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Controlling the Schottky barrier at the Pt/TiO₂ Interface by Intercalation of Self-Assembled Monolayer with Oriented Dipole Moments

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ABSTRACT. Interfacial Schottky barriers can impact the catalytic function of Pt on TiO₂. Since the electronic structure is characteristic of each material, it may be advantageous to tailor the interfacial Schottky barrier by addition of adsorbed layers. Here, we show that the Schottky barrier in Pt/TiO₂ can be mitigated by insertion of self-assembled monolayers (SAM) of carboranethiols which possesses an oriented dipole moment. A Pt substrate with the SAM on which TiO₂ nanoparticles are deposited is used to that effect. Kelvin Probe Force Microscopy shows that *m*-9-carboranethiolate SAM with perpendicular dipole moments decrease the potential difference between TiO₂ and Pt by ~0.3 eV due to the interfacial electric field of the SAM. Our findings open new opportunities for tailoring interfacial electronic structures, not only in metal-semiconductor junction, but also semiconductor heterojunctions.

TOC GRAPHICS

KEYWORDS. Schottky junction, Kelvin probe force microscopy, Pt/TiO₂ interface, Self-assembled monolayer, Carboranethiol.

INTRODUCTION

Recently, the metal-support interaction in heterogeneous catalysts, especially electronic metal-support interaction (EMSI), is gathering attention for development of nonconventional catalysts, where the electronic structure of support materials with nanoparticles of metal catalysts is crucial for adsorption of substances, redox properties, and so on. Especially, Pt/TiO₂ heterojunction system has been widely investigated for applications in (photo-)catalysis²⁻⁶ and as sensors⁷⁻¹⁰. A Schottky barrier is formed at the interface of the Pt/TiO₂ heterojunction structure since the work function (WF) of polycrystalline Pt (ca. 5.7 eV)¹¹⁻¹³ is much larger than that of TiO₂ (ca. 4.5 eV)¹⁴, sometimes leading unique properties at the Pt/TiO₂ junction.¹⁵ Gunasooriya et al. demonstrated the high catalytic performance of a supported Pt catalyst on TiO₂ for ethylene dehydrogenation. The negatively charged surface of Pt can be formed by electron transfer from TiO₂ to Pt, decreasing the ethylene adsorption energy and increasing the reaction turnover frequency⁴. On the other hand, the interfacial Schottky barrier inhibits the dynamic electron transfer reaction from TiO₂ conduction band to Pt, which is an essential reaction step in photocatalysis⁵. Since the electronic structure is an inherent nature of each material, extrinsic ways for tailoring the interfacial Schottky barrier are desired such as interfacial modification and applied bias¹⁶. For example, Deshlahra et al. demonstrated that the infrared peaks of adsorbed CO on a Pt/TiO₂ multilayer diode can be reversibly controlled by applying an external voltage to modify the Pt surface negative charge⁸. In the last two decades, self-assembled monolayers (SAM) have been used to tailor the electronic structure of a metal-semiconductor interface.¹⁷⁻²² Campbell et al. previously demonstrated that metal/organic Schottky barriers can be controlled

by intercalation of SAM of alkanethiols, where the SAM had dipole moments perpendicular to the interface.²³

Here, we use SAMs of 1-mercapto-1,7-dicarba-*closo*-dodecaborane (M1) and 9-mercapto-1,7-dicarba-*closo*-dodecaborane (M9)²⁰ with dipole moments horizontal and perpendicular to the surface, respectively. The position of the two carbon atoms replaced with the boron atoms in the *closo*-carborane cage is crucial to the orientation of the dipole moment, while the molecular structures of M1 and M9 are almost identical. The sulfur moiety in M1 and M9 binds preferentially on the metal surface, resulting in an oriented dipole moment on the metal surface. Previously, the oriented dipoles of M1 and M9 SAM have been demonstrated to modify the WF of Au metal.²⁴ When the SAM is present at the platinum interface, the dipole moments of the adsorbates modify the surface potential without changing the distance between the Pt surface and the TiO₂ surface. By selection of adsorbate, the Schottky junction can therefore be controlled by selecting the substrate without altering the HOMO-LUMO gap, the tunneling charge transfer, or the tunneling distance. Here, we demonstrate that the Schottky barrier at the interface of TiO₂ and Pt can be decreased by intercalation of M9 SAM, because the oriented dipole moment of the M9 molecules decrease the electronic potential difference between TiO₂ and Pt (Figure 1a). On the other hand, an intercalated M1 SAM is expected to not affect the value of the Schottky barrier. It should be noted that the dipole moment of M1 and M9 is drawn as a vector pointing from plus to minus in Figure 1a as customary in organic chemistry.

