Supplementary Materials: Surface Functionalization Utilizing Mesoporous Silica Nanoparticles for Enhanced Evanescent-Field Mid-Infrared Waveguide Gas Sensing

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Figure S1. DLS hydrodynamic diameter size distribution of MSNs at pH 9.

Table 1. Zeta potentials and hydrodynamic diameters for MSN 0.2 wt.% aqueous solutions at pH 7 and 8.

| pH | Zeta (mV)     | Diameter (nm) |
|----|--------------|---------------|
| 7  | −36.1 ± 7.5  | 209 ± 18      |
| 8  | −37.4 ± 6.3  | 246 ± 57      |
Figure S2. X-ray diffractogram of MSNs.

Figure S3. Nitrogen adsorption/desorption isotherm for MSNs using BET method.
Figure S4. Images of 1-BL coatings deposited at pH 7 at different withdrawal substrate speeds: 0.01 cm/s (A), 0.1 cm/s (B), 1 cm/s (C) and 1-BL film deposited at pH 9 at 0.001 cm/s (D).

Table 2. Dry ellipsometric thickness of a BPEI priming layer as a function of solution pH and substrate withdrawal conditions.

| BPEI Deposition Conditions                        | Thickness (nm) |
|--------------------------------------------------|----------------|
| Controlled dipping at 0.001 cm/s – pH 7           | 1.5            |
|                                                 | pH 8           | 2.4            |
|                                                 | pH 9           | 3.6            |
| Conventional dipping (7 min deposition time) –    |                |
| pH 7                                            | 0.7            |
| pH 8                                            | 0.8            |
| pH 9                                            | 1.0            |

Figure S5. Ellipsometric thickness of 1-BL coatings (BPEI/MSN) deposited at pH 7, 8 and 9 using conventional dipping and optimized controlled dipping at 0.001 cm/s. Fitted ellipsometric refractive index of these films is 1.2.

Figure S6. Schematic representation of the effect of BPEI deposition pH on surface coverage with MSNs.
Figure 7. Top-view SEM image of MSNs deposited directly on bare Si substrate at pH 9 using controlled dipping at 0.001 cm/s.

Figure 8. Top-view SEM images of 5-BL MSN coatings deposited at pH 9 using controlled dipping at 0.001 cm/s (A) and conventional dipping (B).

Figure 9. Comparison of controlled and conventional dipping ellipsometric thickness as a function of number of bilayers (A), and cross-sectional SEM images of 1- and 5-BL films at pH 9 (B-E): 1-BL film at 0.001 cm/s (B); 5-BL film at 0.001 cm/s (C); 1-BL film using conventional dipping (D); and 5-BL film using conventional dipping (E). Refractive indices of these films were fitted using the grade layer Cauchy model. Cross-sectional SEM thicknesses were estimated using ImageJ software analysis of 10 images collected from samples prepared by using several repeated coating depositions.
Table 3. Total energy and adsorption energy of ethanol and methane molecule on a-SiO₂ surface with and without dipole correction.

| Analytes  | Method        | \(E_{\text{slab}}\) (eV) | \(E_{\text{molecule}}\) (eV) | \(E_{\text{slab} + \text{molecule}}\) (eV) | \(E_{\text{ads}}\) (meV) |
|-----------|---------------|---------------------------|-----------------------------|---------------------------------|---------------------------|
| Ethanol   | PBE           | −758.896                  | −46.8748                    | −806.496                        | −725.168                  |
|           | PBE+dip. corr.| −758.789                  | −46.8748                    | −806.326                        | −662.595                  |
| Methane   | PBE           | −758.896                  | −24.0373                    | −782.982                        | −47.833                   |
|           | PBE+dip. corr.| −758.789                  | −24.0373                    | −782.870                        | −43.591                   |