# Silylation of halloysite nanotubes with (3-chloropropyl)-trimethoxy silane

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## Introduction:

Modified halloysite nanotubes (HNTs-Cl) was synthesized by a coupling reaction with (3-chloropropyl) trimethoxysilane (CPTMS). The grafting of chloro-silane onto HNTs surface develops chloro-groups, which have a great chemical activity and are considered to be good nominees for employing as active sites that react with other active molecules for further modification of HNTs surface properties. The aim of this study is to determine the best conditions for silylation of HNTs with (3-chloropropyl) trimethoxysilane. A series of parameters including nature of solvent, molar ratio of (HNTs /CPTMS/$H_2O$), refluxing time and the effect of catalyst have been studied. The best modified HNTs sample was evaluated by Elemental analysis, TGA and SEM.

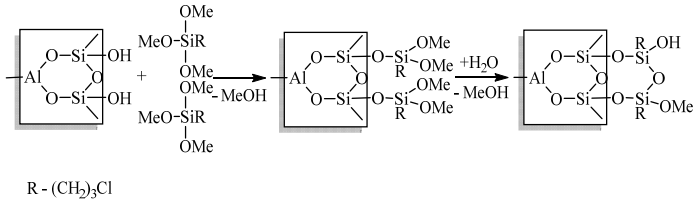


**Figure 1.** Synthetic route that was used during the modification process.

## Materials and Methods:

Halloysite nanotubes was obtained from Sigma-Aldrich and 3-chloro propyl trimethoxy silane was obtained from Alpha- Aser , China.

## Results and discussion:

The results obtained from elemental analysis were used for calculating the degree of functionalization. The highest degree of functionalization was achieved by using toluene as a media for the silylation process, the molar ratio of (HNTs / CPTMS / $H_2O$) was (1:1:3) and the refluxing time was 4 hours. Addition of 7.169 mmol of $Et_3N$ and 25.97 mmol of $NH_4OH$ led to a great effect on increasing the number of silane groups which have been grafted on HNTs surface.

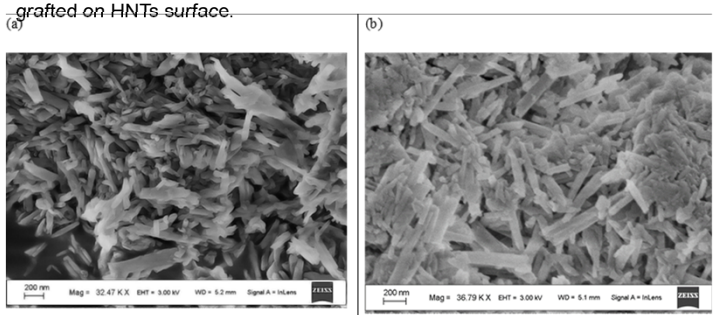


**Figure 2.** SEM image for pristine HNTs (a), SEM image for the best modified HNTs sample (b)

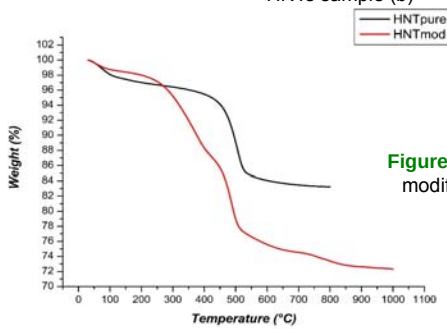


**Figure 3.** TGA for the best modified HNTs sample.

**Table 1.** The different parameters which have been performed for the grafting process and the results obtained from elemental analysis

| Molar ratio (HNTs/CPTMS/ $H_2O$) | Solvent | Catalyst | Refluxing Time | Content, % | | Degree of functionalization % |
|---|---|---|---|---|---|---|
| | | | | C | H | |
| **1:1:0** | 20 ml toluene | | 4 hours | 2.1 | 1.83 | 24.29 |
| **1:1.33:0** | 20 ml THF | | 4 hours | 1.2 | 1.63 | 11.00 |
| **1:1:3** | 20 ml toluene | | 4 hours | 3.2 | 2.22 | 36.5 |
| **1:1:0** | 20 ml ethanol | | 4 hours | 0.9 | 1.53 | 10.75 |
| **1:1.33:0** | 5 ml toluene | | 4 hours | 1.4 | 1.90 | 12.84 |
| **1:1:0** | 20 ml toluene | | 35 hours | 2.0 | 1.86 | 22.5 |
| **1:1:0** | 20 ml toluene | | 48 hours | 1.8 | 1.97 | 21.16 |
| **1:2:0** | 20 ml toluene | | 4 hours | 2.4 | 2.03 | 17.13 |
| **1:2:0** | 17 ml toluene | | 48 hours | 2.9 | 1.95 | 21.19 |
| **1:1:3** | 20 ml toluene | 0.5 ml $Et_3N$ | 7 hours | 4.3 | 2.85 | 48.26 |
| **1:1:3** | 20 ml toluene | 0.2 g urea | 4 hours | 6.6 | 2.97 | 27.77 |
| **1:1.33:0** | 20 ml n-hexane | 1 ml $Et_3N$ | 4 hours | 3.6 | 2.14 | 33.83 |
| **1:1.33:0** | 20 ml 1,4 dioxane | 1 ml $Et_3N$ | 4 hours | 2.6 | 2.17 | 24.34 |
| **1:1.33:0** | 20 ml 1,4 dioxane | | 4 hours | 1.5 | 1.86 | 14.3 |
| **1:1:3** | 20 ml toluene | 0.5 ml $Et_3N$ | 4 hours | 4.8 | 2.22 | 54.19 |
| **1:1:3** | 40 ml toluene | 0.5 ml $Et_3N$ | 4 hours | 4.5 | 2.13 | 50.95 |
| **1:1:3** | 20 ml toluene | 0.5 ml $Et_3N$+ 0.5 ml $NH_4OH$ | 4 hours | 7.2 | 2.55 | 81.35 |
| **1:1:0** | 20 ml toluene | 3drops $(EtO)_4Ti$ | 4 hours | 3.1 | 2.1 | 35.49 |
| **1:1:3** | 20 ml toluene | 0.5 ml $Et_3N$ + 0.138 ml $NH_4OH$ | 4 hours | 4.5 | 2.24 | 50.67 |

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