

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

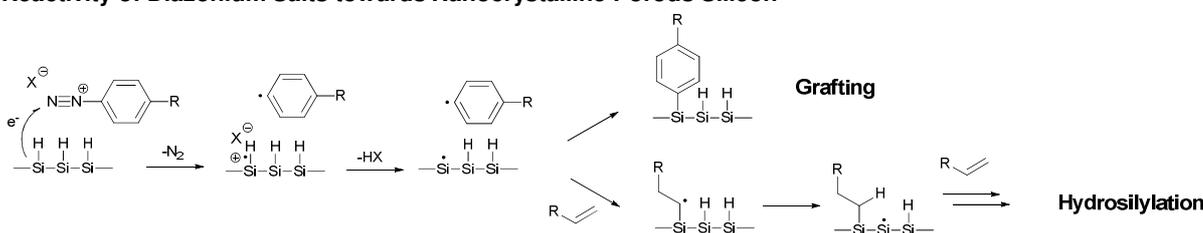
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Silicon nanocrystals (SiNCs) show photoluminescence and have a low toxicity, therefore they are promising materials for the application in solar cells, LEDs or biological probes. Since the silicon surface is drawn to oxidation and the SiNCs tend to 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 covalently 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.

Grafting of diazonium salts on SiNCs

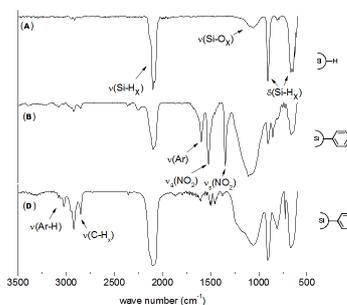
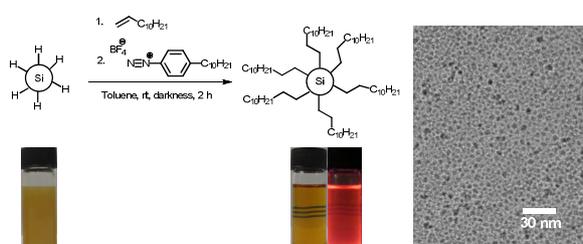


Figure 1: IR spectra of SiNCs directly grafted

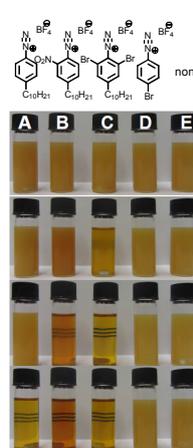
Direct grafting of diazonium salts on SiNCs is achieved via straight forward reaction of the hydride terminated SiNCs with the respective diazonium salts in acetonitrile or toluene. IR (Figure 1) and XPS measurements indicate a surface functionalization, but oxidation of the surface is an occurring side reaction and the functionalized SiNCs are not colloidally stabilized.

Diazonium salt induced hydrosilylation



Scheme 2: Hydrosilylation of dodecene on SiNCs induced with 4-decyl-diazobenzene tetrafluoroborate (left). TEM picture of the functionalized SiNCs (right)

The diazonium salt induced hydrosilylation was found to proceed efficiently on SiNCs. The particles were functionalized with short reaction times at room temperature in darkness and yielded colloidally stable SiNCs (Scheme 2).



Scheme 3: SiNCs hydrosilylated with dodecene using A: 4-decyl B: 2-nitro-4-decyl, C: 2,6-bromo-4-decyl and D: 4-bromo diazobenzene 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 accelerate the reaction. Also a long alkylchain is necessary to render the diazonium salts sufficiently soluble in toluene..

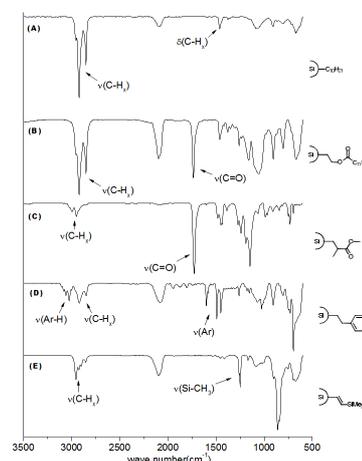


Figure 2: IR-spectra of SiNCs hydrosilylated using 2,6-Br-4-DDB: A: Dodecene, B Vinyl laurate, C : MMA, D: Styrene, E: Ethinyl-TMS

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 functionalization with compounds bearing acidic protons such as alcohols and carboxylic acids could not be achieved.

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