The Pt/TiO₂ catalyst consists of Pt nanoparticles deposited on larger TiO₂ particles. Although there is considerable literature regarding the charge state of metals on semiconductors²⁵, there are few techniques available to determine the electronic structure of a

semiconductor in the vicinity of the Schottky interface in ambient conditions,¹⁵ although it has been investigated by theoretical methods.^{27,28} To explore the electronic structure of TiO₂ locally we deposited TiO₂ nanoparticles onto a flat Pt substrate. In this manner the SAM of thiol molecules form a flat structure which allows easy interrogation with AFM imaging techniques. To investigate the changes in TiO₂ work function by the M1 and M9 SAMs we measured the contact potential as a function of particle size by Kelvin probe force microscopy (KPFM). The setup of the KPFM measurement is shown in Figure 1b. Since the Pt tip has a size comparable to that of the TiO₂ nanoparticles the contact potential measured by the KPFM near the edge of the particles is an average from contributions from the TiO₂ and the Pt substrate. For this reason the WF of TiO₂ nanoparticles we used only the values obtained at the top of the TiO₂ particles.

Figure 1. (a) Illustration of oriented dipole moments formed by carboranethiolate SAM intercalated at Pt/TiO₂ interface. (b) Schematic diagram of the KPFM measurements.

EXPERIMENTAL SECTION

Deposition of TiO₂ nanoparticles on bare Pt film. A P-doped Si wafer with low resistivity (1 mΩ·cm) was purchased from Crystal Base Co., Ltd. A Pt film with a thickness of 80 nm was deposited on the Si wafer by thermal deposition. The flatness of the Pt film were confirmed (Figure S1). The RMS roughness was 1.1 Å. An aqueous TiO₂ nanoparticle dispersion (anatase, 80 ± 30 nm, 15 wt%) was used as received from US Research Nanomaterials, Inc. An SEM image and corresponding EDX spectrum are shown in Figure S2 and S3, respectively. The EDX spectrum shows peaks due to titanium and oxygen. An aluminum from the sample holder is also observed. The TiO₂ dispersion was diluted 400x with deionized water and then sonicated for 10 min, before drop-casting it on the Pt surface and left to dry in air.

Deposition of TiO₂ nanoparticles on Pt film with intercalated carboranethiol SAMs. The template stripping (TS) method was used to obtain ultra-flat TS-Pt samples, as described by Blackstock et al.²⁹ First a P-doped Si wafer was washed with a piranha solution, and a 50 nm Pt layer was formed on the Si wafer by sputtering under 7 mTorr Ar. A second Si wafer was diced into ~10 mm² squares and attached to the Pt layer with epoxy (EPO-TEK377). The epoxy was cured at 150 °C for 2 h. After the excess epoxy was removed using a razor blade, the TS-Pt attached to the Si substrate was lifted with of tweezers, exposing the Pt surface. The RMS roughness of the surface was less than 1 Å, indicating an ultra-flat surface.

The carboranethiol M1 and M9 molecules from Sigma-Aldrich were used as received. The SAM were fabricated by immersing the TS-Pt on the Si substrate in 1 mM solution of carboranethiol in toluene²⁴. After immersing for 24 h, the substrate was removed, rinsed thoroughly with neat toluene and dried with a flow of N₂ gas. The thickness of the M1 SAM was

measured by ellipsometry. Anatase TiO_2 nanoparticle dispersions were dropped on the carboranethiol-SAM-coated TS-Pt. Both samples were left to dry in air.

Kelvin probe force microscopy (KPFM). The KPFM measurement is described in previous studies^{25,30}. The measurement was made in a single pass in frequency modulation mode using an Agilent 5500 atomic force microscope (AFM) and an HF2LI lock-in amplifier with a built-in PID controller from Zurich Instruments. The frequency modulation KPFM has a resolution of ~ 10 mV. Cr/PtIr-coated AFM tips (EFM probe from Nanoworld) with a resonant frequency of $\omega_0 \sim 75$ kHz were used. The tip radius was < 25 nm. While the sample was grounded, a bias $V_{\text{DC}} + V_{\text{AC}} \cos \omega t$, where ω is 2 kHz and V_{AC} is 2 V, was applied to the tip. A DC bias, V_{DC} , was applied to the tip and adjusted by the PID loop to null the amplitude of the sidebands so that $V_{\text{DC}} = \text{CPD}_{\text{tip-sample}}$, which is the contact potential between the tip and the sample. The V_{DC} minimizes the electrostatic force between the tip and surface, allowing determination of the true sample topography. The difference of work function between bare and M1-SAM (M9-SAM) covered Pt substrate is estimated by comparison with the scanned results of a highly oriented pyrolytic graphite (HOPG) reference. All of the samples and HOPG standard were scanned alternatively, and the relative work function value of these Pt substrate was determined.

