

Supporting Information

Surface modification of metal oxides by polar molecules in non-polar, polarizable solvent system

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Surface Modification of nanoparticles:

Surface modification reactions were performed in 20 mL screw-cap vials; 100 mg of nanoparticles and 5 mL of the precursor solution (see table S1 for concentrations of the precursors) in mesitylene (99%, Acros Organics) were loaded into the vials and tightly sealed. Reactions were carried out at 100°C (except phenylarsine oxide (**As2**), which was carried at 50°C) for 2h. Immediately after reaction, the monolayer-containing nanoparticles were removed from the precursor solution by centrifugation, the supernatant phase was discarded, and the nanoparticles were washed in mesitylene and re-dispersed (X3), followed by n-hexane (X2), and finally dried at 115°C for 40minutes. For reactions with **As2** drying was performed under vacuum for 1h at room temperature. The following nanoparticle diameters were used: SiO₂ 15nm; TiO₂ anatase 50nm; Al₂O₃ gamma 15nm and Fe₃O₄ 30nm. All nanoparticles were obtained from MK-nano (oxide pure >99.5%). Commercially available molecular precursors were used as received without further purification: Triphenylphosphineoxide (P1) 99% from Acros Organics, Tris-(4-methylphenyl)phosphineoxide (P2) >98% from TCI, Triphenylarsineoxide (As1) and Phenylarsineoxide (As2) 97% from Acros Organics.

Surface area measurement for SiO₂ nps:

Surface area measurement for SiO₂ nps were obtained from N₂ adsorption isotherm measured at liquid nitrogen temperature with a NOVA-1000 (Quantachrome) system.
Area=142.4 m²/g, correlation coefficient=0.99875.

Computational Analysis

The molecular structures and electronic properties were carried out with B3LYP functional^[S1] using the Gaussian 09 package.^[S2] For geometry optimization 6-311G** basis set^[S3] was used. Frequency calculations were performed in order to check the nature of the stationary points on the potential energy surface. Charge analysis was performed for fully optimized structures using the natural population analysis (NPA) as implemented in G09.^[S4]

