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Diazo Compounds

Diazonium Salts as Grafting Agents and Efficient Radical-Hydrosilylation Initiators for Freestanding Photoluminescent Silicon Nanocrystals

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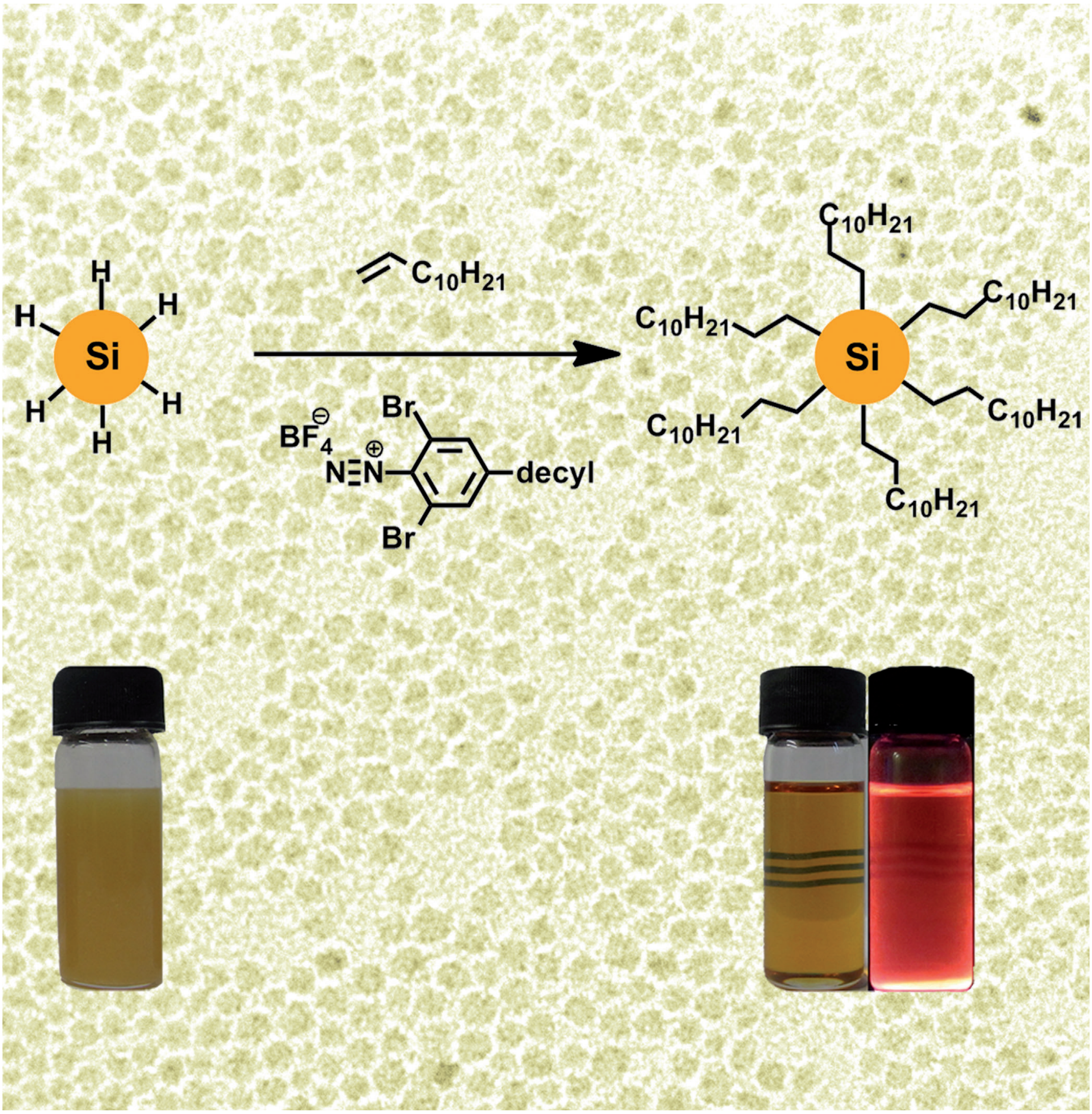
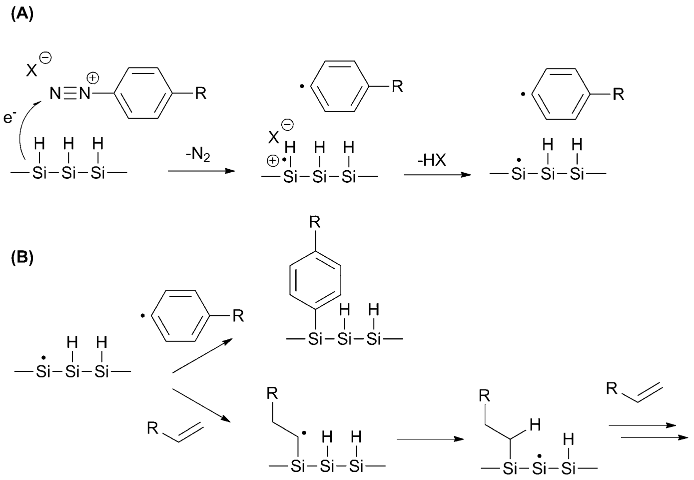


