Articles

Direct Covalent Grafting of Polyoxometalates onto Si Surfaces

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A diazonium salt-derived organoimido hexamolybdate was synthesized and directly covalently immobilized on Si surfaces using diazonium chemistry to form both monolayers and multilayers. These monolayers and multilayers were characterized by ellipsometry, X-ray photoelectron spectroscopy (XPS), and electrochemical analysis. The results of electrochemical analysis have shown a strong electronic interaction between the surface-confined clusters and the Si substrate through the organic conjugated bridge.

Introduction

Polyoxometalates (POMs) are a unique class of inorganic metal–oxygen polyanions formed by early transition metals. They have been widely used in chemical analysis, catalysis, biology, medicine, geochemistry, and material science based on their topological and electronic diversity and fascinating electrical, optical, and magnetic properties.[1-3] Because of their reversible redox behavior, discrete structures in size from subnanometer to a few nanometers, and good solubility and stability in aqueous and organic solvents, POMs have been used widely as the inorganic components in functional molecular materials.[4] Surface-confined thin films and two-dimensional arrays of POMs have been constructed to produce POM-containing molecular materials and devices. Ordered monolayers of POMs on gold or silver were obtained by spontaneous adsorption from solution.[5] By solvent casting, POMs on carbon were prepared with active catalytic properties[6] and ordered mesoporous SiO_2 functionalized with cationic groups was used as substrates for ionic immobilization of POMs.[7] However, the majority of work aimed to make films of POMs utilizes the Langmuir–Blodgett (LB) technique. By taking advantage of the ionic interaction of positively charged organic molecules or polymers and negative charged POM polyanions, both monolayers and multilayers of POMs have been prepared by the LB technique on various substrates including glass, quartz, ITO, glassy carbon, silicon, and silica.[8] These LB films of POMs have been found to have interesting photo and electrical properties.

The majority of these monolayers and multilayers of POMs were deposited on substrates by physical adsorption or electrostatic forces. There are few examples of POMs that were attached through covalent bonds to the substrates to form well-defined monolayers. One example is the bonding of thiol-derived POM clusters to gold nanoparticles.[9] There is one report of covalently bonding POMs to a Si surface by Errington's group, a stepwise method by which $TiWO_{18}$ clusters are attached to Si through covalent Ti–O–C bonds by alcoholysis of the Ti–OR bond in $[(RO)TiW_5O_{18}]^{3-}$ with a preassembled alkanol monolayer on Si.[10]

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Direct Covalent Grafting of POMs onto Si Surfaces

Chem. Mater., Vol. 21, No. 3, 2009 443

Here, we report a one-step method for covalently grafting POMs on a Si surface. Using this method, organically functionalized hexamolybdate clusters were grafted onto Si(111) and Si(100) surfaces through a conjugated linkage by diazonium chemistry. The organic conjugated bridges between the clusters and Si substrates in combination with the Si−C bond of the molecule with the Si surface, without the interfering oxide, could provide better electronic interaction between the electrically active POM clusters and the semiconductor substrate.

It has been demonstrated that hexamolybdates readily react with anilines to form organoimido compounds.[11] The organoimido bonds are very stable toward many functional groups and reaction conditions so that a large number of hybrid molecular materials have been prepared.[12] Surface grafting protocols using aromatic diazonium salts or triazenes have been shown to be mild and efficient methods to form both monolayers and multilayers on Si.[13] To utilize the Si surface grafting protocol with POMs, here we report the synthesis and surface grafting of a diazonium salt-derived organoimido hexamolybdate.

Experimental Section

General. Unless noted otherwise, reactions were performed under a N_2 atmosphere. Triethylamine was distilled from CaH_2. Trimethylsilylacetylene (TMSA) was donated by FAR Research, Inc., or Petra Research, Inc. All other commercially available reagents were used as received unless noted otherwise. ^1H NMR spectra (400 MHz) were collected in $CDCl_3$. The data here are solely for assemblies on Si(111); however, the same assemblies were done on Si(100) and they worked equally well. All the same characterizations were performed except for the CV studies.

