Surface Chemistry

Covalent Immobilization of a TiW_5 Polyoxometalate on Derivatized Silicon Surfaces[**]

R. John Errington, Sagar S. Petkar,*
Benjamin R. Horrocks, Andrew Houlton, Lars H. Lie,
and Samson N. Patole

Polyoxometalates (POMs) are discrete, molecular metal oxides with dimensions ranging from about one to tens of Ångstroms, a wide variety of topologies and compositions, and an extensive range of chemical and electronic properties which, together with their thermal and oxidative stabilities, are leading to applications in catalysis, electrooptics, magnetics, medicine, and biology.[1–3] Consequently, POMs are attractive as functional components of active materials. In recent years, systematic methods for POM synthesis and derivatization have been developed, providing an expanding range of robust "designer" components for "bottom-up" materials synthesis, and a major challenge now facing those engaged in POM research is to devise generic methods for constructing functional nanoscale architectures from these versatile building blocks.

The self-assembly of organic monolayers on surfaces has developed over the last two decades into a powerful strategy for the construction of hierarchical structures from molecular components and, although self-assembled inorganic monolayers have received much less attention, several groups have investigated the incorporation of POMs into surface-confined structures. Ordered monolayers of POMs have been obtained on silver and gold by adsorption from solution,[4,5] and evaporative solution deposition has been used to produce catalytically active POM layers on highly oriented pyrolytic graphite (HOPG).[6–8] Hybrid organic–POM multilayered magnetic structures have been produced by Langmuir–Blodgett techniques,[9–11] while electrostatic layer-by-layer assembly with cationic polyelectrolytes has produced more robust hybrid structures.[12] These approaches rely upon either electrostatic interactions or ill-defined chemisorption for the assembly of POM monolayers or multilayers and, to our knowledge, the only example of well defined covalent attachment to a surface is that of a thiol-derivatized POM on gold nanoparticles.[13] Our previous work has shown that monofunctional alkoxide POM derivatives $[(RO)MW_5O_{18}]^{n-}$ ($M =$ Ti, Zr, Nb) are accessible through hydrolytic aggregation reactions involving metal alkoxides.[14] These species react

---

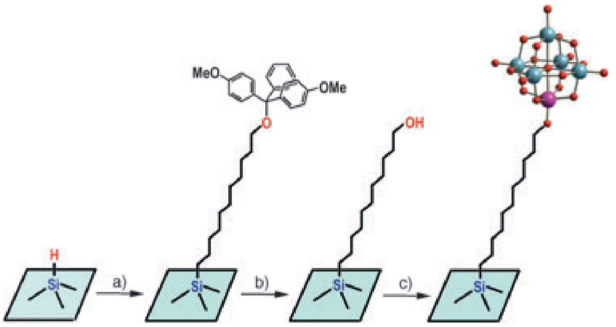
[*] Dr. R. J. Errington, Dr. S. S. Petkar, Dr. B. R. Horrocks,
Prof. A. Houlton, L. H. Lie, Dr. S. N. Patole
School of Natural Sciences, Chemistry
University of Newcastle upon Tyne, NE1 7RU (UK)
Fax: (+44) 191-222-6929
E-mail: John.Errington@ncl.ac.uk

[**] This work was supported by the EPSRC (Grant no. GR/N65028) and by the University of Newcastle upon Tyne. We are grateful to Dr. Lidija Siller and Satheesh Krisnamurthy of the School of Chemical Engineering and Advanced Materials, University of Newcastle upon Tyne for the XPS measurements.

DOI: 10.1002/ange.200461065

with protic reagents HX to provide access to a range of new derivatives $[XMW_5O_{18}]^{n-}$ (for example, X = OR′, OAr, O_2CMe, acac) and we now report the application of this chemistry to the covalent attachment of a TiW_5 hexametalate to single-crystal and porous silicon by reaction with alkanol surface monolayers.

The availability of robust, alkanol-derivatized silicon surfaces from hydrogen-terminated silicon[15] provided the means to attach MW_5O_{18} molecular heterometal oxides to the silicon surface through covalent M-O-C alkoxide bonds by alcoholysis of the M-OR bond in $[(RO)MW_5O_{18}]^{n-}$ (Scheme 1). From EXSY NMR spectroscopy experiments we have determined that the rate of exchange between free methanol and the methoxide in $[(MeO)TiW_5O_{18}]^{3-}$ is approximately 0.03 s^{-1}, so this comparatively inert POM was chosen as the adsorbate in these experiments in the expectation that the resulting POM-derivatized surfaces would be sufficiently stable for subsequent characterization.



