## ChemComm

## COMMUNICATION



View Article Online View Journal | View Issue

Cite this: Chem. Commun., 2014, 50, 5397

Received 18th September 2013, Accepted 10th December 2013

DOI: 10.1039/c3cc47140c

www.rsc.org/chemcomm

polar molecules in a non-polar, polarizable solvent system<sup>†</sup>

Arunava Agarwala, Niv Kaynan, Seva Zaidiner and Roie Yerushalmi\*

Surface modification of metal oxides by

Oxide and metal oxide (MO) nanoparticles are widely used in various applications. A simple yet general approach for modifying MO surfaces using polar compounds in a non-polar but polarizable solvent is presented. Molecular adsorption onto the MO surface is based on dipole-dipole interactions while solvation relies on induced-dipole-dipole interactions.

Oxides and metal oxides (MOs) are an important class of materials used in various fields ranging from microelectronics to optical coatings, photocatalysis and more.<sup>1</sup> MOs readily form non-covalent binding interactions such as H-bonds as well as other polar interactions. In addition, MO surfaces may promote covalent bond formation and cleavage by oxidation, reduction, hydrolysis and other surface catalyzed reactions. The tailoring of MO properties by surface chemistry is a broad research field with applications in microelectronics, photocatalysis, and separation techniques just to name a few.<sup>2–4</sup> The modification of MO surfaces by covalent attachment of organic molecules is of broad interest and extensively studied.<sup>5</sup> The numerous applications of MOs and MO nanoparticles (NPs) encourage the development of diverse approaches for surface modification of these materials.<sup>6</sup>

Here we present a simple yet versatile approach for the formation of molecular films at MO NP surfaces and oxide interfaces in general using organic compounds with the general formula:  $O=X-(Ph-R)_n$ , where X = P and As; R = H and Me; n = 1 and 3 (Fig. 1). Monolayer formation is studied for four types of oxides and four molecular precursors to demonstrate the generality of the approach. Specifically, we demonstrate the approach for SiO<sub>2</sub>, TiO<sub>2</sub> anatase (TiO<sub>2</sub>a), Al<sub>2</sub>O<sub>3</sub> gamma (Al<sub>2</sub>O<sub>3</sub>g) and Fe<sub>3</sub>O<sub>4</sub> NPs. The surface chemistry approach demonstrated here is applicable to a wide variety of organic precursors and MO surfaces. Those MOs are highlighted here because:SiO<sub>2</sub> is widely used as a dielectric layer for electronic devices and more recently for surface doping of Si nanostructures.<sup>2,7</sup> TiO<sub>2</sub> is an important metal oxide used in a wide range of



Fig. 1 Adsorption of molecules with polar head groups onto  $SiO_2$  NPs. Error bars reflect variability in IR peak areas.

applications, for example, photocatalysis and energy related applications.<sup>8</sup> Al<sub>2</sub>O<sub>3</sub> is used as a support for many important industrial catalysts.<sup>9</sup> Fe<sub>3</sub>O<sub>4</sub> is widely used for its magnetic properties, for catalysis, and biomedical applications.<sup>10</sup> Surface reactions were performed in mesitylene, a non-polar, non-protic and highly polarizable solvent. Monolayer formation is driven by polar interactions of the X—O head group at the oxide interface. Mesitylene is used here as a non-polar but polarizable solvent system allowing for sufficient solvation interactions with the polar solute molecules relying on the polarizable medium–permanent dipole interactions that would hamper the adsorption of the polar solute molecules onto the polar oxide interface. This is because the polar molecule adsorption

Institute of Chemistry and the Center for Nanoscience and Nanotechnology, The Hebrew University of Jerusalem, Jerusalem, Israel.

E-mail: roie.yerushalmi@mail.huji.ac.il

 $<sup>\</sup>dagger$  Electronic supplementary information (ESI) available: Experimental details. See DOI: 10.1039/c3cc47140c

process relies on dipole–dipole interactions between the polar X=0 group and polar surface groups typical of MOs while the solvation interactions rely on induced-dipole–dipole interactions between the polarizable solvent molecules and the polar X=0 groups. The surface modified NPs were characterized by FTIR and XPS.