RESULTS AND DISCUSSION

TiO_2 nanoparticles deposited on Bare Pt

The formation of a Schottky junction at the Pt/ TiO_2 interface is confirmed by measuring the CPD on the TiO_2 particles as a function of particle size. When the Schottky junction is formed, the band edge of TiO_2 is curved near the interface due to the fermi level alignment as

determined by the Poisson equation³¹. A relative CPD on TiO₂ compared to the CPD on bare Pt surface (Δ CPD) is determined from KPFM images (Figure S4–S6), plotted against the height of each TiO₂ nanoparticle (Figure 2a). The Δ CPD decreases with the decreasing height of the nanoparticle; as expected from the fact that the TiO₂ surface approaches the Pt/TiO₂ interface. According to the band structure described in Figure 2(b), the built-in potential in TiO₂ nanoparticle (V_{bi}) is corresponding to the Δ CPD. The relation between Schottky barrier height (ϕ_B) and conduction band edge position relative to the Fermi level (V_n) is:

$$\phi_B = V_{bi} + V_n \quad (3)$$

where V_{bi} can be estimated from the KPFM measurement (Δ CPD) and V_n is the intrinsic value of TiO₂ with a specific donor density. We can thus discuss the relative change in the height of the Schottky barrier. From our measurement, V_{bi} at 100 nm from Pt/TiO₂ interface can be estimated to be ~ 0.33 eV as illustrated in Figure 2b, indicating that the height of the Schottky-barrier (ϕ_B) is $0.33 + V_n$ (eV).

Figure 2. (a) Relationship between the ΔCPD of TiO_2 surface and the height of TiO_2 particles measured by KPFM. (b) Electronic structure of Pt/ TiO_2 with Schottky junction.

TiO_2 nanoparticles deposited on SAM modified Pt

The carboranethiolate SAM were deposited on the TS-Pt surface by dipping the substrate in an ethanol solution of the carboranethiol. The SAMs were analysed by attenuated total reflectance infrared (ATR-IR) spectroscopy (Figure S7). The peaks around 2600 cm^{-1} can be attributed B-H stretches for carborane cages.²⁴ Spectroscopic ellipsometry measurements

revealed a thickness of the M1 SAM of 0.58 nm, confirming that the carboranethiolate molecules form a monolayer on the TS-Pt. Topographical images of the M1 and M9 SAM on the TS-Pt surface (Figure S8a and c, respectively), showing that the surface roughness of carboranethiol SAMs (RMS < 0.1 nm) is much smaller than the particle size of TiO₂ (~50 nm). Therefore it can be safely assumed that the roughness of the SAMs plays a negligible role compared to that of the electronic structure of the SAMs. Figure S8b shows the relative surface potential of the M1-SAM-coated TS-Pt, demonstrating that the WF of the M1-SAM-coated TS-Pt is 0.14 V higher than that of the bare TS-Pt. Similarly, the relative surface potential of the M9-SAM-coated TS-Pt (Figure S8d) shows that the WF of M9 is 0.08 V higher than that of the bare TS-Pt. The WF difference of the M1 SAM ($\Delta\Phi_{\text{M1/Pt}}$) is larger than that of the M9 surface ($\Delta\Phi_{\text{M9/Pt}}$), which follows the same trend as that observed for a carboranethiolate SAM on Au, as by photoelectron spectroscopy²⁰ and scanning tunneling microscopy²⁴.

TiO₂ nanoparticles were deposited on SAM-coated TS-Pt particles by the drop-casting of TiO₂ aqueous suspension on the substrates. There is a possibility SAM molecules adsorbed on TiO₂ by dissolution of the molecules to water and then deposition during drop-casting of TiO₂ aqueous suspension. However, the M1 adsorption on TiO₂ substrate was negligible, after TiO₂ substrate was immersed in saturated M1 aqueous solution for 10 min (Fig. S7b). Therefore, M1 adsorption on TiO₂ after the drop-casting of TiO₂ water dispersion on M1-SAM-coated TS-Pt M1 should be negligible, even though the M1 molecules adsorbed on TS-Pt are dissolved in H₂O at saturation concentration. Figure 3a and d show the topographic data of TiO₂ on the M1-SAM-coated TS-Pt and the M9-SAM-coated TS-Pt, respectively. The heights of TiO₂ the nanoparticles vary between 50 and 200 nm. The surface potential of the TiO₂ is higher than that of the