Scheme 1. a) $CH_2{=}CH(CH_2)_9O(DMT)$, toluene, reflux, 18 h; b) Cl_3CCO_2H, CH_2Cl_2; c) 0.05 M $(nBu_4N)_3[(MeO)TiW_5O_{18}]$ (red O, blue W, purple Ti) in MeCN, 85 °C, 24 h. DMT = 1,ω-dimethoxytrityl.

Samples of single-crystal and porous silicon were functionalized with ω-hydroxyundecyl monolayers and then treated with acetonitrile solutions of $(nBu_4N)_3[(MeO)TiW_5O_{18}]$ at 85 °C, washed with MeCN and dried. Figure 1 shows scanning tunneling microscopy (STM) images of a single-crystal Si(111) surface with a ω-hydroxyundecyl monolayer before and after treatment with a MeCN solution of $(nBu_4N)_3[(MeO)TiW_5O_{18}]$ and washing with MeCN. Steps and terraces of the alkanol-modified surface are visible in Figure 1 a, while new features are clearly visible after treatment with the POM solution. X-ray photoelectron spectroscopy (XPS) analysis of the treated monolayer surface confirms the presence of W^{VI} and Ti^{IV} in oxide environments (Figure 2). The W $4f_{7/2}$ and $4f_{5/2}$ binding energies of 36.3 and 38.5 eV and the Ti $2p_{3/2}$ and $2p_{1/2}$ binding energies of 459.6 and 465 eV are comparable with those reported for electrostatically bound $[SiW_{12}O_{40}]^{4-}$ ions (binding energies = 35.3 and 37.3 eV)[16] and for TiO_2 (binding energies = 458.9 and 464.6 eV).[17]

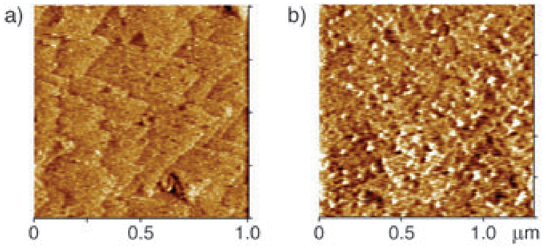


Figure 1. STM images of ω-hydroxyundecyl derivatized Si(111) surface before (a) and after (b) treatment with a MeCN solution of $(nBu_4N)_3[(MeO)TiW_5O_{18}]$.

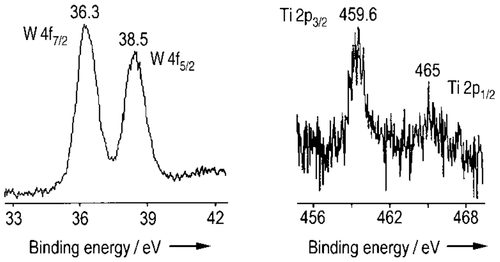


Figure 2. XPS analysis of ω-hydroxyundecyl derivatized Si(111) surface after treatment with $(nBu_4N)_3[(MeO)TiW_5O_{18}]$.

To investigate the nature of the interactions between the POM anions and the organic monolayer in more detail, samples of porous silicon derivatized with ω-hydroxyundecyl groups were prepared and then treated with a solution of $(nBu_4N)_3[(MeO)TiW_5O_{18}]$ in MeCN in a similar fashion to the single-crystal silicon. The FT-IR spectrum of $(nBu_4N)_3[(MeO)TiW_5O_{18}]$ in the region 400–1200 cm^{-1} is shown in Figure 3 a and the FT-IR difference spectrum between a ω-hydroxyundecyl derivatized porous silicon film and the original hydrogen-terminated silicon is shown in Figure 3 b. The difference FT-IR spectrum between the sample after and before treatment with the alkoxohexametalate is shown in Figure 3 c. A comparison of the ν(OH) regions shows that the broad band at 3300 cm^{-1} becomes negative in Figure 3 c, which indicates loss of OH upon reaction between the alkanol surface and the TiOMe group. In addition, the appearance of bands from W=O and W-O-W of the POM at 958, 883, and 795 cm^{-1} confirm the presence of the oxoanion. The ν(CH) region in Figure 3 c contains bands due to the $[nBu_4N]^+$ ion in addition to the undecyl chains and the large peak at 1093 cm^{-1} is from Si–O, formed upon oxidation of residual SiH groups (see below).

