

Supporting information

Time-dependent Fmoc-method for quantification of silane grafting on halloysite's surface

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1.2 Materials and methods

Chemicals

(3-Aminopropyl)triethoxysilane (APTES), pristine halloysite (HNT), toluene and anhydrous toluene, anhydrous dichloromethane (DCM), N,N-Diisopropylethylamine (DIPEA) as well as ethanol (EtOH) were purchased from Sigma Aldrich. Fmoc chloride (Fmoc-Cl) was from Fluka, while piperidine (pip) was from Biosolve.

Reaction steps of Fmoc-method

Synthesis of (3-Triethoxysilylpropyl)carbamic Acid 9H-Fluorenylmethyl Ester (APTES-Fmoc).

The protocol of APTES-Fmoc synthesis was performed according to K. Cheng et al procedure [21]. Specifically, 0.5mL of APTES were dissolved in 7.7mL of anhydrous DCM, under nitrogen flow, while cooling and stirring. To it, 0.38mL of DIPEA were added. In the separate flask 563mg of Fmoc-Cl was dissolved in 3mL of anhydrous DCM, under nitrogen flow. Next, Fmoc-Cl solution was transferred drop by drop to APTES solution. The reaction was kept being stirred at room temperature for 3.5h, while its progress was monitored by TLC (ethyl acetate: hexane (1:4)). Then the solvent was evaporated under the rotavapor, leaving yellow oil. The product was purified by flash chromatography with ethyl acetate: hexane (1:4), yielding to the formation of white rhombic solid (800mg, 1.8mmol, 84% yield). ¹H NMR (300MHz, CDCl₃): δ 7.78 (d, *J* = 7.5Hz, 2H), 7.62 (d, *J* = 7.5Hz, 2H), 7.42 (t, *J* = 7.1Hz, 2H), 7.33 (td, *J* = 7.4, 1.2Hz, 2H), 5.06 (broad s, 1H), 4.42 (d, *J* = 6.9Hz, 2H), 4.24 (t, *J* = 6.8Hz, 1H), 3.84 (q, *J* = 7.0 Hz, 6H), 3.23 (dd, *J* = 12.9, 6.6Hz, 2H), 1.76 – 1.51 (m, 2H), 1.25 (t, *J* = 7.0Hz, 9H), 0.76 – 0.58 (m, 2H). Melting point: 81.3°C. The synthesized product was also characterized with Kaiser test, FT-IR and TGA analysis.

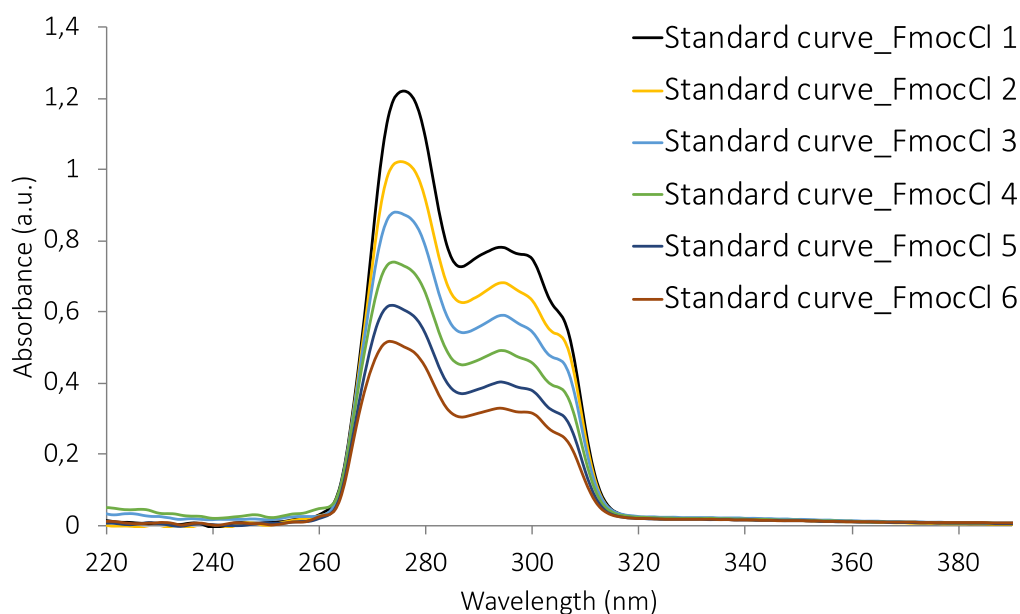
Halloysite nanotubes functionalization with (3-Triethoxysilylpropyl)carbamic Acid 9H-Fluorenylmethyl Ester (APTES-Fmoc).

293mg of APTES-Fmoc were dissolved in 2.5mL of anhydrous toluene, under nitrogen flow. Next, 60mg of pristine halloysite clay and the reaction was kept being stirred for 20h at room temperature. After reaction termination the powder was washed extensively ten times with fresh portions of toluene and dried in air. Next, the dry powder was examined with Kaiser test, FT-IR and TGA analysis.