Abstract: The reactivity of diazonium salts towards free-standing, photoluminescent silicon nanocrystals (SiNCs) is reported. It was found that SiNCs can be functionalized with aryl groups by direct reductive grafting of the diazonium salts. Furthermore, diazonium salts are efficient radical initiators for SiNC hydrosilylation. For this purpose, novel electron-deficient diazonium salts, highly soluble in nonpolar solvents were synthesized. The SiNCs were functionalized with a variety of alkenes and alkynes at room temperature with short reaction times.

Silicon nanocrystals (SiNCs) exhibit properties that differ substantially from their bulk counterpart.[1–3] Their optoelectronic behavior (e.g., photoluminescence) is tunable with size and surface functionality. This, in combination with their low toxicity and biocompatibility, has garnered SiNCs much attention in wide ranging applications, such as solar cells, biological probes, and light-emitting diodes.[4–6]

Most syntheses yield freestanding SiNCs containing a reactive Si–H-terminated surface.[7–10] The surfaces of these particles must be modified, if they are to be useful, because SiNCs are sensitive toward oxidation and difficult to disperse in common solvents. In this context, a variety of hydrosilylation methods have been developed, involving reaction with unsaturated carbon-based compounds (i.e., terminal alkenes and alkynes). These methods generally require high temperatures, UV radiation, and/or metal-based catalysts.[9,11,12] Furthermore, these reactions can lead to multilayer and polymer surfaces that can passivate the SiNC surface.[13] The development of new, mild, and metal-free ways to functionalize SiNCs monolayers and other surface groups is, therefore, a timely and attractive target.

In part, because well-defined SiNCs have not been available, the surface chemistry of hydride-terminated bulk silicon has been more thoroughly investigated than for its nanocrystalline counterpart.[14] An attractive and widely applied method to obtain mono- and multilayers of aryl groups on silicon surfaces involves reductive grafting of diazonium compounds.[15] This assembly can be performed under electrochemically reducing or even at the open-circuit potential conditions.[16,17] The generally accepted reaction mechanism when no bias is applied proceeds by a one-electron reduction of the diazonium salt, release of nitrogen, generation of an aryl radical from the diazonium compound, and formation of a surface-silyl radical cation. After deprotonation, coupling of the two radicals gives a robust silicon–carbon bond (Scheme 1).[17] The formation of silicon-surface radicals during the diazonium reaction offers yet another path to NC surface modification through the attachment of a variety of surface groups—diazonium reagents could reasonably act as radical initiators to induce hydrosilylation reactions. Previously, porous silicon (p-Si), an electrochemically etched form of silicon that exhibits very high surface areas, was functionalized with various compounds in this way at room temperature with short reaction times.[18] In contrast to bulk silicon, reports about the reactivity of colloidal SiNCs with diazonium salts are scarce in literature. To date, only direct grafting was performed, or the diazonium salts were used as linking agents, and only comparably large SiNCs ($d \geq 50$ nm) that do not exhibit size-dependent properties were investigated.[19–21]



Scheme 1. Reaction mechanism of silicon surfaces with diazonium salts. A) Reduction of the diazonium salt and formation of an aryl radical with release of nitrogen and formation of Si-surface radical after deprotonation. B) Possible reactions of the Si-centered radical to form Si–C bonds.

Herein, we report the first investigation into the reactivity of several diazonium salts toward photoluminescent quantum confined SiNCs ($d = 3$ nm). We also demonstrate that the studied diazonium salts give direct, reductive surface grafting, as well as radical hydrosilylation initiation.

