Electronic Supplementary Material (ESI) for Materials Horizons.

Supporting Information for:

Vapor Phase Infiltration (VPI) for Transforming Polymers into Organic-Inorganic Hybrid Materials: A Critical Review of Current Progress and Future Challenges

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In this supporting information file, we attempt to aggregate and classify the processing conditions for various VPI-like schemes that have been reported in the literature but have been described by other names (e.g., ALD, SIS, MPI, or SVI). Based on the reported processing sequences, the table below summarizes key features for each of these processes. Full descriptions for each of these processes are included at the end along with the exact reference.

Table S1: Summary of processing sequences for different VPI-like processes reported in the literature.

Reference	Process name as indicated in reference	Holds during exposures	Evacuate chamber before dose or purge	Repeated precursor exposures per cycle
[1]	ALD			
[2]	ALD			
[3]	ALD			
[4]	ALD			
*[5]	ALD	x		
*[6]	ALD long cycle	x		
[7]	SIS Semi-static mode	x	x	
[8]	SIS Semi-static mode	x	x	
[9]	SIS Semi-static mode	x	x	
[10]	SIS Semi-static mode	x	x	
*[11]	SIS Semi-static mode	x	x	
[12]	SIS Flow mode	x		
[13]	SIS Flow mode	x		
*[14]	SIS			x
*[15]	SIS	x		
[16]	MPI	x		
[17]	MPI	x		
[18]	Vapor-phase processing	x		
*[19]	ALD long cycle, SVI	x		
*[20]	SVI	x		
[21]	SVI	x	Only before co-reactant	x
[22]	SVI	x	Only before co-reactant	x

[23]	SVI	x	Only before co-reactant	x
[24]	SVI	x	Only before co-reactant	x
[25]	SVI	x	Only before co-reactant	x
[26]	SVI	x		x
[27]	SVI	x		x
[28]	SVI	x		x
[29]	SVI	x		x
*[30]	"SVIS"			

Based on this analysis, we have arrived at the following prototypical sequences for each processing scheme:

1. **ALD**: dose A / purge / dose B / purge
2. **SIS Semi-static**: [evac / dose A / hold / evac / purge] + [evac / dose B / hold / evac /purge]
3. **MPI or SIS Flow**: [dose A / hold / purge] + [dose B / hold / purge]
4. **SVI**: N x [dose A / hold / purge] + (possible evac) + M x [dose B / hold / purge]

These prototypical sequences are what have been used to illustrate Figure 4 of the text. Note that in the table and in the list below, we have "asterisked" sequences that do not follow these prototypical schemes.

While every effort is made to accurately describe the sequences, some information such as dose time or purge time may not have been clear in the original references. Sequences that do not follow the prototypical sequences of their respective names are labeled with an asterisk.

"Atomic Layer Deposition (ALD)"

[1] Atomic Layer Deposition of Zinc Oxide onto and into P3HT for Hybrid Photovoltaics
Process Name: ALD
Precursor: DEZ
Co-reactant: H_2O
Dosing sequence: [1 s DEZ, purge] + [1 s H_2O, purge]

[2] Nucleation and Growth during Al_2O_3 Atomic Layer Deposition on Polymers
Process Name: ALD
Precursor: TMA
Co-reactant: H_2O
Dosing sequence: [1 s TMA, 29 s purge] + [1 s H_2O, 29 s purge]

[3] Surface and Sub-surface Reactions during Low Temperature Aluminum Oxide Atomic Layer Deposition on Fiber-forming Polymers
Process Name: ALD

Precursor: TMA
Co-reactant: H_2O
Dosing sequence: [1.2 s TMA, 40 s purge] + [1.2 s H_2O, 50 s purge]

[4] Influence of Subsurface Hybrid Material Growth on the Mechanical Properties of Atomic Layer Deposited Thin Films on Polymers
Process Name: ALD
Precursor: TMA
Co-reactant: H_2O
Dosing sequence: [0.2 s TMA, 30 s purge] + [0.2 s H_2O, 45 s purge]

[5] In Situ Raman Spectroscopic Study of Al-Infiltrated Spider Dragline Silk under Tensile Deformation
Process Name: ALD
Precursor: TMA
Co-reactant: H_2O
***Dosing sequence**: [0.1 s TMA, 30 s hold, 40 s purge] + [1 s H_2O, 30 s hold, 40 s purge]

[6] Quantitative in situ infrared analysis of reactions between trimethylaluminum and polymers during Al2O3 atomic layer deposition
Process Name: ALD "long cycle"
Precursor: TMA
Co-reactant: H_2O
***Dosing sequence**: [60 min TMA hold, 30 min purge] + [60 min H_2O hold, 30 min purge]