Synthesis of Compound 2. To an oven-dried 50 mL round-bottom flask containing a magnetic stir bar were added **1** (800 mg, 0.50 mmol), 4-ethynylphenyldiethyltriazene (13 mg, 0.6 mmol), $Pd(PPh_3)_2Cl_2$ (7 mg, 0.01 mmol), CuI (3 mg, 0.02 mmol), and K_2CO_3 (1000 mg, 3.2 mmol). The flask was then sealed with a rubber septum, evacuated, and backfilled with N_2 (3 ×). Acetonitrile (10 mL) and triethylamine (1 M solution in acetonitrile, 0.5 mL) were then added. The reaction was stirred at room temperature for 0.5 h. The reaction mixture was filtered, and the filtrate was concentrated to about 2 mL before it was poured into diethyl ether. The precipitate was collected and recrystallized from ether/

acetonitrile to yield **2** as dark red crystals. (250 mg, 30%). IR: 2961, 2872, 2189, 1655, 1587, 1481, 1392, 1328, 1237, 975, 952, 778. ^1H NMR ($CDCl_3$, 400 MHz): δ 7.46 (d, $J = 8.7$, Ar−H, 2H), 7.37 (d, $J = 8.7$, Ar−H, 2H), 7.22 (s, Ar−H, 2H), 3.78 (q, $J = 14.3$, NCH_2CH$_3$, 4H), 3.08 (t, $J = 8.8$, NCH_2, 16H), 2.60 (s, Ar-CH$_3$, 6H), 1.60 (q, $J = 8.8$, -CH$_2$, 16H), 1.35 (h, -CH$_2$, 16H), 1.24 (b, NCH$_2$CH$_3$, 6H), 0.96 (t, $J = 8.8$, CH$_3$, 24H). TOF-ESI-MS: 591 ($[Mo_6O_{18}N_4C_{20}H_{22}]^{2-}$, calcd 590.90); 1182 ($[Mo_6O_{18}N_4C_{20}H_{22}]^{2-}H^+$, calcd 1182.90); 1326 ($[Mo_6O_{18}N_4C_{20}H_{22}]^{2-}$ N$^+$Bu$_4$, calcd 1424.09).

Synthesis of Compound 3. To a 25 mL round-bottom flask containing a magnetic stir bar was added **2** (50 mg, 0.03 mmol). The flask was then sealed with a rubber septum, evacuated, and backfilled with N_2 (3 ×). Acetonitrile (2 mL) was added and triethylamine (2 mL) was then added. To this solution, HBF$_4$ (5% in acetonitrile, 0.1 mL) was added dropwise. The reaction was stirred at room temperature for 30 min. Dry ether (10 mL) was then added. The precipitate was collected, washed with dry ether, and dried under nitrogen to yield **3** as an orange/brown solid (25 mg, 30%, mixture with **2**). IR: 2959, 2871, 2242, 2190, 1568, 1457, 1379, 1313, 1078, 976, 950, 776. ^1H NMR ($CDCl_3$, 400 MHz): δ 8.47 (d, $J = 8.5$, Ar−H, 2H), 7.77 (d, $J = 8.5$, Ar−H, 2H), 7.28 (s, Ar−H, 2H), 3.08 (t, $J = 8.8$, NCH_2, 8H), 2.53 (s, Ar-CH$_3$, 6H), 1.60 (q, $J = 8.8$, -CH$_2$, 8H), 1.35 (h, -CH$_2$, 8H), 0.96 (t, $J = 8.8$, CH$_3$, 12H).

Surface Grafting. Caution! *The concentrated piranha solution is very dangerous, particularly when in contact with organic materials, and should be handled extremely carefully.*[18] p-Type Si(111) wafers (prime grade, boron doped) were cleaned in piranha solution (2:1 H_2SO_4:H_2O_2) followed by rinsing with water (resistivity >18 MΩ cm^{-1}) and drying with a stream of N_2. The wafers were then H-passivated by immersing in N_2-sparged 40% NH$_4$F for 15 min, rinsed with water, and dried in a stream of N_2. The cleaned and H-passivated wafers were then brought into a N_2-atmosphere glovebox. Inside the glovebox, a solution of **3** was made to various concentrations in CH$_3$CN, providing enough volume to cover the entire sample inside a reaction container. The substrates were then immersed in the solution of **3**, sealed to prevent evaporation, and kept for various reaction times. After the reaction, the substrates were brought out of the glovebox, rinsed with CH$_3$CN, and dried with a stream of N_2.

