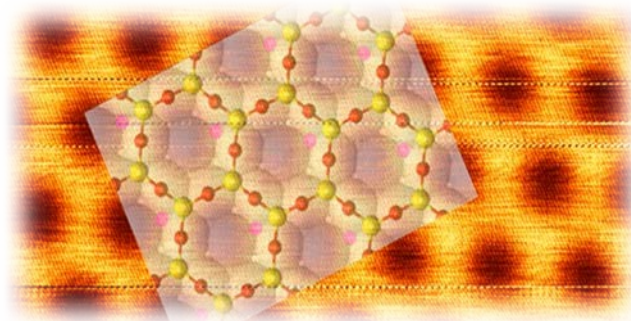
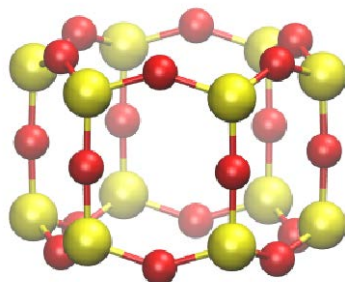

Ultra-thin two-dimensional crystalline nanoporous coatings as cathode protection layers

J. ANIBAL BOSCOBOINIK Center for Functional Nanomaterials
JOHN SMEDLEY Instrumentation Division
Brookhaven National Laboratory



P3, 16th of November 2018

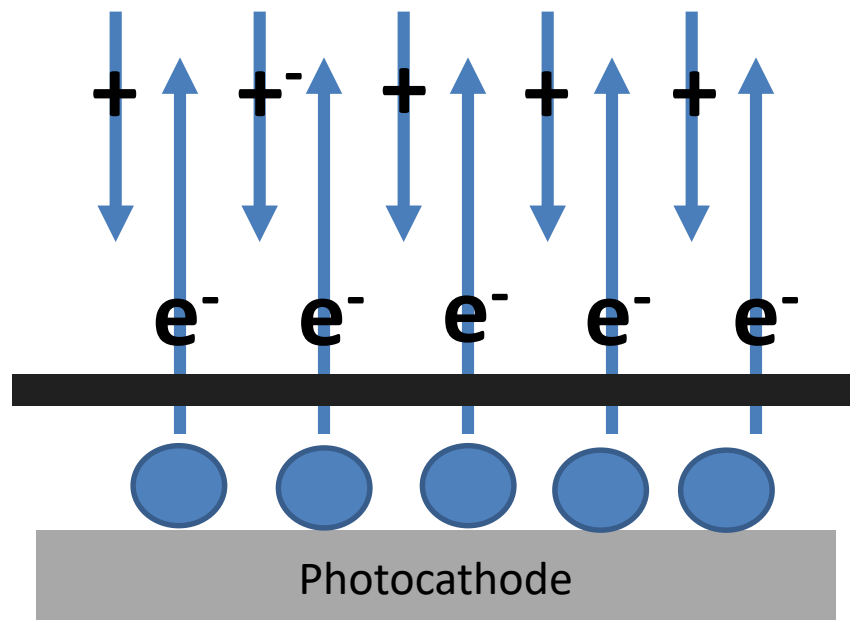
High Brightness Electron Sources

Factors affecting operational lifetime

- Ion bombardment of the cathode
- Chemical contamination
- Thermal decomposition

2D-Material Requirements

- Electron Transparent
- Thermally Stable



Wang, Yang, Moody, Batista, npj 2D Mater. Appl. 2, 17, 2018

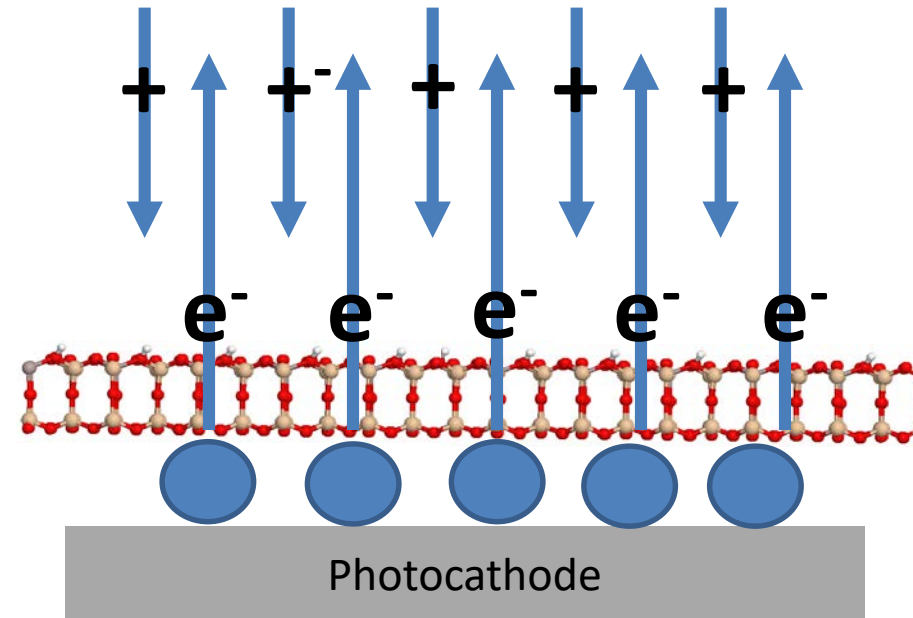
High Brightness Electron Sources

Factors affecting operational lifetime

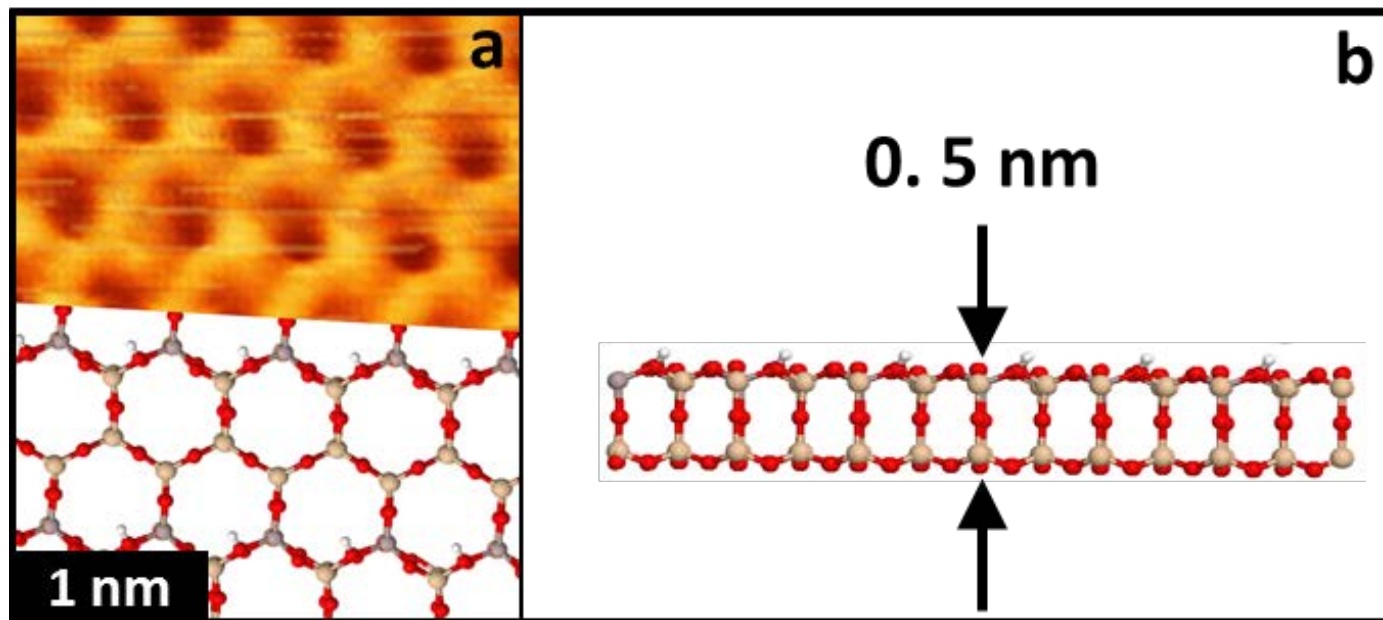
- Ion bombardment of the cathode
- Chemical contamination
- Thermal decomposition

