

## Surface Modification of Nanometer Silica by N, N'-dicyclohexyl-carbodiimide Mediated Amidation

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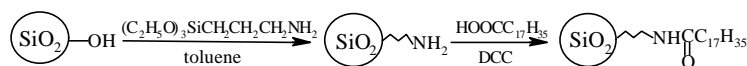
**Abstract:** A potentially versatile procedure for surface modification of nanometer silica is illustrated by N, N'-dicyclohexylcarbodiimide (DCC) mediated amidation of stearic acid.

**Keywords:** Nanometer silica, surface modification, DCC, acid, amidation.

Nanometer silica has gained ever more attention for its superior properties over conventional micrometer particles and has been widely used as a filler in the manufacture of paints, rubber, plastics and so on<sup>1</sup>. However it is difficult to get silica mono-dispersed in the matrix due to heavy agglomeration. Surface modification through organic reactions is an efficient way to improve the dispersibility and compatibility with the matrix, thus improving the mechanical properties of the composite materials<sup>2</sup>. An enormous work on surface modification of silica has been reported, involving mainly treatments with silane reagents and graft polymerizations<sup>3</sup>.

DCC mediated esterification and amidation have been used to introduce active groups and polymers bearing OH and NH<sub>2</sub> groups onto carbon black surface (which has carboxyl groups)<sup>4,5</sup>. In an ongoing project, we need to couple some special polymers bearing carboxyl group onto nanometer silica surface, we thus studied the reaction using cheap readily available stearic acid (SA) as a model compound and DCC as a catalyst.

Scheme 1



Our first attempt to react stearic acid with unmodified silica yielded unsatisfactory results. Functionalization with amino-silane<sup>6</sup> was considered to increase the reactivity of silica by converting silanol into amino groups (**Scheme 1**). The results of amidation are summarized in **Table 1**. A number of factors influence the extent of the reaction. Solvent has a notable effect on the percentage of grafting, dichloromethane being the best, giving grafting about 10% higher than tetrahydrofuran (THF) and 25% higher than N, N-dimethylformamide (DMF). The percentage of grafting increased when the

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amount of stearic acid increased. It is noted that the maximum total grafting is 21%, and the grafting contributed by this amidation step is 14%, indicating that 44% of total amino groups have reacted.

In conclusion, DCC mediated amidation of stearic acid can proceed on amino-silane modified nanometer silica surface in notable amount. The procedure reported here offers the possibility of introducing various organic substituents bearing carboxyl group onto silica surface.

**Table 1** Amidation of stearic acid with amino groups of silica

Entry	solvent	SA (eq)	DMAP (eq)	DCC (eq)	Grafting (%) <sup>a</sup>	Grafted SA (mmol/g) <sup>b</sup>	Reacted NH <sub>2</sub> (%) <sup>c</sup>
1	DMF	4	0	2	17.0/9.6	0.36	31
2	THF	4	0	2	18.2/10.8	0.40	34
3	CH <sub>2</sub> Cl <sub>2</sub>	4	0	2	19.4/12.0	0.45	38
4	CH <sub>2</sub> Cl <sub>2</sub>	0.5	0	2	13.1/5.7	0.21	18
5	CH <sub>2</sub> Cl <sub>2</sub>	1	0	2	18.8/11.4	0.43	37
6	CH <sub>2</sub> Cl <sub>2</sub>	8	0	2	21.3/13.9	0.52	44
7	CH <sub>2</sub> Cl <sub>2</sub>	4	1	2	20.7/13.3	0.50	43
8	CH <sub>2</sub> Cl <sub>2</sub>	4	1	1	18.4/11.0	0.41	35

<sup>a</sup>grafting is defined as the amount of grafted organic molecules to the amount of silica, determined by thermogravimetric analysis, the first value is total grafting, the second value is the contribution by amidation; <sup>b</sup>the amount of SA (in mmol) per gram of original silica; <sup>c</sup>the number of amino groups reacted in amidation to that of initial amino groups.

### General procedure

DCC was added to a stirred mixture of amino-silane modified silica, stearic acid and DMAP in dichloromethane at room temperature (r.t.) under N<sub>2</sub>. The mixture was stirred overnight at r.t. It was then suction filtered and washed with hot THF. The product was purified by Soxhlet extraction with THF for 50 hours<sup>7</sup>.

### Acknowledgment

This project was supported by China Postdoctoral Science Foundation and Tsinghua-Zhongda Postdoctoral Science Foundation.

### References and Notes

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6. It was carried out using a slightly modified literature procedure (N.Tsubokawa *et al.*, *React. Funct. Polym.*, **1998**, 37, 75), the amino group content was 1.08 mmol/g (modified silica) determined by microanalysis and the grafting was 7.4% determined by TGA.
7. All the products show strong peaks at 1640 cm<sup>-1</sup> (amide) and 2940, 2840 cm<sup>-1</sup> (CH<sub>2</sub>) in IR spectrum. The content of carbon has increased remarkably, from 4.8% (for amino-silane modified silica) to 13.2% (Entry 3).

Received 27 March, 2001