The adsorption kinetics of triphenylphosphine oxide (P1), tris-(4-methylphenyl)phosphineoxide (P2), triphenylarsineoxide (As1), and phenylarsineoxide (As2) onto SiO<sub>2</sub> NPs were studied using quantitative FTIR absorption spectroscopy (Fig. 1a-d). The surface density was deduced by quantification of the IR absorption and determination of the SiO<sub>2</sub> NPs surface area by multipoint Brunauer-Emmett-Teller (BET) analysis. Briefly, the IR molar absorption of the molecular precursors was determined with known concentrations in the KBr matrix prepared using an analytical balance. The IR absorption peak area of the monolayer-modified NPs was quantified using standard IR software analysis tools (Bruker OPUS). This analysis yielded the adsorbed molecules concentration for the surface modified NPs. Finally, the coverage was deduced for surface modified SiO<sub>2</sub> NPs using the SiO<sub>2</sub> NPs surface area measured by BET and the IR determined concentrations as explained above (see ESI<sup>+</sup> for more details). The results demonstrate self-limiting surface reactions for all cases studied for the various compounds with molecular surface densities saturating at 0.45–0.66 molecules per nm<sup>2</sup> (Fig. 1). This result suggests that the maximal surface coverage obtained is  $\sim$  42–78% of the oxide surface area (see Table S2 and additional details in the ESI† for calculation of the molecular footprint). We attribute the less than full surface coverage to steric interactions of the bulky phenyl groups or to a limited surface density of adsorption sites. Similarly, the adsorption of P1 onto TiO2a, Al2O3g and Fe3O4 NPs was studied, showing selflimiting characteristics as well (Fig. S1, ESI<sup>+</sup>). All surface reactions were complete within 2 hours.

IR spectra of **P1** (Fig. S2a, ESI<sup>†</sup>) showed a sharp band observed at 1439 cm<sup>-1</sup> for all monolayers on the various MOs assigned to  $\nu$ (C==C), characteristic of a phenyl ring attached to phosphorus (aryl-P). The band at 1121 cm<sup>-1</sup>, observed for TiO<sub>2</sub>a, Al<sub>2</sub>O<sub>3</sub>g and Fe<sub>3</sub>O<sub>4</sub>, is assigned to the  $\nu$ (P=C) stretching mode,<sup>11</sup> where C is part of the aromatic ring. For SiO<sub>2</sub> this peak is obscured by the strong IR absorption band of Si–O. The peak at 1184 cm<sup>-1</sup> for neat **P1**, assigned to  $\nu$ (P==O),<sup>12</sup> became broad on TiO<sub>2</sub>a, Al<sub>2</sub>O<sub>3</sub>g and Fe<sub>3</sub>O<sub>4</sub> indicative of H-bonding interaction of the P==O moiety with polar groups at the oxide surface similar to that previously reported for SiO<sub>2</sub> surfaces.<sup>13</sup>

For **P2** (Fig. S2b, ESI<sup>†</sup>) similar characteristics were observed with an additional sharp band at 1601 cm<sup>-1</sup> for the neat compound and for all monolayers formed on the various MO NPs assigned to  $\nu$ (C==C). The band at 1116 cm<sup>-1</sup>, observed for TiO<sub>2</sub>a, Al<sub>2</sub>O<sub>3</sub>g and Fe<sub>3</sub>O<sub>4</sub>, is assigned to the  $\nu$ (P=C) stretching mode,<sup>11</sup> except for SiO<sub>2</sub> where the IR spectra are obscured, as discussed above. The 1182 cm<sup>-1</sup> peak of neat **P2** assigned to  $\nu$ (P==O)<sup>12</sup> became broad on TiO<sub>2</sub>a, Al<sub>2</sub>O<sub>3</sub>g and Fe<sub>3</sub>O<sub>4</sub> similar to **P1**. XPS showed a P<sub>2p</sub> peak with a single component for all monolayers formed with **P1** and **P2** on the various MOs, similar to that previously reported for **P1** on planar Si/SiO<sub>2</sub> surfaces (Table S3, ESI<sup>†</sup>).<sup>13,14</sup>

IR measurements for arsine oxide compounds, **As1** and **As2**, showed similar adsorption characteristics to the phosphine oxides. For **As1** (Fig. S2c, ESI<sup>†</sup>) the 1085 cm<sup>-1</sup> band assigned to  $\nu$ (As-C)<sup>15</sup> showed little or no change upon monolayer formation on the various MO NPs studied here. A sharp band at 1440 cm<sup>-1</sup> characteristic of

phenyl  $\nu$ (C=C) is observed for neat and **As1** monolayers formed on all MOs studied here. The 880 cm<sup>-1</sup> band assigned to  $\nu$ (As=O)<sup>16</sup> for neat **As1** became broad and shifted to a lower wavenumber following adsorption onto SiO<sub>2</sub> NPs indicative of H-bond formation at the surface similar to the case of **P1** and **P2**.<sup>13</sup> For **As2** a sharp band at 1435 cm<sup>-1</sup> is assigned to the ring vibration mode for neat and all monolayers formed on the various NPs. XPS measurements gave a As<sub>3d</sub> peak for **As1** and **As2** for all MO NP reactions (Table S3, ESI†).<sup>17</sup> For **As2** a single As<sub>3d</sub> peak is present for all MOs studied here.