2D-Material Requirements

- Electron Transparent
- Thermally Stable

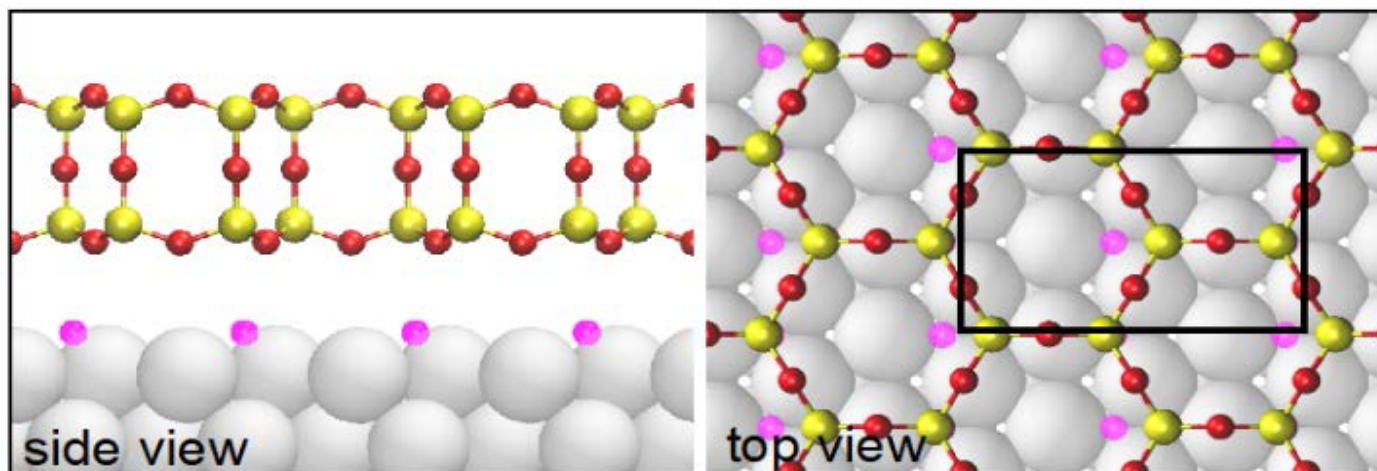
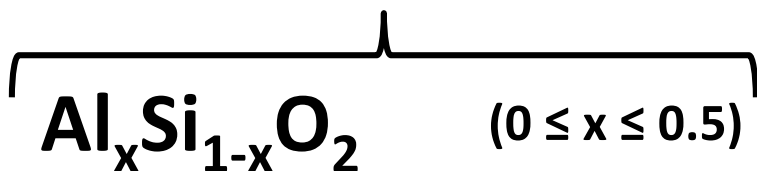


