A Versatile Porous Enrichment Layer for Monitoring Organic Contaminants in Water via ATR Spectroscopy

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INTRODUCTION

- Mid-IR spectroscopy provides access to the information-rich fingerprint region of the electromagnetic spectrum enabling identification and quantification of organic contaminants.
- Strong background absorption of water in the mid-IR region limits sensitivity.
- Sensitivity towards organic contaminants can be increased by coating attenuated total reflectance (ATR) crystals with polymer coatings.
- Analytes are reversibly absorbed and thereby concentrated in the coatings in the region probed by the evanescent wave, while excluding spectral interferences of water.
- Limits of detection (LODs) for chlorinated and brominated hydrocarbons in the mid-low ppb region have been reached.
- Polymer coatings attenuated total reflectance (ATR) crystals with highly ordered mesostructured materials. The variation of used surfactant and precursor/surfactant ratio leads to different mesophases, including 2D hexagonal, 3D hexagonal and 3D cubic.
- Soft templating of sol-gel materials provides access to mesoporous films that can be easily organically modified.

OPTICAL SETUP

A novel flow cell system with easily exchangeable ATR crystals from low-cost silicon wafers allowing for fast screening of an extensive series of enrichment layers.

ENRICHMENT OF BENZONITRILE

- Hydrophobic film repels water, which is largely eliminated from the probing region (comparative absorption band at 1400 cm⁻¹ for coated and uncoated silicon wafer).
- Uncoated wafers show no absorption of benzonitrile at 2230 cm⁻¹ (C≡N mode).
- Limit of detection for benzonitrile is 30 ppm (3 s S/N).
- Response time: < 5 s was measured by displacing pure water in the flow cell with benzonitrile solutions while providing the sensor responds immediately and is just limited by the diffusion of the analyte into the sample chamber.
- Time for regeneration: < 5 s

DESIGN OF ENRICHMENT LAYER

Syntesys of mesoporous silica by templating

Orderly periodic mesoporous materials with controlled pore size are synthesised by using surfactants as sacrificial template e.g. soft templates such as surfactants or amphiphilic block copolymers.

Covariant surface modification

Organosilanes (R'Si(OH)) bearing functional groups R' can be either introduced by co-condensation (pre-functionalisation) or grafted to silanol groups at the surface of porous silica (post-functionalisation).

SYNTHESIS & CHARACTERISATION

Synthesis

Mesoporous silica coatings were synthesised by acidic condensation of tetraethoxysilane in ethanol with cetyltrimethylammonium bromide to co-condensation with methyltriethoxysilane (MTES) or grafting with hexamethyldisilazane (HMDS). The silica films were obtained by spin-coating on polished silicon wafers and subsequent calcination at 400 °C.

Characterisation

Coatings are IR transparent in the information rich region at > 1300 cm⁻¹. FTIR-ATR spectrum of a organically modified film shows absorptions of Si-O-Si stretching modes around 1070 cm⁻¹ and bands that can be assigned to -CH₃ vibrations. Coatings are IR transparent in the information rich region at > 1300 cm⁻¹.

Hydrolysis

\[ Si-OH + H_2O \rightarrow Si-OH + ROH \]

Condensation

\[ Si-OH + Si-OH \rightarrow Si-O-Si + H_2O \]

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CONCLUSION

Organically modified silica with ordered porosity is the material of choice for ATR enrichment coatings.

- Fast diffusion into enrichment layer (response time < 5 s) and fast regeneration.
- IR transparency in the spectral region of organic contaminants.
- Limit of detection of 30 ppm.
- Precise pore design and pore functionality, thereby allowing for selective sample enrichment.

References


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