In contrast, for As1 the As3d peak showed two distinct arsenic species for all MOs except for Fe<sub>3</sub>O<sub>4</sub> NPs that showed a single component (Table S3, ESI<sup>+</sup>). The 0.4-0.8 eV shift to higher binding energy could be assigned to As1 molecules adsorbed via H-bonding interaction with the oxide surface, similar to the previously reported shift of 0.6 eV for P1 on Si/SiO<sub>2</sub> surfaces.<sup>13</sup> The low binding energy peak for reacted As1 is shifted to significantly lower binding energies compared to the unreacted As1 compound with 43.5, 42.7, and 43.7 eV for As1/SiO<sub>2</sub>, As1/TiO<sub>2</sub>a, and As1/Al<sub>2</sub>O<sub>3</sub>g, respectively, which rules out surface induced oxidation of the As1 compound that would lead to higher binding energy (Table S3, ESI<sup>+</sup>). A computational study was performed for considering various surface reactions and assigning the low binding energy species for As1/SiO2. Molecular structures were fully optimized at the B3LYP/6-311G\*\* level of theory and NPA charge analysis was applied to determine the atomic charge of the As atom. The calculated As atomic charges gave a good correlation with binding energies obtained from the NIST database (Fig. 2,  $R^2 = 0.99$ ). The correlation was used to evaluate possible surface species. For SiO<sub>2</sub> NPs we suggest that the low binding energy peak may be assigned to Si-O-As(Ph)2, consistent with the As chemical environment determined by XPS and charge



**Fig. 2** Correlation of XPS As<sub>3d</sub> binding energies with calculated atomic charges of the As atom. Linear correlation obtained for reported binding energies (from NIST database) and calculated atomic charges of the As atom ( $\blacklozenge$ ),  $R^2 = 0.99$ . Measured binding energies, calculated structures, and atomic charges of **As1**/SiO<sub>2</sub> ( $\Box$ ).



Fig. 3 Changes in electron affinity ( $\Delta$ EA) values measured by contact potential difference (CPD) for Si(100) surfaces with a native oxide layer. Error bars represent statistical variation in CPD values for repeating monolayer formation experiments.

analysis (Fig. 2). This result suggests opening of the As=O double bond at the oxide surface and cleavage of one phenyl ring, resulting in Si–O–As covalent bond formation. Notably, for planar Si/SiO<sub>2</sub> surfaces only H-bond formation is observed. The unique reactivity of As1 towards MO NPs reported here is currently under further study.

The surface chemistry presented here for MO NPs may be further utilized for tuning the electronic properties of semiconductor-oxide interfaces, for example Si/SiO<sub>2</sub> surfaces. The adsorption of P1, P2, As1 and As2 from mesitylene was studied for Si(100) surfaces with a native oxide layer. Ellipsometry and XPS measurements confirmed the formation of a self-limiting monolayer for all cases. Contact potential difference (CPD) measurements were performed for studying the changes in the semiconductor electronic properties as a result of the adsorption of the polar molecules. The modulation of the semiconductor electronic properties by monolayers is a versatile handle reflected in tuning of the electron affinity (AEA) values measured.<sup>18</sup> All monolayers yielded negative  $\Delta EA$  values in accordance with the expected changes for surface dipole orientation pointing towards the Si/SiO<sub>2</sub> interface (Fig. 3). This result is in line with the IR data for SiO<sub>2</sub> NPs where the polar molecules studied here adsorb onto the surface via X=O···HO-Si interactions. The tuning of the Si work function reflected in the relatively large magnitudes of  $\Delta EA$  is measured by CPD exceeding 750 mV for As1. Thus, the new surface chemistry presented here may be utilized for tailoring the surface properties of NPs as well as the electronic properties of semiconductor-oxide interfaces.

In summary, we have demonstrated a general method for modification of various MO surfaces with phosphine oxide and arsine oxide polar compounds in a non-polar yet polarizable solvent system for the assembly process. The adsorption processes for the various compounds and oxides studied here show quite similar characteristics regardless of the specific MO details. All MOs and molecular precursors studied here exhibit self-limiting surface adsorption *via* specific interaction of the X=O moiety with polar surface groups of the oxides. For As1 an additional surface reaction mode is studied that is not found for planar Si/SiO<sub>2</sub> surfaces where only H-bonding interactions are involved. Monolayer formation is driven by dipole–dipole interactions between the polar X=O group and polar surface groups typical of oxide interfaces in general while the solvation interactions rely on induced-dipole–dipole interactions between the polar X=O groups. A generalization of the applicability of the surface chemistry presented here is demonstrated for tuning of the semiconductor–oxide electronic properties for planar Si/SiO<sub>2</sub> interfaces.