2D-Silicates and Aluminosilicates



Boscoboinik, Shaikhutdinov, Catal. Lett. **2014** DOI: 10.1007/s10562-014-1369-3

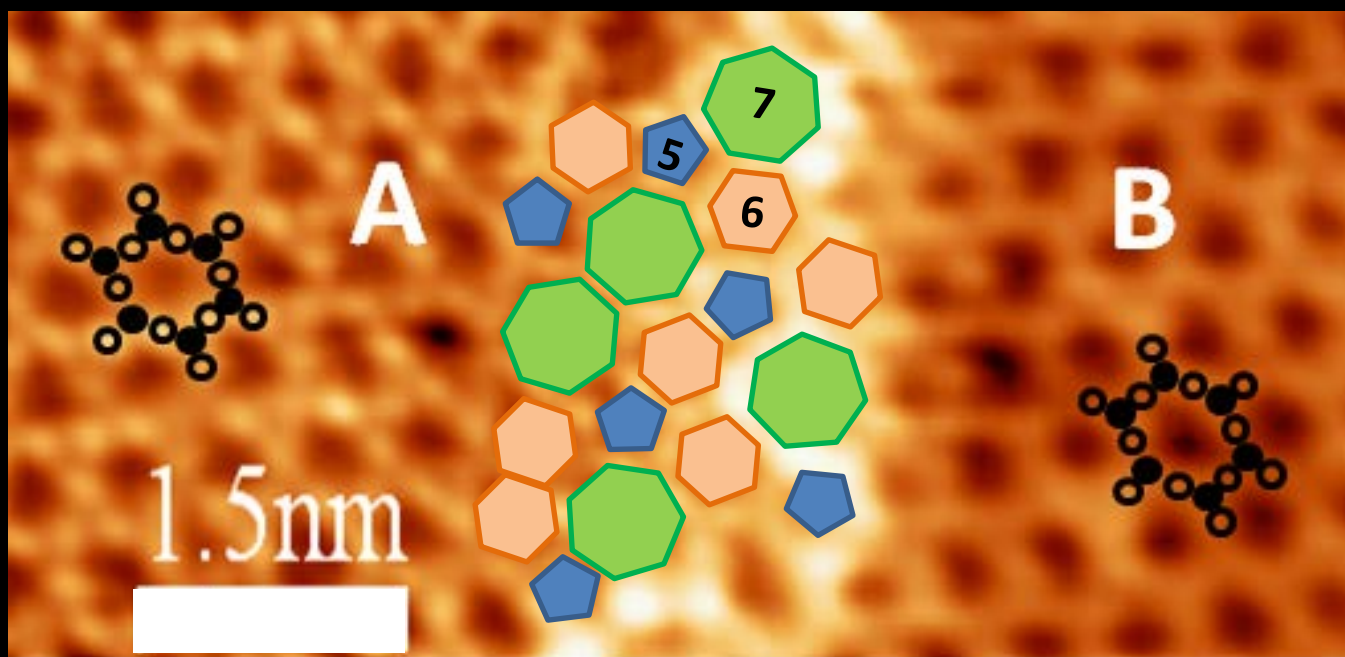
Composition

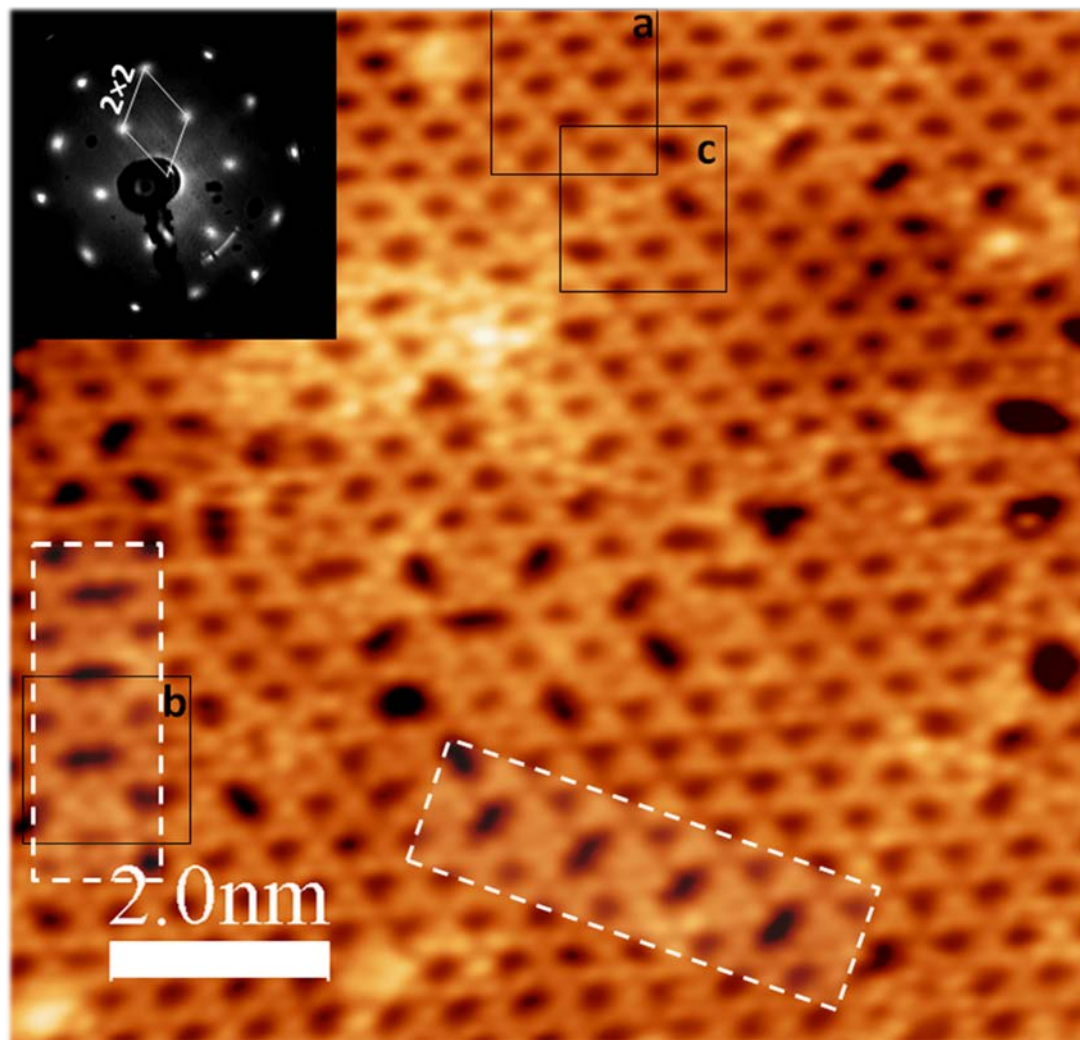


Ru(0001), Pt(111), Pd(100), Pd(111)

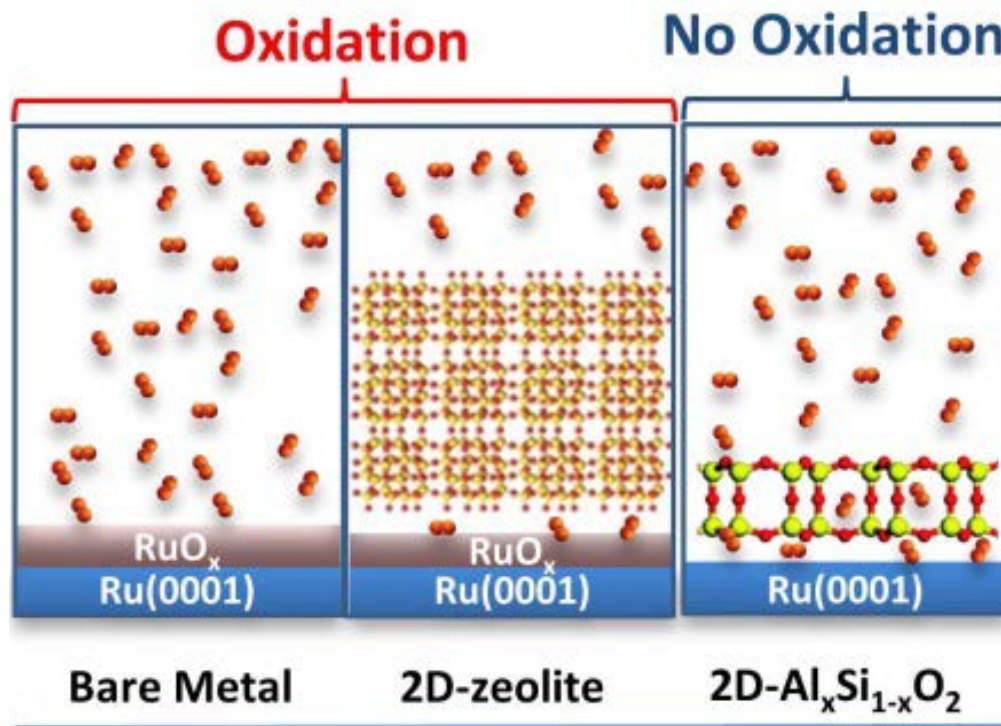
Supports

Scanning Tunneling Microscopy





Corrosion Resistance



820 K

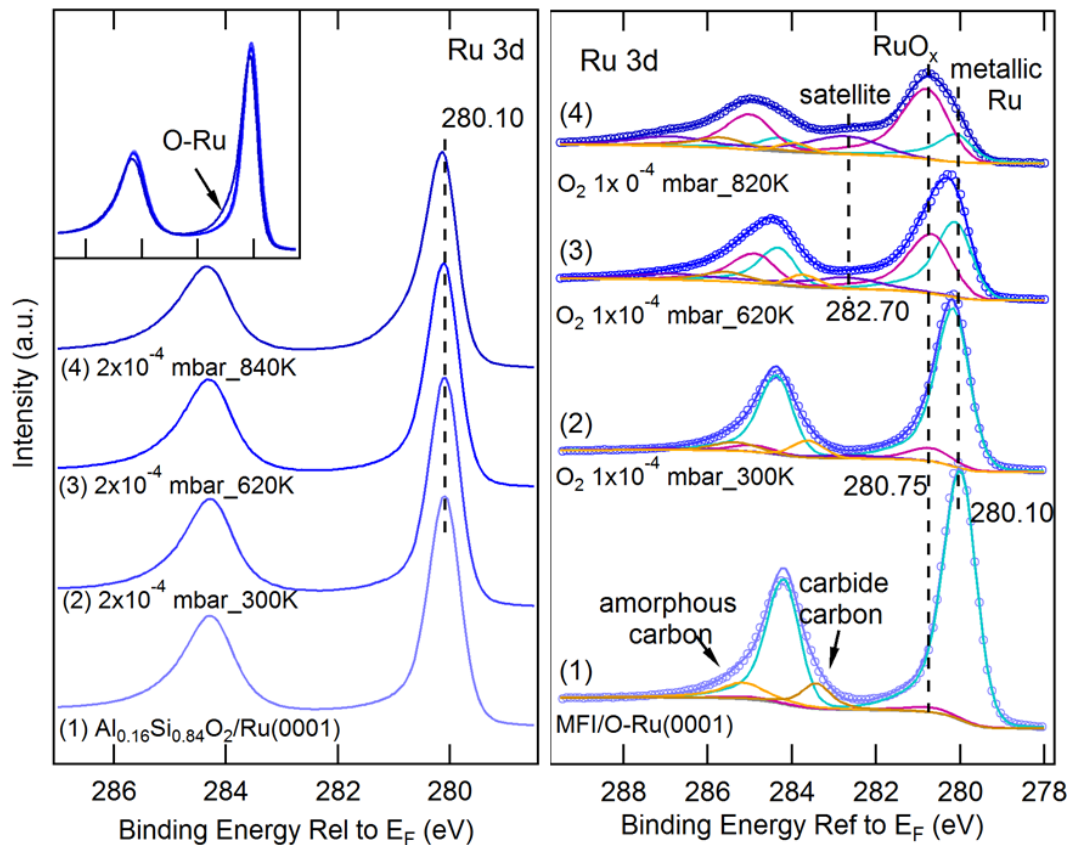
10⁻⁴ mbar O₂

● Silicon or Aluminum

● Oxygen

Zhong, Boscoboinik et al. *J. Phys. Chem. C*, **2016**, 120, 8240.