<u>"Sequential Infiltration Synthesis (SIS)"</u>

[7] Enhanced Block Copolymer Lithography Using Sequential Infiltration Synthesis
Process Name: SIS Semi-static mode
Precursor: TMA
Co-reactant: H_2O
Dosing sequence: [evac chamber, 0.5 Torr TMA, 80 s hold, evac chamber, 10 Torr 30 s purge] + [evac chamber, 80 s H_2O hold, evac chamber, 10 Torr 30 s purge]

[8] Enhanced Polymeric Lithography Resists via Sequential Infiltration Synthesis
Process Name: SIS Semi-static mode
Precursor: TMA
Co-reactant: H_2O
Dosing sequence: [evac chamber, 5 Torr TMA, 20 min hold, evac chamber, 1 Torr purge] + [evac chamber, 5 Torr H_2O, 500 s hold, evac chamber, 1 Torr purge]

[9] Nanoscopic Patterned Materials with Tunable Dimensions via ALD on Block Copolymers
Process Name: SIS Semi-static mode
Precursor: TMA
Co-reactant: H_2O
Dosing sequence: [evac chamber, 5 Torr TMA, hold, evac chamber, 1 Torr purge] + [evac chamber, H_2O exposure, evac chamber, 1 Torr purge]

[10] A Route to Nanoscopic Materials via Sequential Infiltration Synthesis on Block Copolymer Templates
Process Name: SIS Semi-static mode
Precursor: TMA
Co-reactant: H_2O
Dosing sequence: [evac chamber, 5 Torr TMA, hold, evac chamber, 1 Torr purge] + [evac chamber, H_2O exposure, evac chamber, purge]

[11] Characterizing the 3D Structure of Block Copolymers via Sequential Infiltration Synthesis and Scanning Transmission Electron Tomography
Process Name: SIS Semi-static mode
Precursor: TMA
Co-reactant: H_2O
***Dosing sequence**: [evac chamber, 5 Torr TMA, 60 s hold, 300 s purge] + [evac chamber, 60 s H_2O hold, 300 s purge]

[12] New Insight into the Mechanism of Sequential Infiltration Synthesis from Infrared Spectroscopy
Process Name: SIS Flow mode
Precursor: TMA
Co-reactant: H_2O
Dosing sequence: [6 Torr TMA, hold, 3.5 Torr purge] + [H_2O hold, 3.5 Torr purge]

[13] Kinetics for the Sequential Infiltration Synthesis of Alumina in PMMA: An Infrared Spectroscopic Study
Process Name: SIS Flow mode
Precursor: TMA
Co-reactant: H_2O
Dosing sequence: [6 Torr TMA, hold, 3.5 Torr purge] + [H_2O hold, 3.5 Torr purge]

[14] Etch properties of resists modified by sequential infiltration synthesis
Process Name: SIS
Precursor: TMA
Co-reactant: H_2O
***Dosing sequence**: [100x(0.4 s TMA, 0.4 s purge), 60 s purge] + [100x(0.4 s H_2O, 0.4 s purge), 60 purge]
Note: *This sequence is somewhat similar to SVI.*

[15] Sequential Infiltration Synthesis for the Design of Low Refractive Index Surface Coatings with Controllable Thickness
Process Name: SIS
Precursor: TMA
Co-reactant: H_2O
***Dosing sequence**: [10 mTorr TMA, 400 s hold, evac chamber] + [10 mTorr H_2O, 120 s hold, evac chamber, purge]

“Multiple Pulsed Infiltration (MPI)” and Vapor-Phase Processing

[16] Greatly Increased Toughness of Infiltrated Spider Silk

Process Name: MPI
Precursor: TMA
Co-reactant: H_2O
Dosing sequence: [0.3 s TMA, 30 s hold, 30 s purge] + [1.5 s H_2O, 40 s hold, 40 s purge]

[17] Improved Mechanical Stability of Dried Collagen Membrane after Metal Infiltration
Flow mode
Process Name: MPI
Precursor: TMA
Co-reactant: H_2O
Dosing sequence: [0.3 s TMA, 30 s hold, 30 s purge] + [1.5 s H_2O, 40 s hold, 40 s purge]

[18] An Alternative Route Towards Metal-Polymer Hybrid Materials Prepared by Vapor-Phase Processing
Process Name: Vapor-Phase Processing
Precursor: DEZ
Co-reactant: H_2O
Dosing sequence: [0.2 s DEZ, 5 s hold, 150 s purge] + [1.5 s H_2O, 30 s hold, 40 s purge]

“Sequential Vapor Infiltration (SVI)”

