Novel Silane Coupling Agents Containing a Photolabile 2-Nitrobenzyl Ester for Introduction of a Carboxy Group on the Surface of Silica Gel

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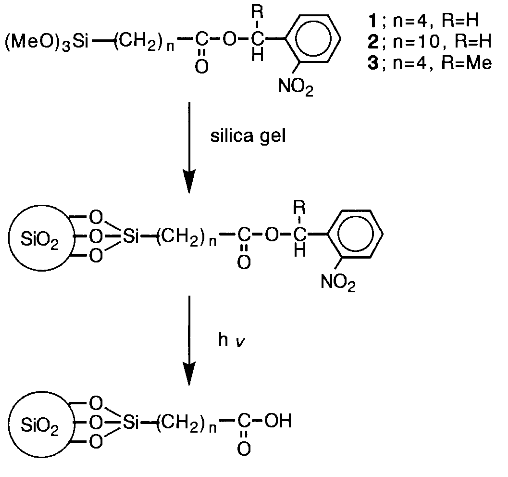
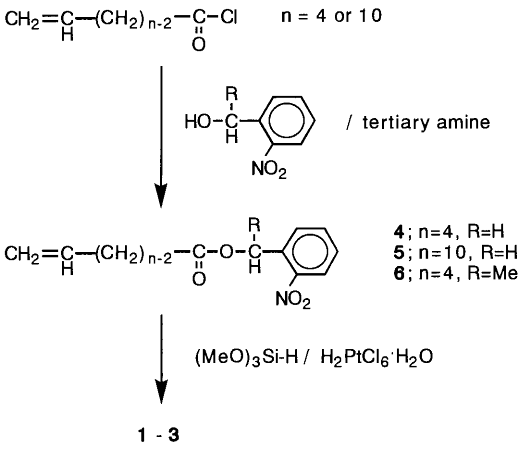
Silane coupling agents containing a carboxy group are not known because the chloro- or alkoxy group is reactive to the carboxylic acid. In this study, silane coupling agents bearing a 2-nitrobenzyl ester as a protecting group of carboxylic acid were synthesized and applied for surface modification of silica gel followed by uv irradiation under neutral conditions to generate carboxy groups on the surface.

Silane coupling agents, which are organic compounds with a chloro- or alkoxysilyl group, are applied for surface modification of inorganic materials by covalent bonding to hydroxy groups on the surface.[1] It is demonstrated that mixed self-assembled monolayers on the silica gel surface derived from two silane coupling agents with different chain lengths are effective for the separation of biomolecules.[2] Many compounds containing organic functional groups such as chloro, vinyl, ester, epoxy, amino, and mercapto groups as well as reactive silyl groups are also commercially available to introduce these functional groups on the surface which are employed for immobilization of a variety of organic compounds.[3-6] Silane coupling agents with more complex structures have also been synthesized.[5-9] However, silane coupling agents bearing carboxy and hydroxy groups have not been reported since these groups are incompatible with a chloro- or alkoxysilyl group. Compounds bearing other groups are used for the surface modification and subsequent chemical reaction to generate carboxy groups on the surface.[10] We report here the synthesis of novel silane coupling agents **1** - **3** containing 2-nitrobenzyl and 1-(2-nitrophenyl)ethyl esters to be converted into carboxylic acid by photoirradiation[11] and the surface modification of silica gel with **1** - **3** as shown in Scheme 1.



Scheme 1. Surface modification of silica gel with **1** - **3**.

The compounds, **1** - **3**, were synthesized by esterification and hydrosilylation from 4-pentenoyl chloride or 10-undecenoyl chloride as shown in Scheme 2. Acid chlorides were reacted with 2-nitrobenzyl alcohol in the presence of triethylamine to obtain the corresponding 2-nitrobenzyl esters **4** and **5**. 1-(2-Nitrophenyl)ethyl ester, **6**, was given from 4-pentenoyl chloride and 1-(2-nitrophenyl)ethanol with 4-dimethylaminopyridine instead of triethylamine. These compounds, **4** - **6**, were purified by silica gel column chromatography.[12] The final products, **1** - **3**, obtained by the reaction of **4** - **6** with trimethoxysilane in the presence of $H_2PtCl_6{\cdot}6H_2O$ as a catalyst were isolated by Kugelrohr vacuum distillation.[13]



Scheme 2. Synthesis of **1** - **3**.