Corrosion Resistance

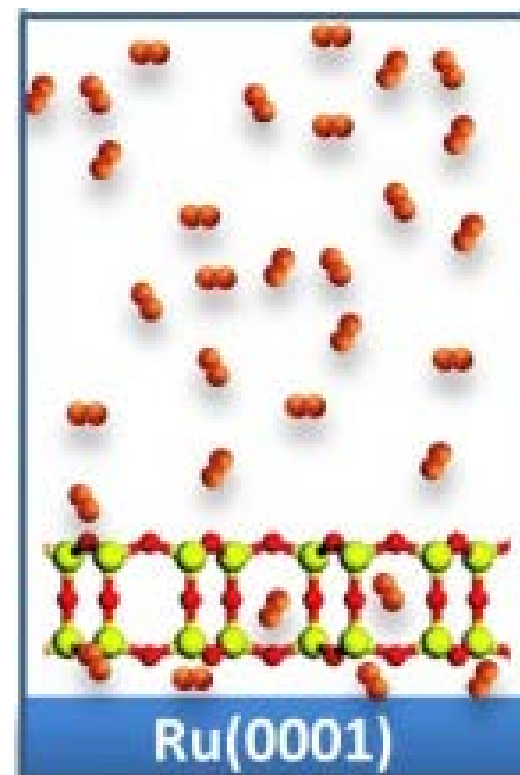
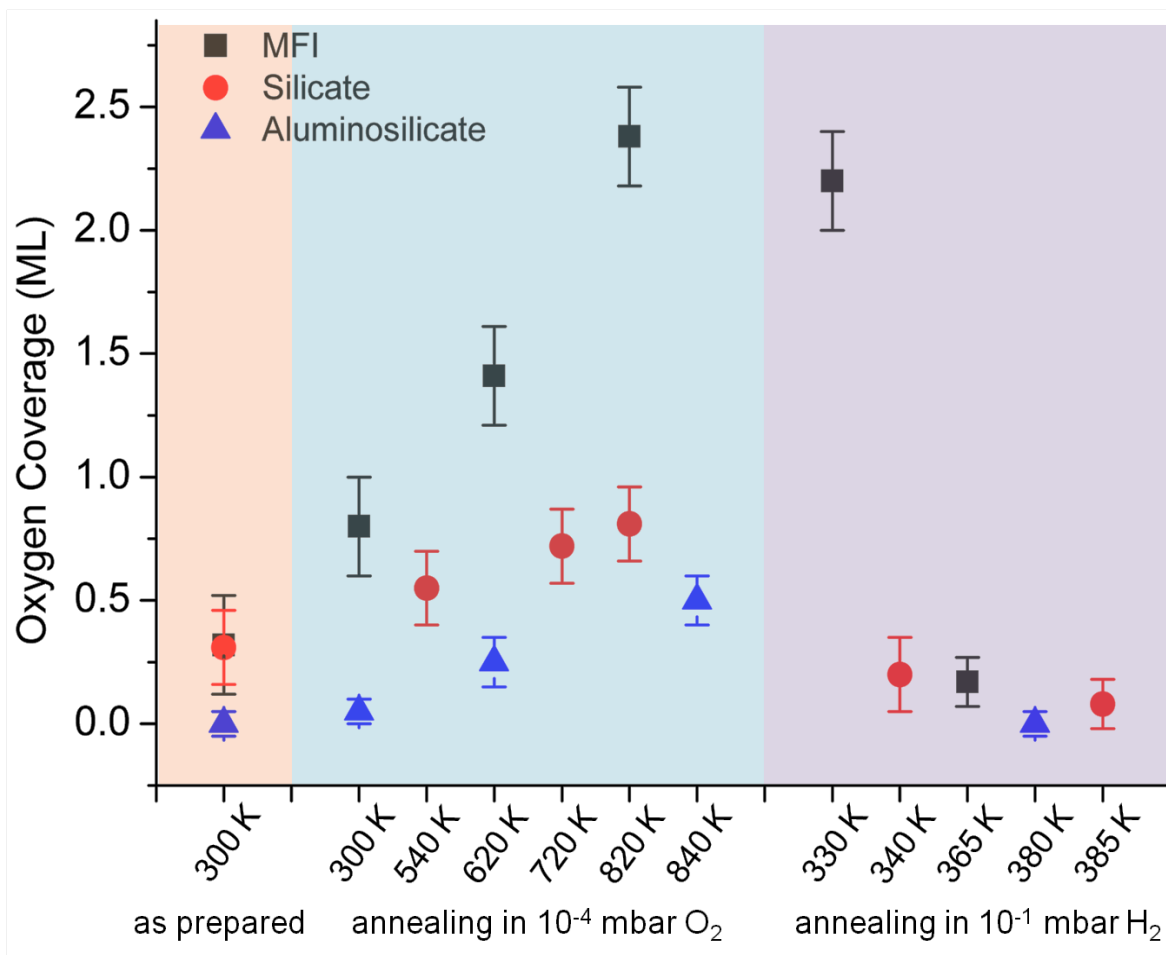


Aluminosilicate 2dH

MFI Nanosheet

Zhong, Boscoboinik et al. *J. Phys. Chem. C*, **2016**, 120, 8240.

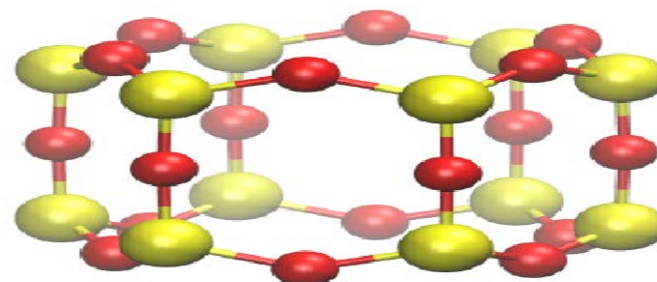
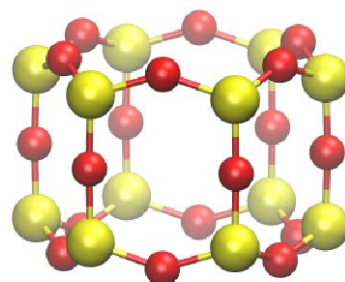
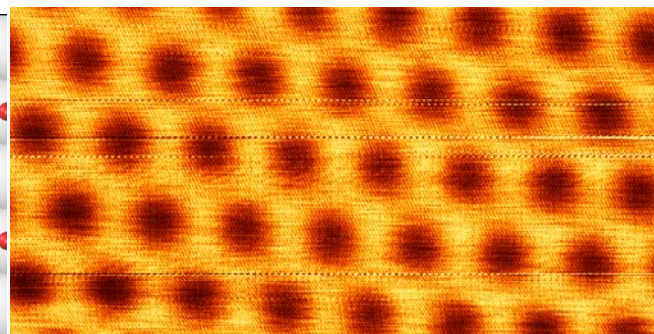
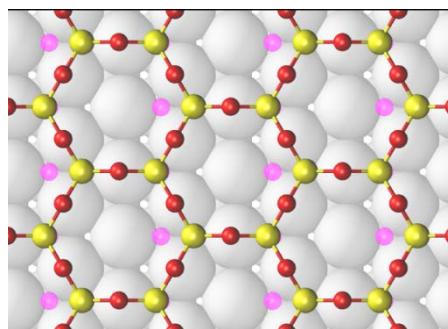
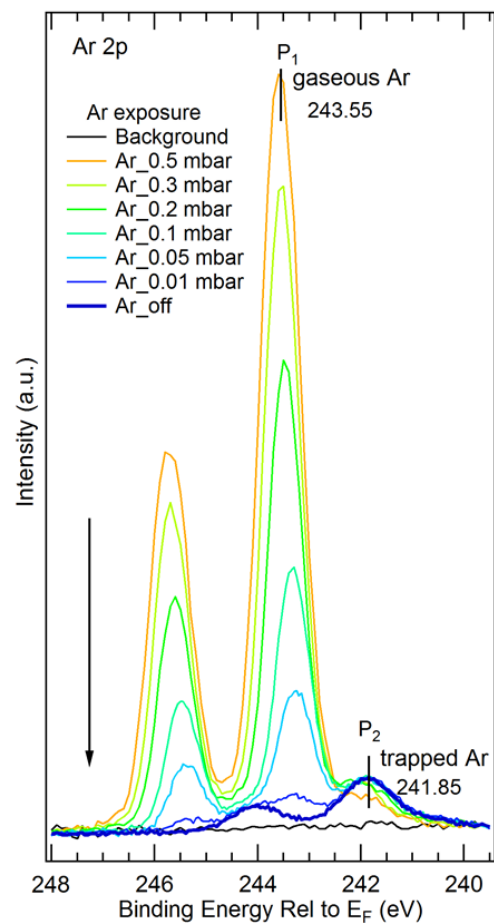
Corrosion Resistance



Zhong, Boscoboinik et al. *J. Phys. Chem. C*, **2016**, 120, 8240.