Ellipsometric Measurements. Measurements of surface optical constants and molecular layer thicknesses were taken with a single-wavelength (632.8 nm) laser Gaertner Stokes ellipsometer. The n value for the H-passivated Si(111) substrate was 3.83 and k was −0.02. The surface thickness was modeled as a single absorbing layer atop an infinitely thick substrate (fixed n_s). The observed range in repeated measurements of the same spot was typically less than 0.2 nm, and the typical experimental error is ±5%.

XPS Measurements. A Quantera XPS scanning microprobe was used to collect the XPS data. The takeoff angle was 45°, and a 114.8 W monochromatic Al X-ray source was applied for all the measurements. All XPS peaks were referenced to the C_{1s} major peak at 284.5 eV.

Electrochemical Characterization. The cyclic voltammetry was performed with a Bioanalytical Systems (BAS CV-50W) analyzer in a self-designed three-electrode cell. The working electrode, cluster grafted Si(111), was sealed against an opening in the cell bottom by epoxy resin. An ohmic contact was made on the previously polished rear side of the sample by applying a drop of an In−Ga eutectic. The counter electrode was a platinum wire and the system 1×10^{-2} M Ag$^+$/Ag in acetonitrile was used as the reference electrode (+0.29 V vs aqueous SCE). 0.1 M tetra-n-butylammonium perchlorate Bu$_4$NClO$_4$ in acetonitrile was used as the electrolytic

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Scheme 1. Synthesis and Surface Grafting of Diazonium Derived Hexamolybdates; Compound 3 was Contaminated by 2
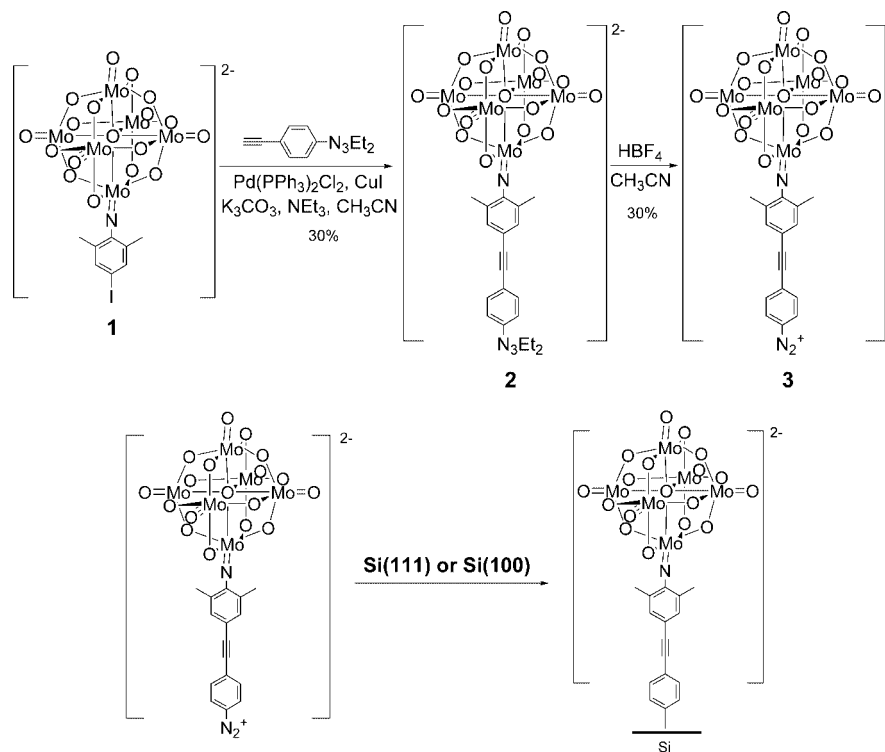
medium. All electrochemical measurements were carried out at room temperature under a constant flow of nitrogen.