Immobilization of 2-nitrobenzyl esters on the surface of silica gels and transformation of the esters to carboxylic acids by uv irradiation were carried out. Dry benzene solutions of **1** - **3** with silica gel (Wakogel C-300) were refluxed for 2 h and the modified silica gel was filtered and washed with dry benzene. The resulting silica gel was suspended in ethanol and irradiated at room temperature with a 500-W ultrahigh-pressure mercury lamp through a water filter followed by filtration and ethanol washing to afford carboxy-terminated silica gel. The results are shown in Table 1. Loading of the photolabile ester on the surface of silica gel measured by thermogravimetry up to 500 °C was around 200 μmol/g. The carboxy group generated by photoirradiation was determined by back titration. The carboxy group increased with uv irradiation time. Photolysis of the 1-(2-nitrophenyl)ethyl ester from **3** is faster than that of the 2-nitrobenzyl ester from **1** and **2**, consistent with the reported data.[14] Most of the ester moieties are decomposed within 1 h, and carboxy groups are almost quantitatively generated after 3-h irradiation. FT-IR diffuse reflectance spectra of the silica gel

Table 1. Characterization of silica gel modified with **1** - **3**

Compound	Loading /μmol/g	Amount of COOH generated / μmol/g				
		Irradiation time / min				
		5	15	30	60	180
1	185	60	94	114	155	184
2	316	-	176	237	247	283
3	205	127	166	171	178	203

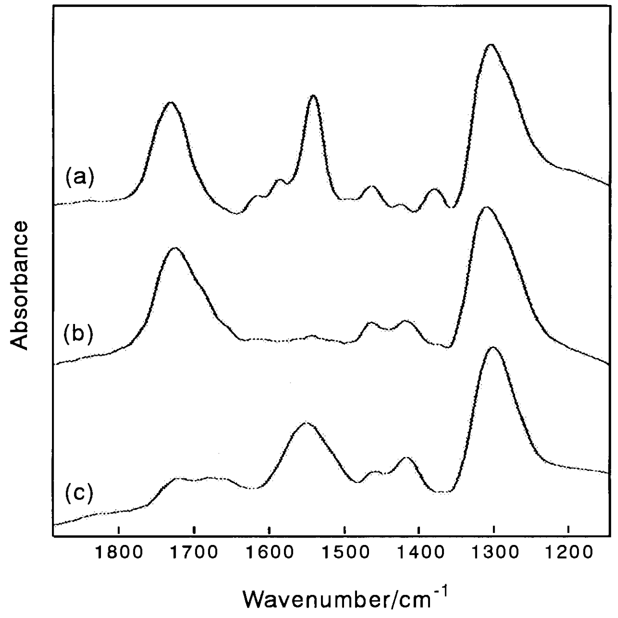


Figure 1. FT-IR diffuse reflectance spectra of 1-(2-nitrophenyl)ethyl ester (a), carboxylic acid (b), and the sodium salt (c) immobilized with **3** on the surface of silica gel.

modified with **3** are shown in Figure 1. Signals of 1724 cm^{-1} and 1534 cm^{-1} for the carbonyl and nitro groups were observed on the modified silica gel with **3** (Figure 1(a)), while only the carbonyl group remained at 1720 cm^{-1} on the irradiated surface (Figure 1(b)). The treatment of the silica gel with sodium hydrogencarbonate solution resulted in a shift of absorption of the carbonyl group to 1540 cm^{-1} for the sodium salt as shown in Figure 1 (c). This spectral change indicates that the 2-nitrobenzyl ester immobilized on the surface is converted to a carboxy group by photoirradiation.

