER rate increased) as the number of the viologen/Pt layers increased. This shows
that the Pt particles dispersed within the viologen multilayers effectively acted as the HER catalyst although the distance from the electrode to the Pt particles increased with number of layers, confirming that viologen groups within the multilayer formed a network for a supply of electrons from the Si(111) electrode to the Pt particles. Thus, HER is efficiently accelerated at the Pt particles.

**Photoelectrochemical Hydrogen Evolution at Modified p-Si(111) Electrodes.** Figure 10 shows quasi-steady-state $I-V$ curves of the p-type $H^-$ (○), EBC–(●), $V_{2}^{2-}$ (△), Pt–$V_{2}^{2-}$ (●), 3L–Pt–$V_{2}^{2-}$ (○), and 5L–Pt–$V_{2}^{2-}$–Si(111) (●) electrodes under photoillumination in 0.1 M Na$_2$SO$_4$ aqueous solution. Inset: Energy diagram for the hydrogen evolution reaction at the p-Si(111) modified with Pt/viologen layers. The dotted line shows the reversible potential of $H^+$/H$_2$.

**Conclusions.** Mono- and multiviologen layers were constructed on hydrogen-terminated Si(111) surfaces via a Si–C bond in a layer-by-layer fashion, and electron mediation capability of the viologen moiety was demonstrated. Very small, well-dispersed Pt particles were formed within the viologen layers by ion exchange of halide ions by PtCl$_4^{2-}$ followed by reduction hydrogen gas. Electrocatalytic HER rates in the dark and under illumination were significantly enhanced by the Pt deposition. HER rate increased with the increase of the number of viologen/Pt layers, showing that all attached viologen moieties and Pt particles served as electron mediator and catalyst for HER, respectively.

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**References and Notes**