Results and Discussion

Synthesis. The diazonium salt-derived organoimido hexamolybdate was synthesized as shown in Scheme 1. The Pd-catalyzed coupling reaction of iodo-derived organoimido hexamolybdate **1** and 4-ethynylphenyltriazene gave the triazene functionalized cluster **2** as dark red crystals, which were converted to the diazonium salt **3** using HBF$_4$. Because the hexamolybdate cluster is not stable toward acid, only 1 equiv. of HBF$_4$ was used. Therefore, **3** was usually obtained as a mixture with the triazene **2**.

The diazonium salt **3**, containing unreacted **2**, was characterized by ^{1}H NMR and FTIR. As shown in Figure 1, two sets of signals in the ^{1}H NMR spectra could be clearly assigned to compounds **2** and **3**, with the signals due to the diazonium arene **3** further downfield than those of the triazene **2**. FTIR confirmed the presence of diazonium salt **3** in the mixture. As shown in Figure 2, compared to the spectrum of **2**, the N≡N stretch of the diazonium group appeared at 2242 cm^{-1} in the IR spectrum of **3**. The peaks
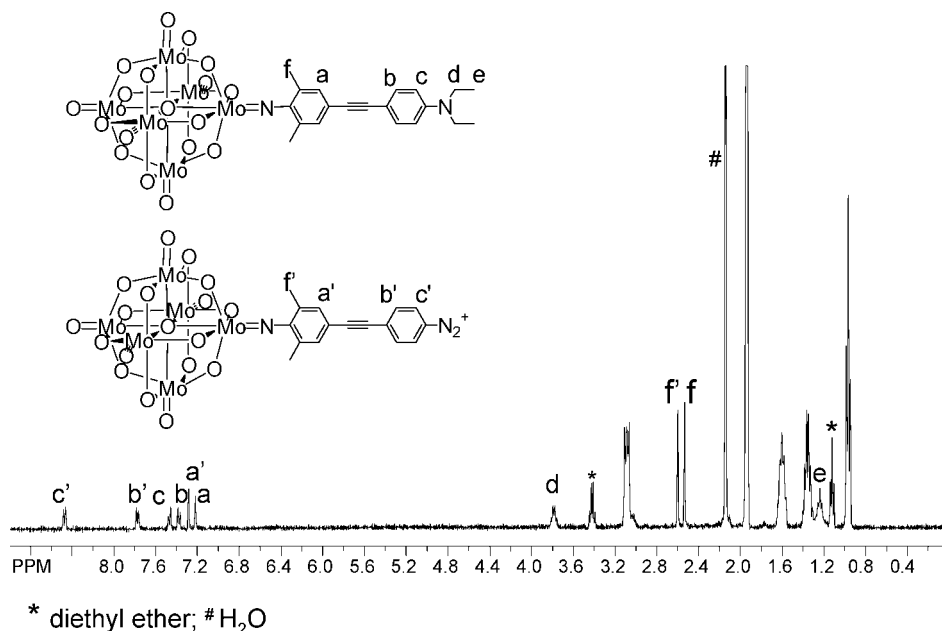

* diethyl ether; # H$_2$O

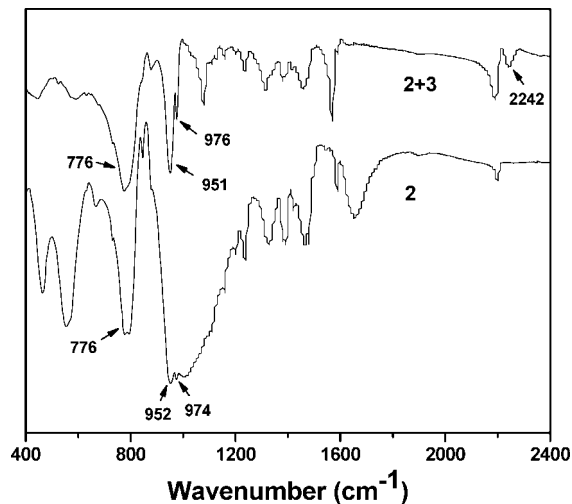**Figure 1.** ^{1}H NMR of the mixture of triazene **2** (top structure) and diazonium salt **3** (bottom structure).