[19] Directed inorganic modification of bi-component polymer fibers by selective vapor reaction and atomic layer deposition
Process Name: SVI, ALD “long cycle”
Precursor: TMA
Co-reactant: H_2O
***Dosing sequence**: [5 s TMA, 60 s hold, 60 s purge] + [5 s H_2O, 60 s hold, 60 s purge]

[20] Hydrophilic mechanical buffer layers and stable hydrophilic finishes on polydimethylsiloxane using combined sequential vapor infiltration and atomic/molecular layer deposition
Process Name: SVI
Precursor: TMA
Co-reactant: H_2O
***Dosing sequence**: [5 hour TMA exposure, 30 min purge] + [30 min H_2O exposure]

[21] Temperature and Exposure Dependence of Hybrid Organic−Inorganic Layer Formation by SVI into Polymer Fibers
Process Name: SVI
Precursor: TMA
Co-reactant: H_2O
Dosing sequence: N x [0.5 s TMA dose, 30 s hold, 30 s purge] + evac chamber + M x [0.2 s H_2O dose, 30 s hold, 30 s purge]

[22] Depth Profiling Trimethylaluminum-Modified PET Fibers by Nanoscale Infrared Spectroscopy
Process Name: SVI
Precursor: TMA

Co-reactant: H_2O
Dosing sequence: Nx[0.5 s TMA dose, 30 s hold, 30 s purge] + evac chamber + Mx[0.2 s H_2O dose, 30 s hold, 30 s purge]

[23] Organometallic exposure dependence on organic-inorganic hybrid material formation in polyethylene terephthalate and polyamide 6 polymer fibers
Process Name: SVI
Precursor: TMA
Co-reactant: H_2O
Dosing sequence: Nx[TMA dose, hold, purge] + evac chamber + Mx[H_2O dose, hold, purge]

[24] Formation of novel photoluminescent hybrid materials by sequential vapor infiltration into polyethylene terephthalate fibers
Process Name: SVI
Precursor: TMA
Co-reactant: H_2O
Dosing sequence: Nx[0.5 s TMA dose, 30 s hold, 30 s purge] + evac chamber + Mx[0.2 s H_2O dose, 30 s hold, 30 s purge]

[25] Photoluminescence Mechanism and Photocatalytic Activity of Organic-Inorganic Hybrid Materials Formed by Sequential Vapor Infiltration
Process Name: SVI
Precursor: TMA
Co-reactant: H_2O
Dosing sequence: Nx[0.5 s TMA dose, 30 s hold, 30 s purge] + evac chamber + Mx[0.2 s H_2O dose, 30 s hold, 30 s purge]

[26] Comparison of precursor infiltration into polymer thin films via atomic layer deposition and sequential vapor infiltration using in-situ quartz crystal microgravimetry
Process Name: SVI
Precursor: TMA
Co-reactant: H_2O
Dosing sequence: 10x[0.2 s TMA dose, 30 s hold, 90 s purge] + 5x[0.2 s H_2O dose, 30 s hold, 90 s purge]

[27] Atmospheric pressure synthesis of photoluminescent hybrid materials by sequential organometallic vapor infiltration into polyethylene terephthalate fibers
Process Name: SVI
Precursor: TMA
Co-reactant: H_2O
Dosing sequence: Nx[0.5 s TMA dose, 30 s hold, 30 s purge] + evac chamber + Mx[0.2 s H_2O dose, 30 s hold, 30 s purge]

[28] Sequential Vapor Infiltration of Metal Oxides into Sacrificial Polyester Fibers: Shape Replication and Controlled Porosity of Microporous/Mesoporous Oxide Monoliths
Process Name: SVI
Precursor: TMA
Co-reactant: H_2O

Dosing sequence: 60x[10 s TMA dose, 60 s hold, 20 s purge] + 20x[10 s H_2O dose, 60 s hold, 20 s purge]

[29] Temperature-dependent reaction between trimethylaluminum and poly(methyl methacrylate) during sequential vapor infiltration: experimental and *ab initio* analysis
Process Name: SVI
Precursor: TMA
Co-reactant: H_2O
Dosing sequence: Nx[1 s TMA dose, 60 s hold, 30 s purge] + 1x[1 s H_2O dose, 45 s purge]

[30] Investigating Sequential Vapor Infiltration Synthesis on Block-Copolymer-Templated Titania Nanoarrays
Process Name: SVIS
Precursor: $TiCl_4$
Co-reactant: H_2O
***Dosing sequence**: [0.2 s $TiCl_4$ dose, 30 s purge] + [0.2 s H_2O dose, 30 s purge]

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