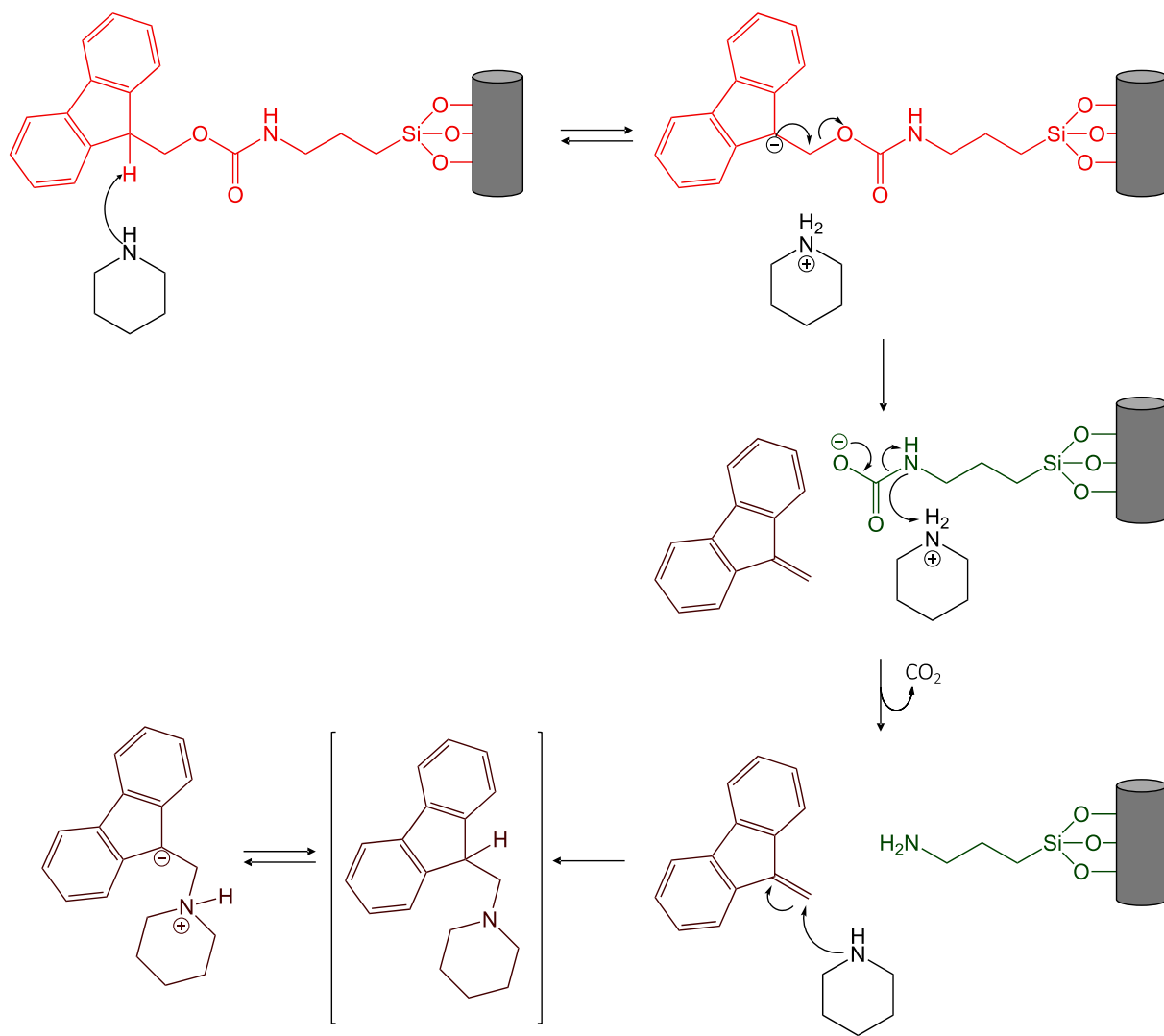
Fmoc adduct deprotection. Approximately 6mg of HNT-APTES-Fmoc powder were resuspended in 1mL of piperidine in EtOH (20%) and let to react while mixing for 1 - 5h. Next, mixtures were centrifuged at 45000r.p.m. for 10 minutes. Then supernatants were separated from precipitates and further characterized with UV-vis spectrophotometer. While precipitated powders were washed extensively with ammonium chloride (1M) and dried in air, to be further characterized. Washed and dried powders after the deprotection reaction were examined with Kaiser test and FT-IR.

Measurements

Kaiser tests were performed using Kaiser test kit (Sigma Aldrich) and its standard protocol. Briefly, 1mg of the powder under analysis was resuspended in 1.5mL of Kaiser solution in a glass tube and heated up for 1 minute at 100°C. The color of such treated suspension was under analysis. The IR spectra were recorded on powders using ATR Fourier Transform Infrared (FTIR) spectrometer (PerkinElmer spectrum 100) in the transmittance mode, in the range of 4000 - 500cm⁻¹. Thermogravimetric analysis (TGA) was conducted using Mettler-Toledo Stare System TGA/DSC3+ instrument, heating the sample in a crucible from 30,0–900,0°C at the rate 5K/min in air. The characterization of supernatants was done using spectrophotometer (500 Evolution Thermo Electron Corporation) on their absorbance values at 300nm, when placed in quartz cuvettes of 1cm light path.



UV absorbance spectra of FmocCl in piperidine in EtOH solution (2:8), which were used for standard curve preparation.



Scheme representing Fmoc adduct removal in piperidine: ethanol solution (2:8) from modified halloysite support. Formation of DBF and further DBF-pip in the presence of piperidine excess.