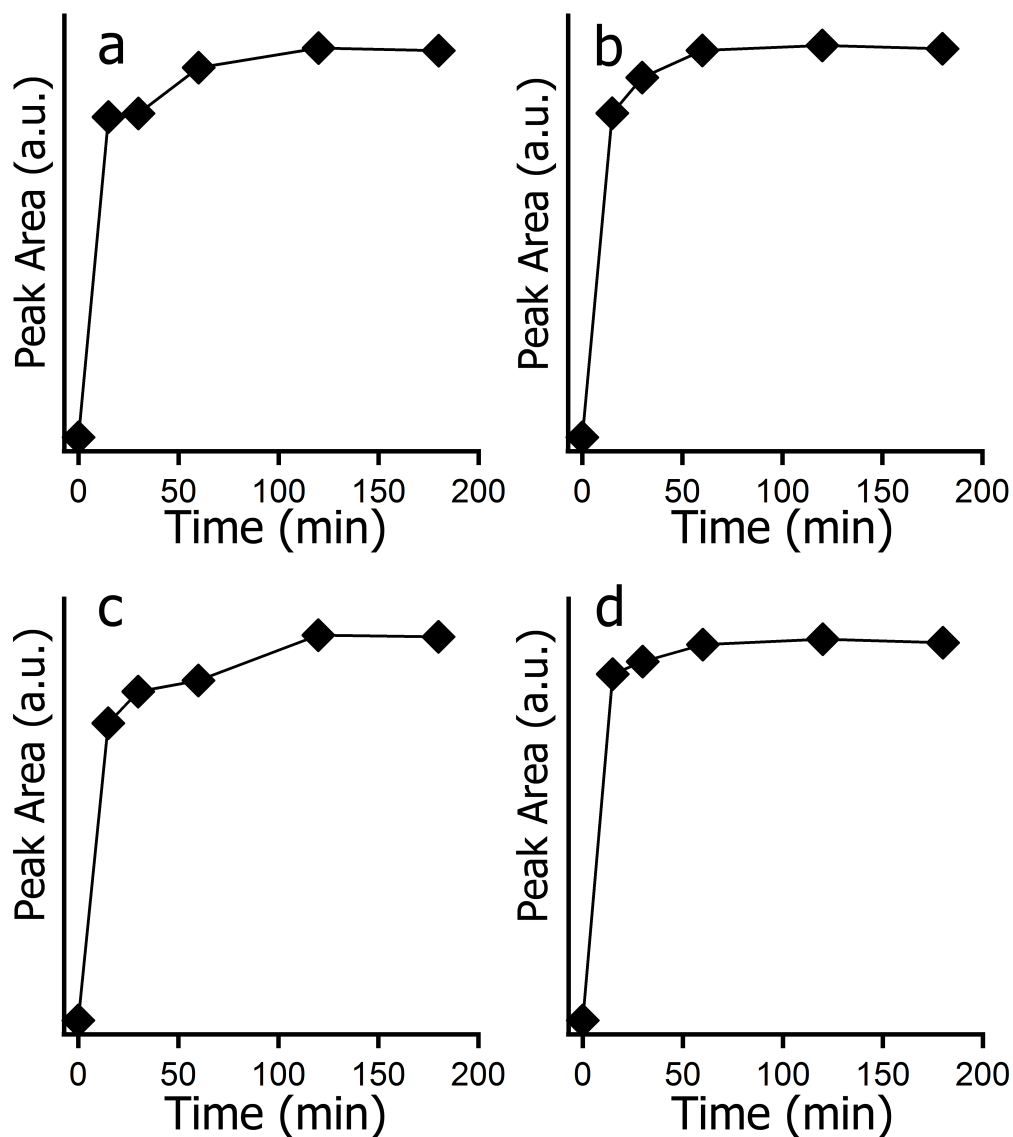


Figure S1. Peak area (1439cm⁻¹) vs. reaction time for **P1** monolayer on (a) SiO₂, (b) TiO₂a, (c) Al₂O₃g, and (d) Fe₃O₄ nanoparticles. Lines connecting the data points serve as a guide to the eye.