Gas trapping

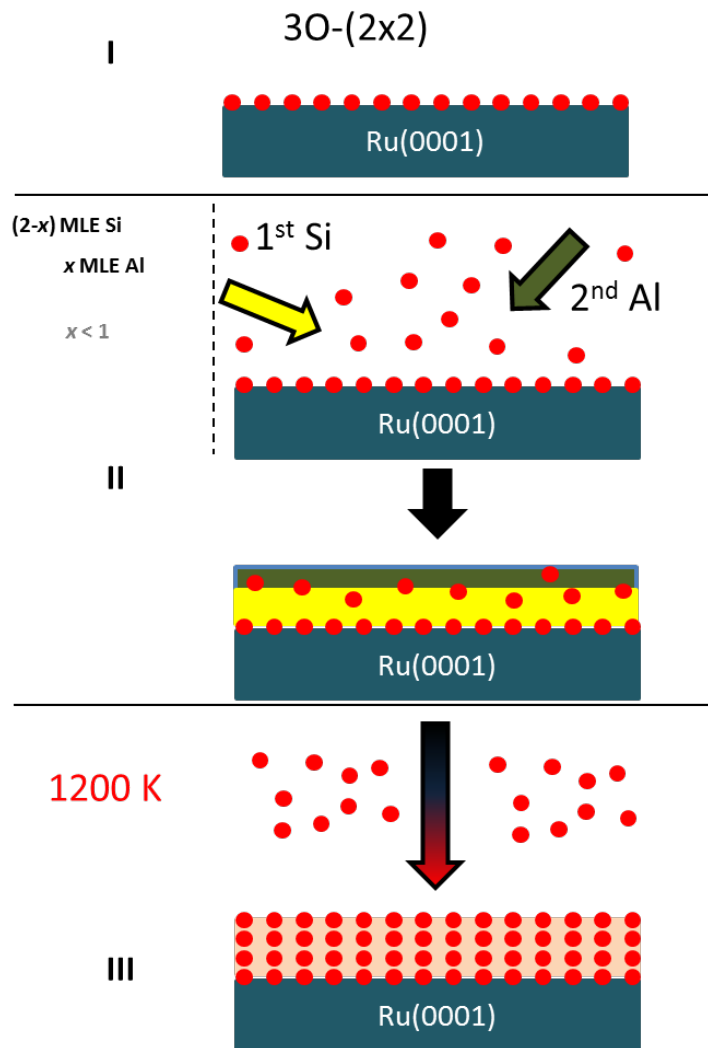
- Exposure to Argon gas



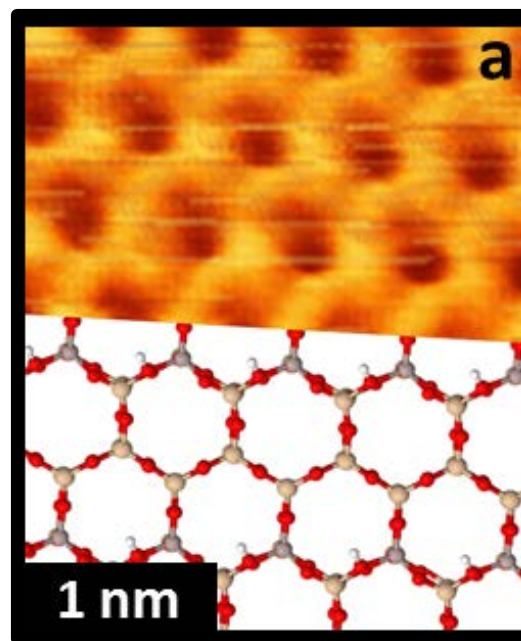
Zhong, Boscoboinik et al., *Nat. Commun.* 8, 16118 (2017)

Synthesis and Alternatives

Current Synthesis Method (UHV conditions)



Base pressure 10^{-9} mbar
E-beam evaporation



Resulting film stable in air

Alternative #1.1: Exfoliation

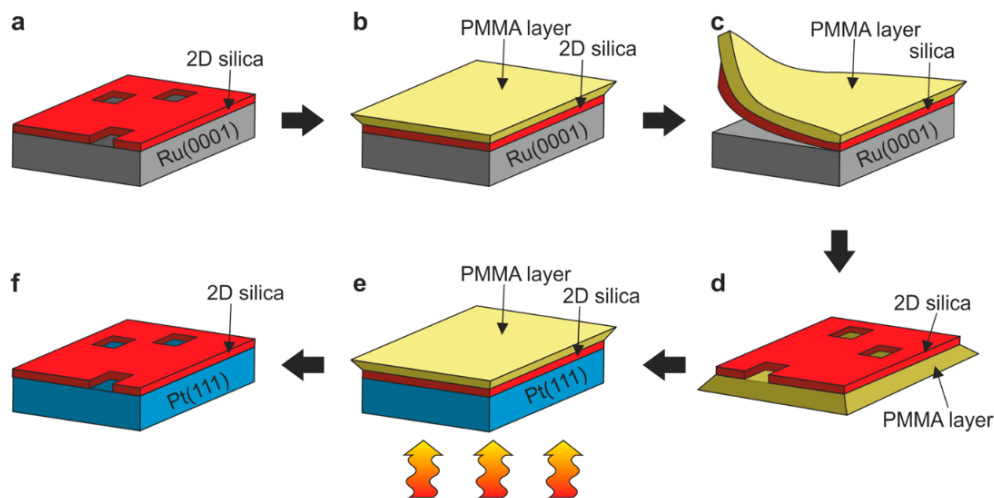
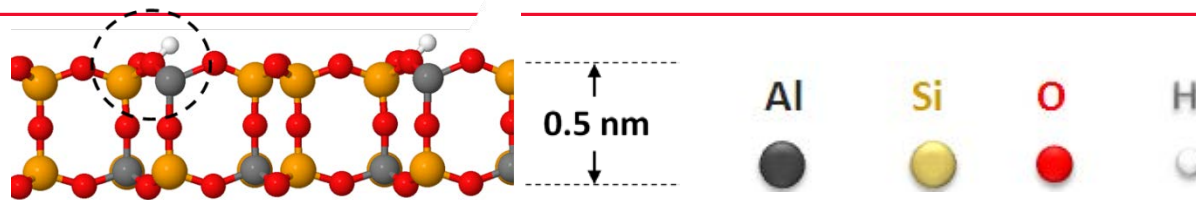


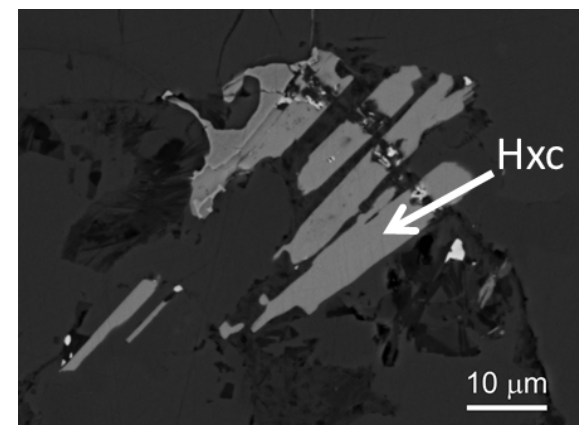
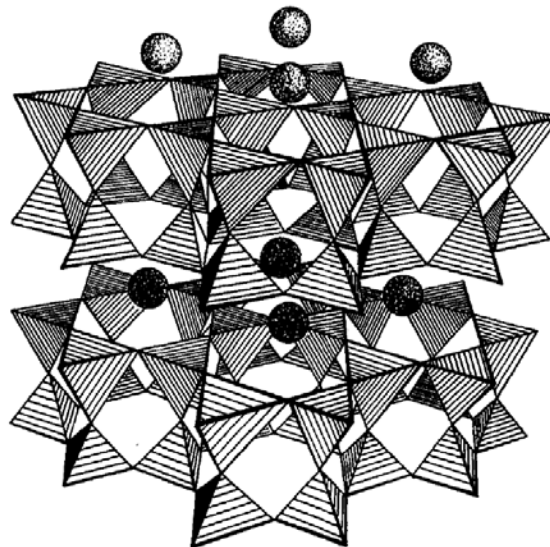
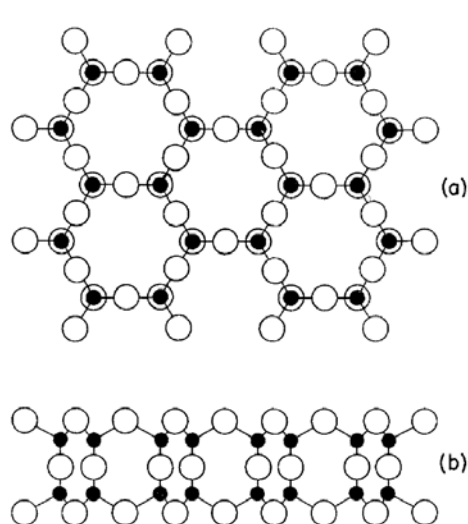
Figure 3. Schematic of the transfer procedure. (a) Silica bilayer on ruthenium substrate. (b) Spin coating of system with PMMA layer. (c) Mechanical exfoliation of PMMA; silica adheres to PMMA layer. (d) Silica supported on PMMA layer. (e) Placing the PMMA-supported silica layer on clean Pt(111) substrate. subsequent heat treatment. (f) After PMMA removal. silica is supported on Pt(111) substrate.