The STM image in Figure 1 b shows the surface features to have diameters of 35–50 nm and profile analysis shows heights of approximately 4 nm. Assuming that the optimum packing of $[nBu_4N]^+$ ions and $[(MeO)TiW_5O_{18}]^{3-}$ ions is that observed in the crystal structure,[14] the fraction of ω-hydroxyundecyl groups that would be required to react with the Ti–OMe groups to achieve this packing density can be estimated by mapping the plane containing the methoxide oxygen atoms in the unit cell of $(nBu_4N)_3[(MeO)TiW_5O_{18}]$ onto the Si(111) surface. As during preparation of the ω-hydroxyundecyl monolayer the packing constraints of the dimethoxytrityl-protected alkanol groups restrict functionalization to, at most, every second SiH site,[18,19] the Si:POM ratio of 11.4:1 derived by this mapping would mean that only around 17.5 % of available undecanol groups in the monolayer would be derivatized in the formation of a close-packed layer of $(nBu_4N)_3[(RO)TiW_5O_{18}]$ ($R = Si(CH_2)_{11}$). This situation would leave residual undecanol groups on the surface,

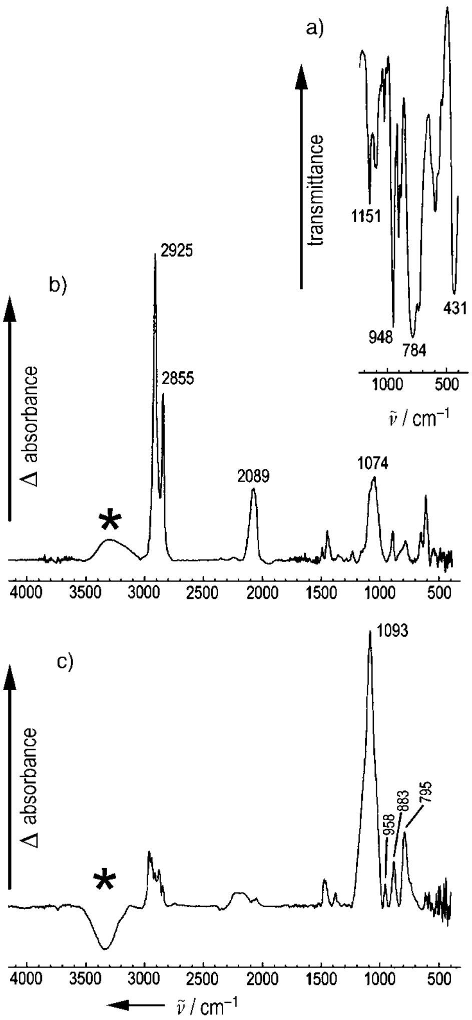


Figure 3. a) Section of the FT-IR spectrum of $(n\mathrm{Bu}_4\mathrm{N})_3[(\mathrm{MeO})\mathrm{TiW}_5\mathrm{O}_{18}]$ as a Nujol mull, b) FT-IR difference spectrum between ω-hydroxyundecyl derivatized porous silicon film and hydrogen-terminated silicon, c) FT-IR difference spectrum between ω-hydroxyundecyl derivatized porous silicon film after and before treatment with $(n\mathrm{Bu}_4\mathrm{N})_3[(\mathrm{MeO})\mathrm{TiW}_5\mathrm{O}_{18}]$; ν(OH) regions marked with an asterix.

while the remaining SiH groups may be susceptible to oxidation. The heights of the surface features in Figure 1b suggest greater than monolayer coverage in these areas, probably a result of electrostatic interactions. The unit cell volume ($Z=4$) of $(n\mathrm{Bu}_4\mathrm{N})_3[(\mathrm{MeO})\mathrm{TiW}_5\mathrm{O}_{18}]0.5\,\mathrm{MeCN}$, is 6852(8) Å^3 and, if the surface features observed in Figure 1b were composed of close-packed $[n\mathrm{Bu}_4\mathrm{N}]^+$ ions and $[(\mathrm{RO})\mathrm{TiW}_5\mathrm{O}_{18}]^{3-}$ ions, they should therefore contain between 2000 and 4700 hexametalate ions together with their associated cations. If these larger features are indeed a result of a "surface crystallization" process it may be that electrostatic aggregation around an initial covalently bound POM serves to direct subsequent covalent attachment at other alkanol sites, which results in "island" growth. We are now investigating whether the degree of electrostatic aggregation can be controlled by ion exchange or by varying the POM solution concentration, the reaction times, or the washing process in attempts to move towards monolayer coverage.