surrounding M1-SAM-coated TS-Pt area (Figure 3b), similar to the case of TiO_2 nanoparticles on bare Pt substrate (Figure S4–6). Figure 3c, showing the line scan data as shown in Figure 3a–b, indicates that there is large surface potential difference between the M1-SAM-coated TS-Pt surface and the TiO_2 surface. Figure S9 also shows a data set of TiO_2 nanoparticles on the M1-SAM-coated TS-Pt substrate. On the other hand, the surface potential difference between TiO_2 nanoparticles and Pt substrate is reduced in the case of M9-SAM-coated TS-Pt (Figure 3e). Figure 3f shows the line scan data as shown in Figure 3d–e. The lines 4 and 5 in Figure 3f show that the surface potential difference between the M9-SAM-coated TS-Pt surface and the TiO_2 surface is almost disappeared demonstrating that the insertion of M9-SAM causes a substantial reduction of the Schottky barrier at the interface of TiO_2 and Pt. The slight potential difference is observed when the TiO_2 nanoparticle is getting large (line 6 in Figure 3f). This is the evidence of the formation of the Schottky junction, while the Schottky barrier height of TiO_2 nanoparticles and the M9-SAM-coated TS-Pt is much smaller than that of TiO_2 nanoparticles and the M1-SAM-coated TS-Pt.

Figure 3. KPFM data of TS-Pt/carboranethiolate SAM/TiO₂ surface. (a) Topography of TiO₂ and M1 SAM. (b) Surface potential of TiO₂ and M1 SAM. (c) Topography profiles along lines 1–3 in Figure 3a and Surface potential profiles along lines 1–3 in Figure 3b. (d) Topography of TiO₂ and M9 SAM. (e) Surface potential of TiO₂ and M9 SAM. (f) Topography profiles along lines 4–6 in Figure 3d and Surface potential profiles along lines 4–6 in Figure 3e.

In order to discuss the electronic structure of the Pt/TiO₂ interface, ΔCPD on TiO₂ nanoparticles is plotted as a function of the particle size of TiO₂ (Figure 4a). When the M1 SAMs are placed at the Pt/TiO₂ interface, the ΔCPD on TiO₂ nanoparticles is drastically changed. On the other hand, the extent of the ΔCPD change is relatively small when M9 SAMs are placed at the Pt/TiO₂ interface, meaning that the Schottky barrier height of the M1-SAM-intercalated Pt and TiO₂ interface is larger than that of the M9-SAM-intercalated Pt and TiO₂ interface. Figure 4b and c describes the electronic structure of the Pt/TiO₂ heterojunction. According to the above discussion, ΔCPD equals to V_{bi} . According to eq. (2), the Schottky barrier height at the M1-SAM-intercalated Pt and TiO₂ interface can be estimated as $\phi_{\text{B}} = 0.20 + V_{\text{n}}$ (eV), which is 0.13 eV lower than the Schottky barrier height at the bare Pt and TiO₂ interface, $\phi_{\text{b}} = 0.33 + V_{\text{n}}$ (eV). On the other hand, the Schottky barrier height is drastically decreased as $\phi_{\text{b}} = 0.05 + V_{\text{n}}$ (eV) by the insertion of the M9 SAM layer at the interface of Pt and TiO₂. The larger effect of M9 in reducing the Schottky barrier compared to M1 is due to the nearly horizontal dipole moment of M1 SAM compared to the nearly vertical direction in M9. Tachikawa et al. reported that the Schottky barrier height at Pt and TiO₂ can be modulated by the insertion of atomic layer thickness LaAlO₃ layers with a potential gradient perpendicular to the interface³². In the current system, the interfacial electronic field created by intercalated of M9 SAM compensates the built-in potential at the Schottky-junction due to the charge transfer from TiO₂ to Pt.

Figure 4. (a) Summary of the relationship between WF and TiO_2 nanoparticle height from Figure 3c, 3f, and Figure S9c–e. (b) Electronic structure of Pt/M1 SAM/ TiO_2 . (i) Electronic structure of Pt/M9 SAM/ TiO_2 .

CONCLUSIONS

From these results, we can conclude that the Schottky barrier of Pt/TiO₂ interface can be reduced strongly by insertion of dipolar spacer molecules that create an interfacial electric field, like those provided by intercalated SAMs with oriented permanent dipole moments. Insertion of M1 SAM with a horizontal dipole in the Pt/TiO₂ interface has a smaller effect on the Schottky barrier than M9 SAM with a vertical dipole, which reduced the Schottky barrier by approximately 0.3 eV. The electronic structure of TiO₂ could be directly investigated by the current configuration where the TiO₂ nanoparticles are deposited on flat Pt substrates. Applying this molecular level fabrication method with various types of heterojunction structures, the interfacial electronic properties can be tailored precisely, resulting in new nanomaterials with advanced electronic properties.

ASSOCIATED CONTENT

Supporting information for this article is consisting of following information.

KPFM data of HOPG, Pt, M1 SAM, M9 SAM and TiO₂ nanoparticles deposited on Pt and M1 SAM, SEM and EDX of TiO₂ nanoparticles, and ATR-IR spectrum of M1 and M9 modified TS-Pt substrate (PDF)

AUTHOR INFORMATION

The authors declare no competing financial interests.

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