In conclusion, we have demonstrated that silane coupling agents with 2-nitrobenzyl groups are effective for introduction of carboxy groups on the surface of silica gel. This method has an advantage over reported methodology in that the 2-nitrobenzyl ester can be converted under neutral conditions by photochemical reaction. The photochemical technique should be useful for formation of patterned functionalized monolayers.[15] More detailed elaboration of this approach for silica gel and the surface modification and patterning of silicon wafers are now under investigation.

References and Notes

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12 **4**: 61%; ^{1}H NMR($CDCl_3$, δ, 90 MHz) 2.26-2.65 (m, 4H, CH_2), 5.01 (d, *J*=9.8, 1H, *cis*-H_2C=C<), 5.05 (d, *J*=16.5, 1H, *trans*-H_2C=C<), 5.51 (s, 2H, benzyl), 5.63-6.00 (m, 1H, >C=CH-), 7.30-8.13 (m, 4H, aromatic); Anal. Calcd for $C_{12}H_{13}NO_4$: C, 61.27; H, 5.57; N, 5.95%. Found: C, 61.10; H, 5.70; N, 5.70%. **5**: 61%; ^{1}H NMR($CDCl_3$, δ, 90 MHz) 1.30-2.07 (m, 14H, CH_2), 2.41(t, *J*=7.5, 2H, CH_2CO,), 4.92(d, *J*=9.9, 1H, *cis*-H_2C=C<), 4.96(d, *J*=16.7, 1H, *trans*-H_2C=C<), 5.50(s, 2H, benzyl), 5.59-5.85(m, 1H, >C=CH-), 7.44-8.12(m, 4H, aromatic); Anal. Calcd for $C_{18}H_{25}NO_4$: C, 67.69; H, 7.89; N, 4.39%. Found: C, 67.53; H, 7.81; N, 4.07%. **6**: 43%; ^{1}H NMR($CDCl_3$, δ, 90 MHz) 1.65(d, *J*=6.5, 3H, CH_3), 2.26-2.53 (m, 4H, CH_2), 4.99(d, *J*=11.2, 1H, *cis*-H_2C=C<), 5.09(d, *J*=16.9, 1H, *trans*-H_2C=C<,), 5.60-5.97(m, 1H, >C=CH-), 6.36(q, *J*=6.5, 1H, methine), 7.29-7.98(m, 4H, aromatic); Anal. Calcd for $C_{13}H_{15}NO_4$: C, 62.64; H, 6.07; N, 5.62%. Found: C, 62.60; H, 6.15; N, 5.42%.

13 **1**: 46%; Bp 200 °C(oven)/0.3 mmHg; ^{1}H NMR ($CDCl_3$, δ, 90 MHz) 0.57-0.72 (m, 2H, -CH_2Si), 1.2-1.8 (m, 4H, -CH_2C), 2.35(t, *J*=7.4, 2H, CH_2CO), 3.58(s, 9H, CH_3O), 5.53(s, 2H, benzyl), 7.29-8.17 (m, 4H, aromatic). **2**: 54%; Bp 250 °C(oven)/0.4 mmHg; ^{1}H NMR($CDCl_3$, δ, 90 MHz) 0.60-0.75 (m, 2H, -CH_2Si), 1.2-1.8 (m, 16H, -CH_2C), 2.38(t, *J*=7.7, 2H, CH_2CO), 3.57(s, 9H, CH_3O), 5.51(s, 2H, benzyl), 7.57-8.13 (m, 4H, aromatic). **3**: 37%; Bp 200°C(oven)/0.3 mmHg; ^{1}H NMR($CDCl_3$, δ, 90 MHz) 0.61-0.72 (m, 2H, -CH_2Si), 1.2-1.8 (m, 4H, -CH_2C), 1.62 (d, *J*=6.5, 3H, CH_3), 2.33 (t, *J*=6.8, 2H, CH_2CO), 3.55(s, 9H, CH_3O), 6.32 (q, *J*=6.5, 1H, methine), 7.41-7.96 (m, 4H, aromatic).

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