The H-terminated SiNCs used in this work were synthesized by following a known procedure through disproportion of hydrogen silsesquioxane (HSQ) giving SiNCs embedded in a silicon oxide matrix. The SiNCs were subsequently liberated by etching with hydrofluoric acid and final extraction in toluene.[7]

Direct reductive grafting of diazonium salts was first investigated by using commercially available 4-nitro (4-NDB) and 4-bromobenzene diazonium tetrafluoroborate (4-BDB). For these

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grafting experiments, SiNCs (150 mg etched SiO_2/SiNC compound) were suspended in a dry and degassed 0.1 м solution (2 mL) of the diazonium salt in acetonitrile and stirred for 6 h. In each stage of the reaction, the SiNCs formed turbid suspensions, so the SiNCs could be separated and purified with several centrifugation and ultrasonication steps in acetonitrile, toluene, and dichloromethane. FTIR analyses confirmed surface modification with clear evidence of C–C ring-stretching bands (1400–1600 cm^{-1}), and in the case of 4-NDB, the spectral signature of the NO_2 moiety (1350, 1500 cm^{-1}; Figure 1 B and C). However, strong residual Si–H bands (2100 cm^{-1}) imply the coverage of the SiNCs is poor. Further supporting partial surface modification, surface oxidation evidenced by Si–O bands (1050 cm^{-1}), was observed for all samples. The present oxidation of SiNC surfaces is consistent with published reports of diazonium-based modification of p-Si.[18]

It is possible that the incomplete functionalization is a manifestation of the divergent solubility properties of the diazonium salts and the H-terminated SiNCs. Acetonitrile is commonly used solvent when manipulating diazonium compounds because of their solubility properties. Unfortunately, H-terminated SiNCs are hydrophobic/nonpolar and do not disperse well in this solvent system. In an effort to minimize the impact of solvent polarity and improve SiNC surface coverage, we turned to an organic-soluble diazonium salt (i.e., 4-decylbenzene diazonium tetrafluoroborate (4-DDB)) known to give toluene-dispersible hydrophobic aryl-grafted Au and Pt nanoparticles.[22] SiNC modification and product isolation were performed by using conditions identical to those described herein (see below) for the other diazonium salts. Unfortunately, the IR spectrum of the SiNCs showed evidence of limited functionalization, and Si–H and Si–O bands were dominant (Figure 1 D).

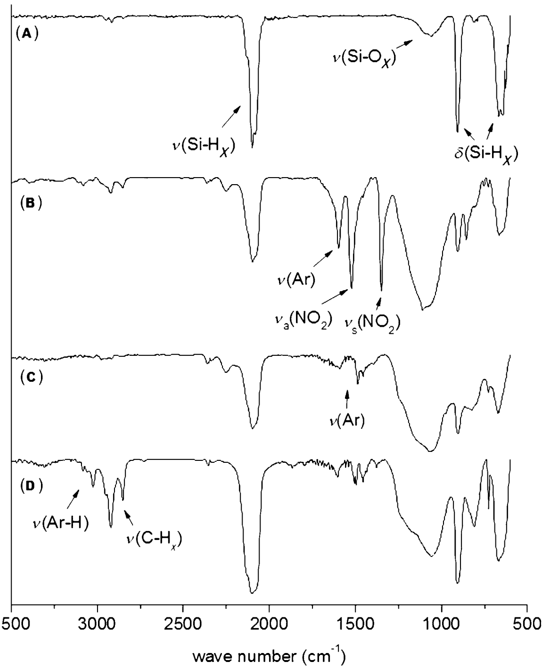

Figure 1. FTIR spectra of A) freshly etched hydride terminated SiNCs; B) reacted with 4-NDB; C) with 4-BDB; and D) with 4-DDB.

Clearly, an extensive surface modification of small SiNCs is not straightforward for this reaction system. It is reasonable that surface reactivity differences noted for bulk Si and SiNCs may result from the limited ability of the SiNC to support the required radical cation intermediate noted in Scheme 1.

Because the surface modification of colloidal SiNCs through direct reductive grafting of diazonium species is inefficient and led to substantial surface oxide that can influence the optoelectronic properties of SiNCs, we turned to the application of diazonium salts as radical initiators.

Diazonium salts have proven to be efficient radical initiators of hydrosilylation on p-Si surfaces.[18] It was illustrated above that reactions suitable for modifying bulk and p-Si are not always directly transferable to colloidal SiNCs. In this context, we explore the application of diazonium salts as radical initiators in the surface modification of freestanding SiNCs. Hydride-terminated SiNCs tend to agglomerate in solution giving turbid dispersions. Alkyl-surface modification achieved upon reaction with α-olefins (e.g., dodecene) gave clear colloidal dispersions.[5,23] For ease of comparison, dodecene was used for the present hydrosilylation experiments.