<https://pubs.acs.org/doi/pdf/10.1021/acсна no.6b03929>

Alternative #2: Exfoliation



Hexacelsian (a multilayered version)

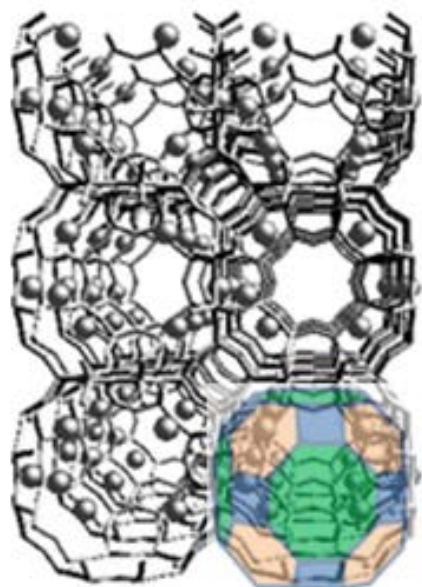


Irina Galuskina

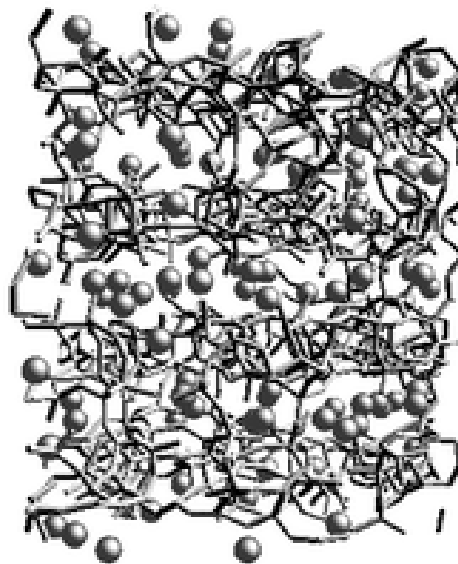
B. Yoshiki, K. Matsumoto

J. Am. Ceram. Soc., 34 (1951), pp. 283–286

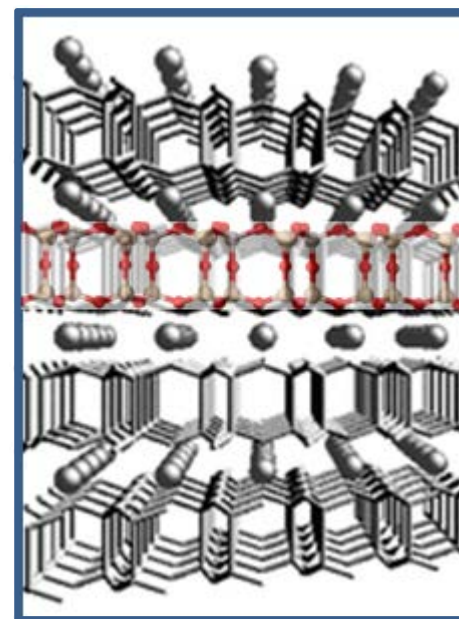
Can be synthesized from Zeolite A!



Ba-LTA zeolite



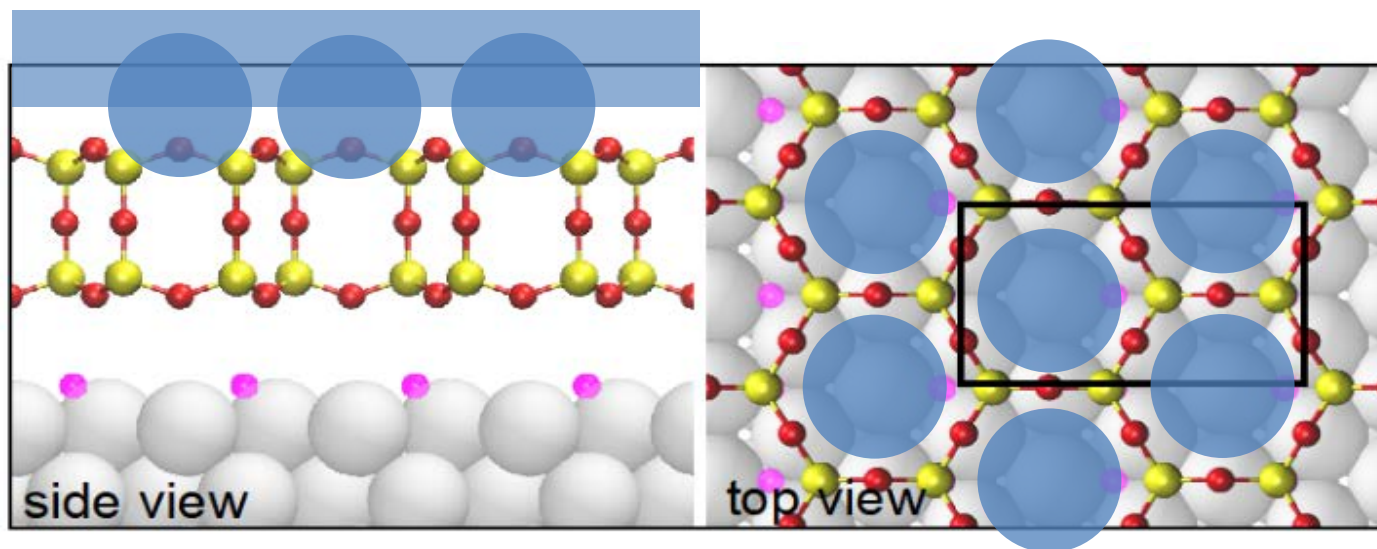
Glass



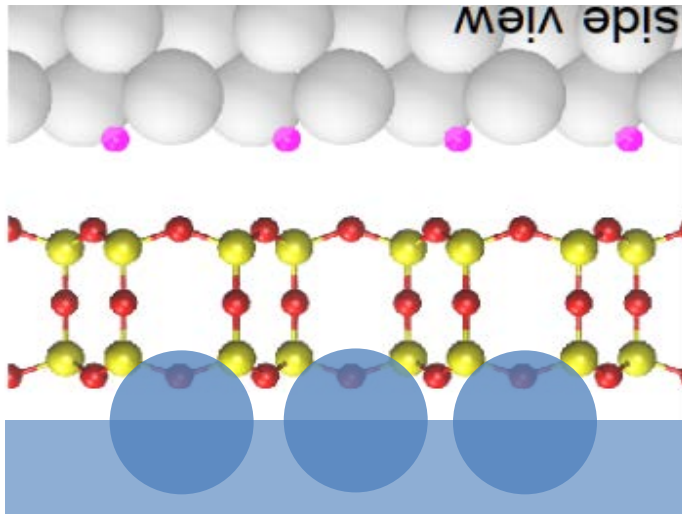
Hexacelsian

Djordjevic et al. *Phys. Chem. Chem. Phys.*, 2001, 3, 1560-1565

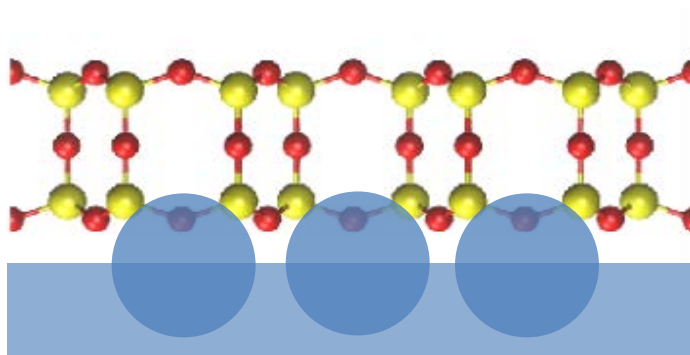
Alternative #1.2: Grow cathode on silicate