In conclusion, these results demonstrate that covalent metal alkoxide bonding can be used to immobilize a polyoxometalate on alkanol-derivatized silicon surfaces, although further aggregation beyond the monolayer also occurs, probably through electrostatic interactions. After 6 h reaction time, the POMs were localized in clusters on the surface containing between 2000 and 5000 TiW_5 units, and further studies are in progress to investigate the factors affecting POM clustering and surface coverage. In an extension of this covalent approach to larger POMs our initial experiments with Keggin $[(\mathrm{RO})\mathrm{TiPW}_{11}\mathrm{O}_{39}]^{4-}$ and Wells–Dawson $[(\mathrm{R}_2\mathrm{Si}_2\mathrm{O})\mathrm{P}_2\mathrm{W}_{17}\mathrm{O}_{61}]^{6-}$ derivatives appear promising and results will be described in due course.

Experimental Section

$(n\mathrm{Bu}_4\mathrm{N})_3[(\mathrm{MeO})\mathrm{TiW}_5\mathrm{O}_{18}]$ was prepared as described elsewhere.[14] STM images of silicon surfaces were collected in air and in constant current mode using a Multimode Nanoscope III (DI Digital Instruments). The Pt/Ir tips used for STM imaging were prepared by electrochemical etching of 80/20 Pt/Ir alloy wire in 1 M HCl/saturated CaCl_2 using approximately 20 V a.c. FT-IR Spectra (unpolarized) of porous Si samples were obtained using a Biorad Excaliber series spectrometer fitted with mercury cadmium telluride (MCT) detector in the normal transmission alignment. Features owing to water vapor and CO_2 were minimized by purging the sample compartment with dry N_2. Spectra of (modified minus hydrogen-terminated) porous silicon were referenced to an unetched piece of Si ⟨100⟩ wafer. The difference spectra (modified minus hydrogen-terminated) were then baseline corrected prior to the integration. The resolution was 2 cm^{-1} and 64 scans were summed and averaged.

Preparation of hydrogen-terminated Si (111) wafers: ⟨111⟩ Oriented silicon wafers (phosphorus-doped, n-type 1–20 Ω cm resistivity, Compart Technology) were first cut into 1 cm^2 pieces and then degreased with acetone. An oxide layer was formed by immersing the chips in freshly prepared "piranha" solution (4:1 v/v conc. $\mathrm{H}_2\mathrm{SO}_4$:30 % $\mathrm{H}_2\mathrm{O}_2$) for 1 h at 80 °C. The oxide was removed and a hydrogen-terminated surface was formed by etching in N_2-purged 40 % w/v aqueous $\mathrm{NH}_4\mathrm{F}$ for 3 min with the chip held in a vertical orientation as suggested elsewhere.[20] Wafers were then rinsed for 20 s in deionized water (Millipore, nominal 18 MΩ cm) and blown dry with N_2.

Preparation of porous silicon: Porous silicon was formed by galvanostatic anodization of silicon wafers (⟨100⟩ oriented; boron-doped, p-type, 10 Ω cm resistivity, Compart Technology). Chips (≈1.0 cm × 1.0 cm) were degreased in acetone and then oxidised in freshly prepared "pirhana" solution (4:1 v/v conc. $\mathrm{H}_2\mathrm{SO}_4$:30 % $\mathrm{H}_2\mathrm{O}_2$) for at least 10 min at room temperature. The oxide was removed and a hydride layer was formed by a subsequent immersion in 48 % w/w aqueous HF (10 min). Wafers were then rinsed for 20 s in deionized water (Millipore, nominal 18 MΩ cm) and blown dry with N_2. Ohmic contact to the back of the chip was made by rubbing with In/Ga eutectic. The chip was then placed in a polytetrafluoroethylene (PTFE) cell with an electrolyte consisting of a 1:1 v/v solution of 48 % aqueous HF:ethanol and a current density of 12.7 mA cm^{-2} was applied until the charge passed reached 5.0 C cm^{-2} (ca. 6.5 min). The porous silicon was then washed in deionized water to remove ethanol and then immersed for a few seconds in 48 % aqueous HF to remove any residual oxide. The chip was finally rinsed with distilled water and dried in a stream of dry N_2.

Reaction between 1,ω-dimethoxytritylundecenol and porous silicon or Si(111) and subsequent deprotection: Porous silicon was treated with the protected alkene by heating in a 10 % v/v solution of undecenol-DMT in toluene (predistilled over Na) under reflux for approximately 18 h under nitrogen. The chips were then rinsed with toluene, CH_2Cl_2 (× 2) and dried in a stream of N_2. The presence of the monolayer was confirmed by normal transmission FT-IR spectroscopy (ν = aromatic C–H 3074, 3040, 3000 cm^{-1}, alkyl C–H 2927, 2854 cm^{-1}, C═C 1641, 1608, CH_2(scissor) 1465 cm^{-1}. Washing with 3% trichloroethanoic acid in CH_2Cl_2 quantitatively removed all the bands associated with the DMT group and produced a broad band centred at about 3300 cm^{-1} assigned to ν(OH).