Figure 2. FTIR of triazene **2** and that of **2** mixed with diazonium salt **3**.

Table 1. Thicknesses of Hexamolybdates Films on Si(111)

entry	concentration (mM)	reaction time (min)	thickness (nm)[a]
1	0.1	20	1.1 ± 0.3
2	0.1	40	1.8 ± 0.1
3	0.1	60	2.8 ± 0.2
4	0.1	120	5.4 ± 0.1
5	0.1	240	6.1 ± 0.1
6	0.2	30	1.9 ± 0.2
7	0.2	60	2.3 ± 0.2

[a] The measured values are the average of four different spots on the same film, with the $\pm$ values indicating the range of measurements.
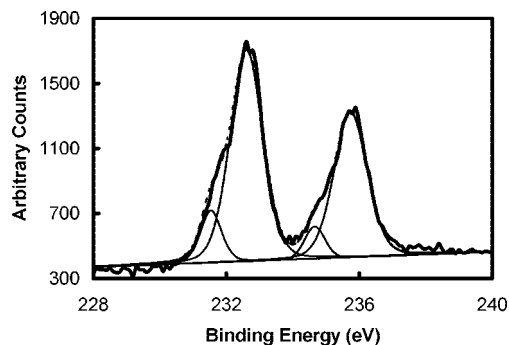

Figure 3. Mo_{3d} region in the XPS spectra of a hexamolybdate film (2.1 nm) on Si(111). The lighter lines are the curve fittings.

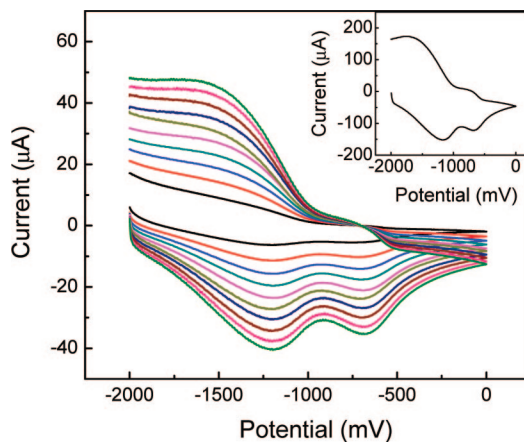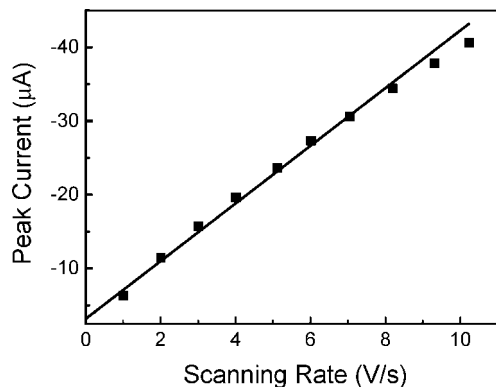**Figure 4.** Cyclic voltammograms of a hexamolybdate film (1.8 nm in thickness) on p-type Si(111) in 0.1 M NBu_4ClO_4/CH_3CN. The scan rates are from 1 V s^{-1} (black line) to 10 V s^{-1} (green line) with increments of 1 V s^{-1}. Inset is a representative cyclic voltammogram with a scan rate of 10 V s^{-1}.

at ~776 and ~951 cm^{-1} are characteristic for hexamolybdate clusters with the Mo−N stretches showing at around 978 cm^{-1}.[14] These peaks clearly indicate the integrity of the organoimido hexamolybdate clusters in compounds **2** and **3**.

