Diazonium salts – Grafting Agents and Radical-
Hydrosilylation Initiators for Photoluminescent
Silicon Nanocrystals


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Silicon nanocrystals (SiNCs) show photoluminescence and have a low toxicity, therefore they are promising materials for the application in solar cells, LEDs or biological probes. Since the silicon surface is drawn to oxidation and the SiNCs tend to agglomerate in solution, control over the surface chemistry of SiNCs is a timely and attractive target.

Reactivity of Diazonium Salts towards Nanocrystalline Porous Silicon

Scheme 1: Reactions with diazonium salts and nanocrystalline silicon.

Diazonium salts are reduced by nanocrystalline porous silicon forming aryl radicals. On the silicon, a surface radical is generated. The radicals can combine giving covalentyl grafted aryl groups on the silicon surface. If an excess of unsaturated carbon compounds is present, the silicon surface radicals can be trapped, inducing a radical hydrosilylation reaction. This reactivity was known on porous silicon but was never investigated on freestanding SiNCs. The SiNCs for this work were prepared via pyrolysis of hydrogen silsesquioxane followed by etching with HF. Their diameter is 3 nm, they have a Si-H terminated surface and the SiNCs show red photoluminescence.

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Figure 1: IR spectra of SiNCs directly grafted

Scheme 2: Hydrosilylation of dodecane on SiNCs induced with 1-decyldiazobenzene tetrafluoroborate.

Several diazonium salts were synthesized and tested for their hydrosilylation reactivity. The dispersions become non-opalescent upon functionalization, therefore the reaction can be followed qualitatively. Electronwithdrawing groups excelerate the reaction. Also a long alkylchain is necessary to render the diazonium salts sufficiently soluble in toluene.

The diazonium salt induced hydrosilylation was performed with a variety of unsaturated carbon compounds. IR spectra of some of the resulting functionalized SiNCs are shown in Figure 2. It has to be noted that a sufficient funcitonalization with compounds bearing acidic protons such as alcohols and carboxylic acids could not be achieved.