RY acknowledges financial support from the European Research Council (ERC) under the European Community's Seventh Framework Programme Grant agreement no. 259312, the Israel Science Foundation (ISF) under Grant (690/09) and the Israeli National Nanotechnology Initiative (INNI, FTA project). We thank Prof. Miron Landau for his kind assistance with BET measurements and Prof. Shlomo Yitzchaik for assistance with CPD measurements.

## Notes and references

- 1 (a) F. Caruso, Adv. Mater., 2001, 13, 11; (b) D. S. Hecht, L. Hu and G. Irvin, Adv. Mater., 2011, 23, 1482.
- 2 (a) J. C. Ho, R. Yerushalmi, Z. A. Jacobson, Z. Fan, R. L. Alley and A. Javey, *Nat. Mater.*, 2008, 7, 67; (b) O. Hazut, A. Agarwala, I. Amit, T. Subramani, S. Zaidiner, Y. Rosenwaks and R. Yerushalmi, *ACS Nano*, 2012, **6**, 10311.
- 3 H. Zhang, G. Chen and D. W. Bahnemann, J. Mater. Chem., 2009, 19, 5089.
- 4 P. K. Jal, S. Patel and B. K. Mishra, Talanta, 2004, 62, 1005.
- (a) A. Ulman, *Chem. Rev.*, 1996, **96**, 1533; (b) P. H. Mutin, V. Lafond,
   A. F. Popa, M. Granier, L. Markey and A. Dereux, *Chem. Mater.*, 2004,
   **16**, 5670; (c) T. Rajh, L. X. Chen, K. Lukas, T. Liu, M. C. Thurnauer
   and D. M. Tiede, *J. Phys. Chem. B*, 2002, **106**, 10543.
- 6 (a) A. K. Gupta and M. Gupta, *Biomaterials*, 2005, 26, 3995;
  (b) D. Toulemon, B. P. Pichon, X. Cattoen, M. Wong Chi Man and S. Begin-Colina, *Chem. Commun.*, 2011, 47, 11954; (c) R. A. Sperling and W. J. Parak, *Philos. Trans. R. Soc. London, Ser. A*, 2010, 368, 1333;
  (d) E. Galoppini, *Coord. Chem. Rev.*, 2004, 248, 1283.
- 7 R. Cohen, N. Zenou, D. Cahen and S. Yitzchaik, *Chem. Phys. Lett.*, 1997, **279**, 270.
- 8 A. L. Linsebigler, G. Lu and J. T. Yates Jr., *Chem. Rev.*, 1995, 95, 735.
  9 R. S. Varma, *Green Chem.*, 1999, 1, 43.
- 10 (a) R. Hao, R. Xing, Z. Xu, Y. Hou, S. Gao and S. Sun, Adv. Mater., 2010, 22, 2729; (b) M. Mikhaylova, D. K. Kim, N. Bobrysheva, M. Osmolowsky, V. Semenov, T. Tsakalakos and M. Muhammed, *Langmuir*, 2004, 20, 2472.
- 11 G. Socrates, Infrared and Raman Characteristic Group frequencies Tables and Charts, John Wiley&Sons, West Sussex, 2001.
- 12 (a) M. Halmann and S. Pinchas, J. Chem. Soc., 1958, 3264;
   (b) L. C. Thomas and R. A. Chittenden, Spectrochim. Acta, 1964, 20, 467.
- 13 R. Yerushalmi, J. C. Ho, Z. Fan and A. Javey, *Angew. Chem., Int. Ed.*, 2008, 47, 4440.
- (a) M. Pelavin, D. Hendrickson, J. Hollander and W. Jolly, *J. Phys. Chem.*, 1970, 74, 1116; (b) J. R. Blackburn, C. R. Nordberg, F. Stevie, R. G. Albridge and M. M. Jones, *Inorg. Chem.*, 1970, 9, 2374.
- 15 L. D. Pettit and D. Turner, Spectrochim. Acta, 1968, 24A, 999.
- 16 G. V. Howell and R. L. Williams, J. Chem. Soc. A, 1968, 117.
- (a) W. J. Stec, W. E. Morgan, R. G. Albridge and J. R. Van Wazer, Inorg. Chem., 1972, 11, 219; (b) M. K. Bahl, R. O. Woodall, R. L. Watson and K. J. Irgolic, J. Chem. Phys., 1976, 64, 1210.
- 18 L. Kronik and Y. Shapira, Surf. Sci. Rep., 1999, 37, 1.