Modification of Si(111) single-crystal chips was by the same method, except that it was not possble to obtain the FT-IR spectrum in the normal transmission alignment for reasons of instrumental sensitivity. After alkylation, the surface was washed with excess toluene and dried under N_2 before storing under N_2 prior to use.

Reaction between $(nBu_4N)_3[(MeO)TiW_5O_{18}]$ and undecanol-derivatized Si: The undecanol-derivatized single-crystal or porous Si chips were immersed in a MeCN solution of $(n\mathrm{Bu}_4\mathrm{N})_3[(\mathrm{MeO})\mathrm{TiW}_5\mathrm{O}_{18}]$ (0.05 M, 5 mL) under dry N_2 in a Schlenk flask. The flask was then heated to 85 °C for 6 h. After cooling, the chip was removed, washed with dry acetonitrile, and dried in a stream of dry N_2.

Received: June 24, 2004
Revised: November 11, 2004

Keywords: alkoxides · polyoxometalates · surface chemistry · titanium · tungsten

---

[1] M. T. Pope, A. Müller, *Angew. Chem.* **1991**, *103*, 56; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 34.
[2] *Polyoxometalates: From platonic solids to anti-retroviral activity* (Eds.: M. T. Pope, A. Müller), Kluwer, Dordrecht, Netherlands, **1994**.
[3] *Polyoxometalate Chemistry: From topology via self-assembly to applications* (Eds.: M. T. Pope, A. Müller), Kluwer, Dordrecht, Netherlands, **2001**.
[4] W. G. Klemperer, C. G. Wall, *Chem. Rev.* **1998**, *98*, 297.
[5] M. Ge, B. Zhong, W. G. Klemperer, A. A. Gewirth, *J. Am. Chem. Soc.* **1996**, *118*, 5812.
[6] B. Keita, L. Nadjo, *Surf. Sci. Lett.* **1991**, *254*, L443.
[7] M. S. Kaba, I. K. Song, D. C. Duncan, C. L. Hill, M. A. Barteau, *Inorg. Chem.* **1998**, *37*, 398.
[8] M. A. Barteau, J. E. Lyons, I. K. Song, *J. Catal.* **2003**, *216*, 236.
[9] M. Clemente-Leon, C. Mingotaud, B. Agricole, C. J. Gomez-Garcia, E. Coronado, P. Delhaes, *Angew. Chem.* **1997**, *109*, 1143; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1114.
[10] M. Clemente-Leon, E. Coronado, P. Delhaes, C. J. Gomez-Garcia, C. Mingotaud, *Adv. Mater.* **2001**, *13*, 574.
[11] M. Clemente-Leon, B. Agricole, C. Mingotaud, C. J. Gomez-Garcia, E. Coronado, P. Delhaes, *Langmuir* **1997**, *13*, 2340.
[12] S. Liu, G. D. Kurth, B. Bredenkotter, D. Volkmer, *J. Am. Chem. Soc.* **2002**, *124*, 12279.
[13] C. R. Mayer, S. Neveu, V. Cabuil, *Angew. Chem.* **2002**, *114*, 519; *Angew. Chem. Int. Ed.* **2002**, *41*, 501.
[14] W. Clegg, M. R. J. Elsegood, R. J. Errington, J. Havelock, *J. Chem. Soc. Dalton Trans.* **1996**, 681.
[15] A. R. Pike, L. H. Lie, R. A. Eagling, L. C. Ryder, S. N. Patole, B. A. Connelly, B. R. Horrocks, A. Houlton, *Angew. Chem.* **2002**, *114*, 637; *Angew. Chem. Int. Ed.* **2002**, *41*, 615.
[16] Y. Wang, C. Guo, Y. Chen, C. Hu, W. Yu, *J. Colloid Interface Sci.* **2003**, *264*, 176.
[17] D. Gonbeau, C. Guimon, G. Pfister-Guillouzo, A. Levasseur, G. Meunier, R. Dormoy, *Surf. Sci.* **1991**, *254*, 81.
[18] A. B. Sieval, B. v. d. Hout, H. Zuilhof, E. J. R. Sudhölter, *Langmuir* **2000**, *16*, 2987.
[19] A. B. Sieval, B. v. d. Hout, H. Zuilhof, E. J. R. Sudhölter, *Langmuir* **2001**, *17*, 2172.
[20] C. P. Wade, C. E. D. Chidsey, *Appl. Phys. Lett.* **1997**, *71*, 1679.