Alternative #1.2: Grow cathode on silicate



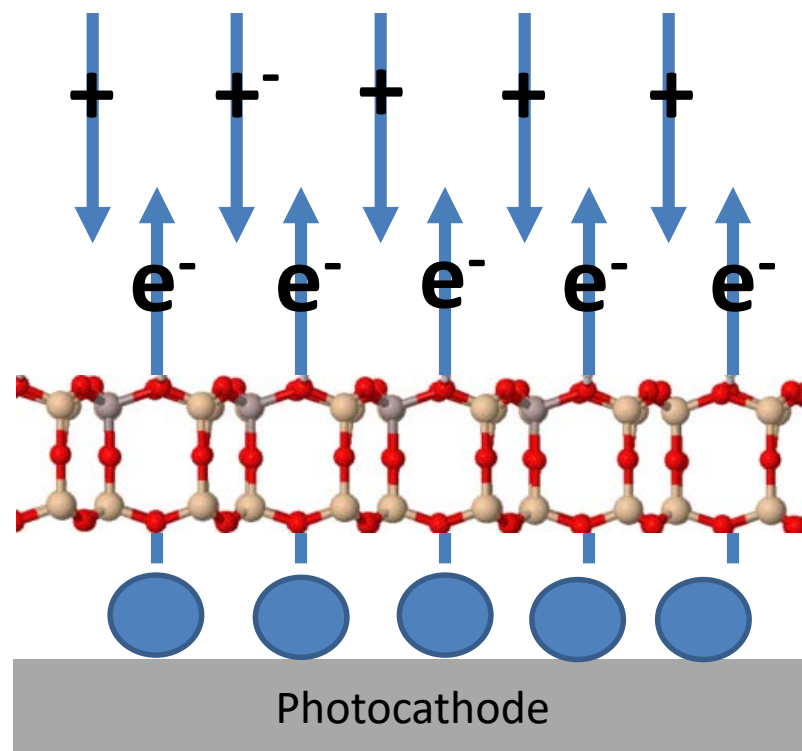
Alternative #1.2: Grow cathode on silicate



Summary

37 Rb Rubidium 85.47	38 Sr Strontium 87.62
55 Cs Cesium 132.91	56 Ba Barium 137.33
87 Fr Francium 223.02	88 Ra Radium 226.03

- Stable ultra-thin silicates
- Potentially reducing:
 - Ion bombardment of the cathode
 - Chemical contamination
 - Thermal decomposition
- Directional electron emission
- Tunability of work function
- **Challenging preparation or deposition on photocathodes**
 - **alternatives are being explored**



Acknowledgements



Center for Functional Nanomaterials at Brookhaven National Laboratory

A DOE Office of Science User Facility for Nanoscience Research

About the CFN:

A national user facility

A portfolio of world-class instruments and expertise under one roof

All facilities and staff expertise available to Users *for free*

Proprietary rate available



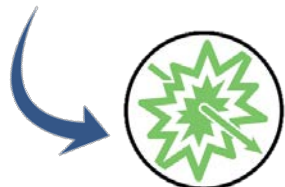
Strategic Themes:



Self-Assembled
Nanomaterials by Design



Nano-Architectures for
Energy Solutions



Nanomaterials in
Operando Conditions

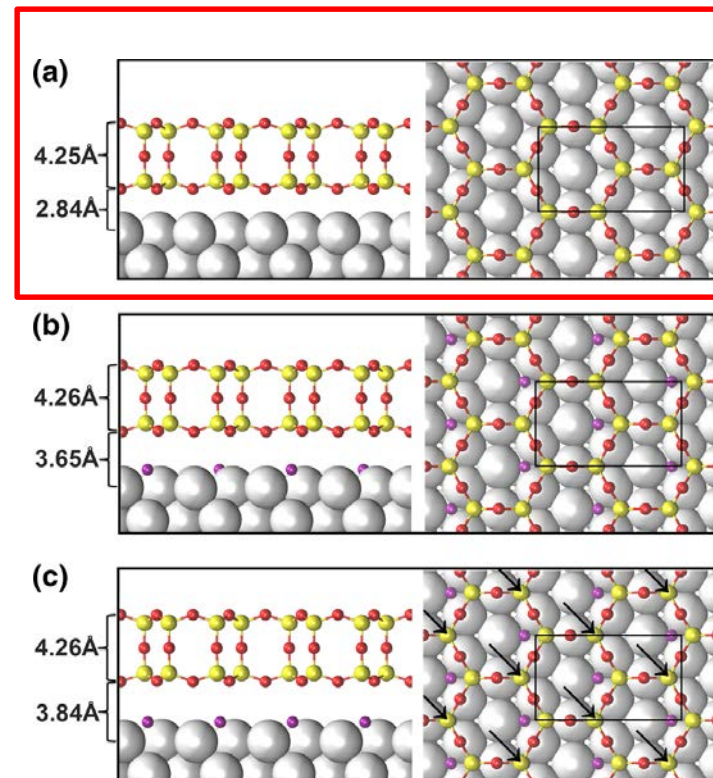
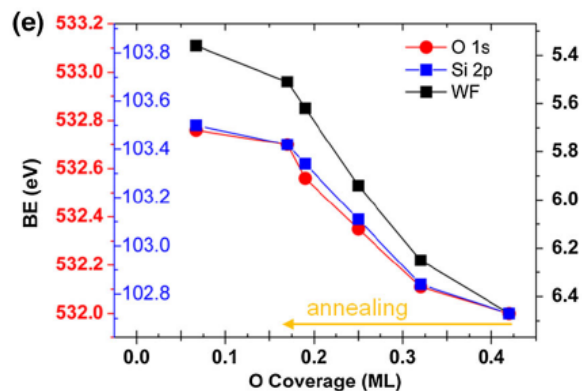
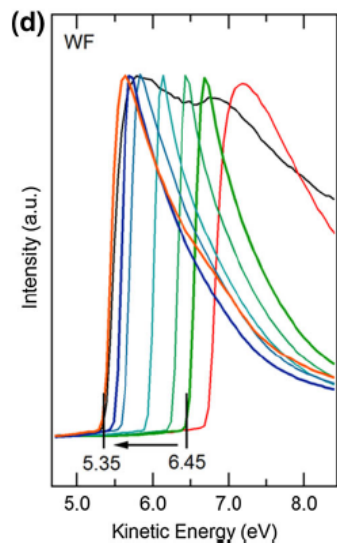


Facilities for creating, characterizing, and understanding nanomaterials:

- Materials Synthesis
- Nanofabrication
- Proximal Probes
- Electron Microscopy
- Advanced Optical Spectroscopy and Microscopy
- Advanced X-ray and UV Probes
- Theory and Computation

Thank you

2D-silica on Ru(0001)



	Ru(0001)	$(\text{SiO}_2)_8/00/\text{Ru}(0001)$		$(\text{SiO}_2)_8/20/\text{Ru}(0001)$		$(\text{SiO}_2)_8/40/\text{Ru}(0001)$	
	Ru	Ru	Ru/(SiO ₂)	Ru/O	Ru/O/(SiO ₂)	Ru/O	Ru/O/(SiO ₂)
<i>p</i>	0.02	0.02	0.38	-0.03	0.03	-0.18	-0.18
Φ	5.12 [†]	5.12	3.88	5.32	5.16	5.89	5.93
	(5.37)						