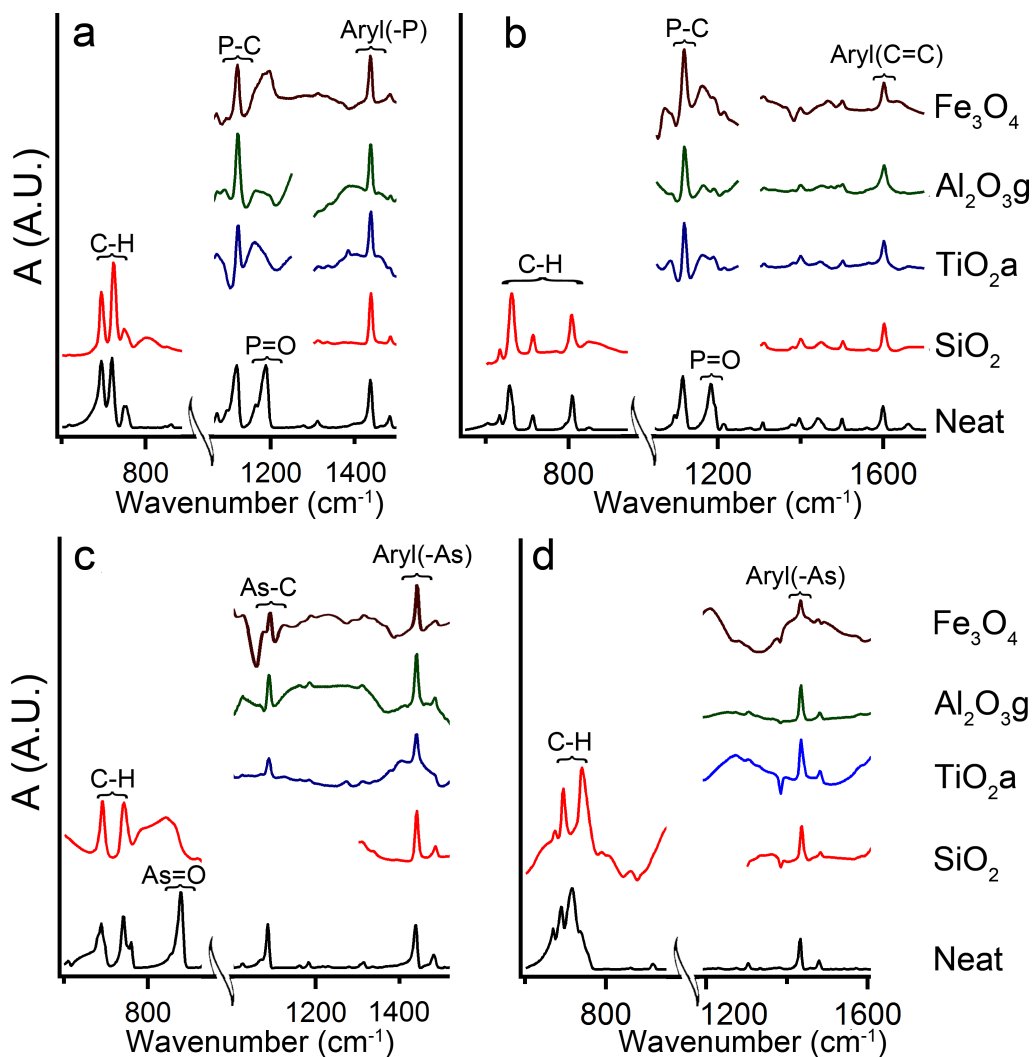


Figure S2. FTIR spectra of MO nps reacted with **P1** (a), **P2** (b), **As1** (c), and **As2** (d). Spectra normalized by 1439cm⁻¹, 1601cm⁻¹, 1440 cm⁻¹, and 1435 cm⁻¹ peaks for **P1**, **P2**, **As1**, and **As2**, respectively.

Table S1:

Molecular precursors used and concentrations of mesitylene solutions used for monolayer formation.

Precursor	Mesitylene Solution	
	MW	Concentration
	[g/mol]	[mM]
Triphenylphosphineoxide (P1)	278.28	44.9
Tris-(4-methylphenyl)phosphineoxide (P2)	320.36	10.4
Triphenylarsineoxide (As1)	322.03	1.6
Phenylarsineoxide (As2)	168.02	14.8

Table S2:

Surface coverage analysis.

Molecule	Molec Footprint molecules/nm ²	Film Density molecules/nm ²	Coverage θ
P1	1.04	0.53	0.51
P2	0.84	0.65	0.78
As1	1.07	0.45	0.42
As2	0.93	0.66	0.71

The molecular footprint values are obtained by fully optimized molecular structures calculated by DFT and assuming rotational degree of freedom of the molecules on the surface around the -X=O axis. The coverage is obtained by the molecular footprint and the experimentally determined surface densities. The molecular footprint variation for the set of molecules studied here is $\sim 104 \pm 12 \text{ \AA}^2$ per molecule.

Table S3:

X-ray Photoelectron Spectroscopy summary for the nanoparticles and precursors studied.

Monolayer/NP	XPS Signal	Binding Energy 1		Binding Energy 2	
		(eV)	Fraction	(eV)	Fraction
P1/SiO₂	P2 _p	133.4	1.0	-	-
P1/TiO₂a	P2 _p	133.9	1.0	-	-
P1/Al₂O₃g	P2 _p	132.8	1.0	-	-
P1/Fe₃O₄	P2 _p	133.2	1.0	-	-
P2/SiO₂	P2 _p	133.4	1.0	-	-
P2/TiO₂a	P2 _p	133.8	1.0	-	-
P2/Al₂O₃g	P2 _p	132.7	1.0	-	-
P2/Fe₃O₄	P2 _p	133.3	1.0	-	-
As1/SiO₂	As _{3d}	45.2	0.3	43.2	0.7
As1/TiO₂a	As _{3d}	44.9	0.7	42.7	0.3
As1/Al₂O₃g	As _{3d}	44.7	0.6	43.7	0.4
As1/Fe₃O₄	As _{3d}	44.8	1.0	-	-
As2/SiO₂	As _{3d}	44.6	1.0	-	-
As2/TiO₂a	As _{3d}	43.7	1.0	-	-
As2/Al₂O₃g	As _{3d}	44.8	1.0	-	-
As2/Fe₃O₄	As _{3d}	43.8	1.0	-	-

Table S4:

Calculated atomic charges and X-ray Photoelectron Spectroscopy binding energies.

Molecular Structure	Calculated charge of As ^a (e ⁻)	As _{3d}		Ref.
		Binding Energy (eV)	Error (eV)	
(C ₆ H ₅) ₃ As	0.882	42.4	0.2	NIST ^b
(C ₆ H ₅) ₃ AsO	1.897	44.4	0.2	NIST
(OH) ₂ As(C ₆ H ₅) ₃	1.889	44.5	0.2	NIST
(C ₆ H ₅)As(O)(OH) ₂	2.229	45.1	0.2	NIST
(C ₆ H ₅) ₃ AsO-HB	1.922	45.2	0.2	This work ^c
Si-O-As(C ₆ H ₅) ₂	1.170	43.2	0.2	This work ^c

^aAtomic charges were calculated for fully optimized structures at the B3LYP/6-311G** level of theory. NPA charge analysis was applied.

^bValues obtained from the NIST database:

NIST X-ray Photoelectron Spectroscopy Database, Version 4.1 (National Institute of Standards and Technology, Gaithersburg, 2012); <http://srdata.nist.gov/xps/>.

^cSee Table S3, **As1/SiO₂**.

References

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