Surface Grafting. The surface grafting of the compound **3** on Si surfaces was achieved by using a known protocol for the surface grafting of aryl diazonium salts. H-passivated Si(111) wafers were immersed in the solutions of compound **3** in acetonitrile at various concentrations for different reaction times. The thicknesses of the resulted films are summarized in Table 1. Both monolayers and multilayers were prepared by controlling the concentration of **3** and the reaction times. For example, a monolayer was formed (a monolayer was assumed considering the calculated length 1.8 nm of **3** after grafting on Si(111)) at a concentration of **3** of 0.1 mM and a reaction time of 40 min (entry 2) or 0.2 mM and 30 min (entry 6). At longer times (entries 3−5) or higher concentration (0.2 mM) of **3** (entry 7), the film growth was faster, and multilayers could be easily formed with thicknesses up to several nanometers. According to the proposed mechanism of grafting on Si−H surface by diazonium salts,[13a] the formation of multilayers resulted from the reaction of diazonium molecules with the molecules that had already been grafted to the Si surface. Therefore, the multilayers are present due to the formation of covalent bonds between molecules. In addition to the concentration and grafting time, the thickness of multilayer may also be limited by the stability of the diazonium salts in solution. In this work, the thickest multilayer produced is ~6 nm thick, which contains ~3 layers of molecules. Hence, this grafting method

can be used for grafting of compound **3** on Si(111) to form both monolayers and multilayers.

XPS Studies. These monolayers and multilayers of hexamolybdates were characterized by X-ray photoelectron spectroscopy (XPS). The characteristic signals in the Mo_{3d} region are shown in Figure 3. By curve fitting, two pairs of peaks could be observed. The pair of peaks at lower binding energy were assigned to the Mo atoms in the Mo=N bonds, whereas the peak at higher binding energy to all of the other Mo atoms. The ratio of the peak areas between these two sets of peaks was around 1:5, which indicated the structures of monofunctionalized organoimido hexamolybdates existing in the film. In the XPS spectra, we also observed signals for C_{1s} and O_{1s}. The N_{1s} signals were buried under the Mo_{3p} signal.

Electrochemical Studies. Cyclic voltammetry was used to study the electrical properties of the covalently surface attached hexamolybdate clusters, and the results are summarized in Figure 4. Monoorganoimido hexamolybdate clusters in acetonitrile solution usually have one reversible one-electron redox wave within the potential range of −1.5 to 0 V. However, two reversible redox waves were observed for the surface-bonded hexamolybdates. According to the peak potentials shown in the inset of Figure 4, the formal potentials of these two redox waves were estimated to be −0.73 and −1.45 V versus Ag/Ag$^+$. For the redox wave at −1.45 V, which was assigned to the redox pair of the

Figure 5. Cathodic peak current as a function of potential scan rate of the hexamolybdate redox peaks derived from the cyclic voltammograms in Figure 4.

hexamolybdate clusters, the cathodic peak current exhibits a linear dependence on the scan rate, indicating a surface confined redox process, as shown in Figure 5. For the redox wave at -0.73 V, constant cathodic peak currents were found under different potential scan rates. These constant cathodic peak currents may have resulted from the limited electron transfer from the electron-deficient p-Si substrate to the clusters, therefore, we assigned the redox wave at -0.73 V to the reversible electron transfer between the hexamolybdates clusters and the Si substrate. From these cyclic voltammetry results, the surface coverage Γ was estimated to be 1.1×10^{13} molecules cm^{-2}.[15] The apparent rate constant of electron transfer, k_{app}, was calculated to be $\sim$25 s^{-1} using Laviron's approach.[16] These electrochemical results indicate that the hexamolybdate clusters covalently bonded onto Si surfaces are electrochemically accessible, and there are strong electronic interactions between the clusters and the Si substrate.

Conclusion

In summary, using diazonium chemistry, we have covalently immobilized organically functionalized hexamolybdates on Si surfaces to form both monolayers and multilayers. By electrochemical analysis, a strong electronic interaction between the surface-confined clusters and the Si substrate through the organic conjugated bridge was observed. This electronic interaction, in addition to the accessible and reversible redox behavior of hexamolybdates, could have applications in the bottom-up design of functional molecular materials or future generation of hybrid molecular/semiconductor electronic devices.[17]

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