The number in parenthesis is the experimental value

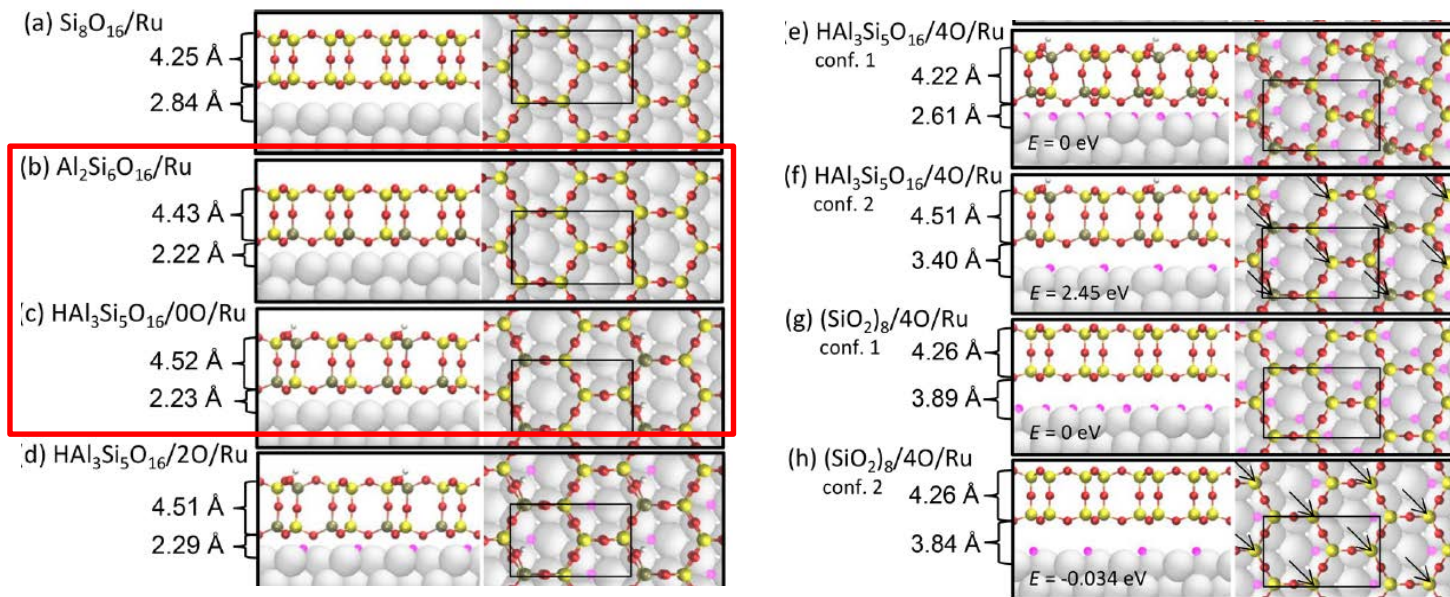
[†] The work function of the clean Ru(0001) with top two layers allowed to relax. $\Phi = 5.03$ eV was reported by Kim et al. [42]

Wang, Boscoboinik et al. Top. Catal., 2017, DOI: 10.1007/s11244-016-0704-x

2D-aluminosilicate on Ru(0001)

Table 1. Dipole Moment (p in $e\text{\AA}$) and the Work Function (Φ in eV) of $n\text{O}/\text{Ru}(0001)$, $(\text{H})\text{Al}_x\text{Si}_{8-x}\text{O}_{16}$ (bilayer) and $(\text{H})\text{Al}_x\text{Si}_{8-x}\text{O}_{16}/n\text{O}/\text{Ru}(0001)$ (total) for $n = 0, 2$, and 4

	dipole moment (p in $e\text{\AA}$)				work function (Φ in eV)		
	$n\text{O}/\text{Ru}$	bilayer	interface	total	$n\text{O}/\text{Ru}$	bilayer	total
$\text{Al}_2\text{Si}_6\text{O}_{16}/\text{Ru}(0001)$	0.02	0.21	-0.28	-0.05	5.15	8.10	5.50
$\text{HAl}_3\text{Si}_5\text{O}_{16}/\text{Ru}(0001)$	0.03	0.42	-0.25	0.20	5.15	7.39	4.61
$\text{HAl}_3\text{Si}_5\text{O}_{16}/2\text{O}/\text{Ru}(0001)$	0.01	0.41	-0.40	0.02	5.24	7.42	5.24
$\text{HAl}_3\text{Si}_5\text{O}_{16}/4\text{O}/\text{Ru}(0001)$	-0.10	0.46	-0.74	-0.38	5.66	7.11	6.69



Wang, Boscoboinik et al. J. Phys. Chem. C 2018, DOI: 10.1021/acs.jpcc.8b05853

Permeability of single atoms (or ions)

Periodic Table of the Elements

1 H Hydrogen 1.01																	18 He Helium 4.00
3 Li Lithium 6.94	4 Be Beryllium 9.01											5 B Boron 10.81	6 C Carbon 12.01	7 N Nitrogen 14.01	8 O Oxygen 16.00	9 F Fluorine 19.00	10 Ne Neon 20.18
11 Na Sodium 22.99	12 Mg Magnesium 24.31											13 Al Aluminum 26.98	14 Si Silicon 28.09	15 P Phosphorus 30.97	16 S Sulfur 32.06	17 Cl Chlorine 35.45	18 Ar Argon 39.95
19 K Potassium 39.10	20 Ca Calcium 40.08	21 Sc Scandium 44.96	22 Ti Titanium 47.88	23 V Vanadium 50.94	24 Cr Chromium 51.99	25 Mn Manganese 54.94	26 Fe Iron 55.85	27 Co Cobalt 58.93	28 Ni Nickel 58.69	29 Cu Copper 63.55	30 Zn Zinc 65.38	31 Ga Gallium 69.72	32 Ge Germanium 72.63	33 As Arsenic 74.92	34 Se Selenium 78.97	35 Br Bromine 79.90	36 Kr Krypton 84.80
37 Rb Rubidium 85.47	38 Sr Strontium 87.62	39 Y Yttrium 88.91	40 Zr Zirconium 91.22	41 Nb Niobium 92.91	42 Mo Molybdenum 95.95	43 Tc Technetium 98.91	44 Ru Ruthenium 101.07	45 Rh Rhodium 102.91	46 Pd Palladium 106.42	47 Ag Silver 107.87	48 Cd Cadmium 112.41	49 In Indium 114.82	50 Sn Tin 118.71	51 Sb Antimony 121.76	52 Te Tellurium 127.6	53 I Iodine 126.90	54 Xe Xenon 131.29
55 Cs Cesium 132.91	56 Ba Barium 137.33	57-71 Lanthanides	72 Hf Hafnium 178.49	73 Ta Tantalum 180.95	74 W Tungsten 183.85	75 Re Rhenium 186.21	76 Os Osmium 190.23	77 Ir Iridium 192.22	78 Pt Platinum 195.08	79 Au Gold 196.97	80 Hg Mercury 200.59	81 Tl Thallium 204.38	82 Pb Lead 207.20	83 Bi Bismuth 208.98	84 Po Polonium [209]	85 At Astatine 209.98	86 Rn Radon 222.02
87 Fr Francium 223.02	88 Ra Radium 226.03	89-103 Actinides	104 Rf Rutherfordium [261]	105 Db Dubnium [262]	106 Sg Seaborgium [266]	107 Bh Bohrium [264]	108 Hs Hassium [269]	109 Mt Meitnerium [278]	110 Ds Darmstadtium [281]	111 Rg Roentgenium [280]	112 Cn Copernicium [285]	113 Nh Nihonium [286]	114 Fl Flerovium [289]	115 Mc Moscovium [289]	116 Lv Livermorium [293]	117 Ts Tennessine [294]	118 Og Oganesson [294]
57 La Lanthanum 138.91	58 Ce Cerium 140.12	59 Pr Praseodymium 140.91	60 Nd Neodymium 144.24	61 Pm Promethium 144.91	62 Sm Samarium 150.36	63 Eu Europium 151.96	64 Gd Gadolinium 157.25	65 Tb Terbium 158.93	66 Dy Dysprosium 162.50	67 Ho Holmium 164.93	68 Er Erbium 167.26	69 Tm Thulium 168.93	70 Yb Ytterbium 173.05	71 Lu Lutetium 174.97			
89 Ac Actinium 227.03	90 Th Thorium 232.04	91 Pa Protactinium 231.04	92 U Uranium 238.03	93 Np Neptunium 237.05	94 Pu Plutonium 244.06	95 Am Americium 243.06	96 Cm Curium 247.07	97 Bk Berkelium 247.07	98 Cf Californium 251.08	99 Es Einsteinium [254]	100 Fm Fermium 257.10	101 Md Mendelevium 258.10	102 No Nobelium 259.10	103 Lr Lawrencium [262]			

Alkali Metal
Alkaline Earth
Transition Metal
Basic Metal
Metalloid
Nonmetal
Halogen
Noble Gas
Lanthanide
Actinide

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