Diazonium salt induced hydrosilylation was achieved upon dispersing H-terminated SiNCs (150 mg etched SiO_2/SiNC compound) in 3 mL of a toluene solution of dodecene (3 mmol). The reaction at room temperature was initiated upon addition of 4-DDB (15 μmol; Note: diazonium salts without long alkyl chains, such as 4-NDB and 4-BDB, are ill-suited for reactions in toluene because of their limited solubility). After stirring for 2 h at room temperature and in complete darkness, the functionalized SiNCs were isolated and purified by established antisolvent precipitation with methanol. In contrast to the SiNCs containing Si–H surfaces, the present dodecyl-terminated SiNCs form a stable clear colloidal dispersion (Figure 2). The resulting SiNCs showed red photoluminescence (PL) with an emission maximum at approximately 700 nm, which is typical for their size.[24]

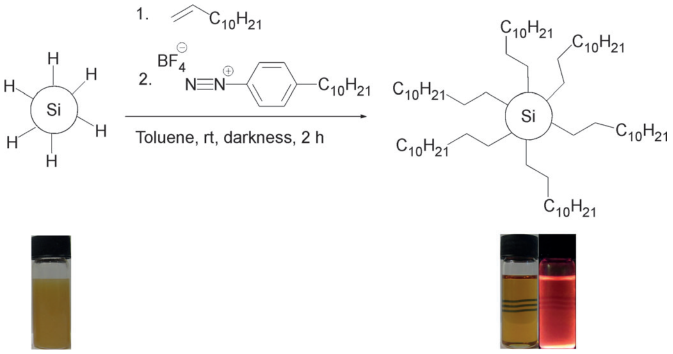

Figure 2. Unfunctionalized SiNCs in toluene (left), dodecyl functionalized SiNCs in toluene under visible light and UV radiation (right).

FTIR analysis showed clear evidence of dodecyl surface termination: the C–H stretching band (2900 cm^{-1}) dominates the spectrum, whereas substantially weaker features attributable to trace Si–H and Si–O bands are also present (Figure 3 A). In contrast, the reference sample without the addition of the di-

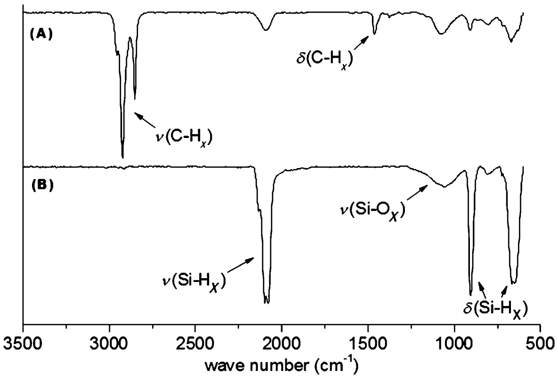

Figure 3. A) Dodecyl-functionalized SiNCs with 4-DDB as radical-hydrosilylation initiator; B) reference sample without the addition of 4-DDB.

azonium salt showed no evidence of functionalization (Figure 3 B).

Having established diazonium reagents do initiate surface modification of SiNCs, we explored the influence of the diazonium structure on the present reaction. Electron-deficient diazonium salts were reported to be more reactive towards homolytic dediazotation.[25] Thus, diazonium salts containing electron-withdrawing groups are expected to be even more effective initiators for the present reactions. To test this hypothesis, the heretofore unknown diazonium salts 2-nitro-4-decyl (2-NO_2-4-DDB) and 2,6-bromo-decyl-diazobenzene tetrafluoroborate (2,6-Br-4-DDB) were synthesized and applied as hydrosilylation radical initiators, and their reactivity was compared to that of 4-DDB and 4-BDB. Conveniently, because the reaction dispersions become non-opalescent upon functionalization, the progress of the reaction can be readily monitored qualitatively (Figure 4).

As was expected, the more electron-deficient 2-NO_2-4-DDB and 2,6-Br-4-DDB reacted faster than 4-DDB, as was evidenced by the transparency of the reaction mixture. With 2,6-Br-4-DDB being the most reactive, the suspension started to turn transparent after only 30 min. Compounds 2-NO_2-4-DDB and 4-DDB needed 60 or 90 min, respectively, to reach this point. No reaction, in comparison to the reference sample without diazonium salt, was observed with 4-BDB, presumably due to its low solubility in toluene.

If the present SiNC reactivity is to find wide application, it is necessary to demonstrate a broad applicability and functional group tolerance of the diazonium-salt-induced hydrosilylation. In this context, we explored reactions with dodecyne, vinyl laurate, methyl methacrylate (MMA), styrene, and ethinyltrimethylsilane (ethinyl-TMS) by using 2,6-Br-4-DDB as radical initiator (Figure 5).

The reaction times differ for each the compounds with dodecyne being the most reactive and turning transparent after only 10 min, whereas vinyl laurate showed the lowest reactivity and needed 6 h until reaching this point. These differences are possibly due to different stabilities of the carbon-centered radicals, which are formed during hydrosilylation (Scheme 1 B) and are subject of ongoing investigations. We also noted that alkenes containing acidic protons, such as alcohols and amines, seem to hamper the hydrosilylation reaction. This issue will be addressed in future work.

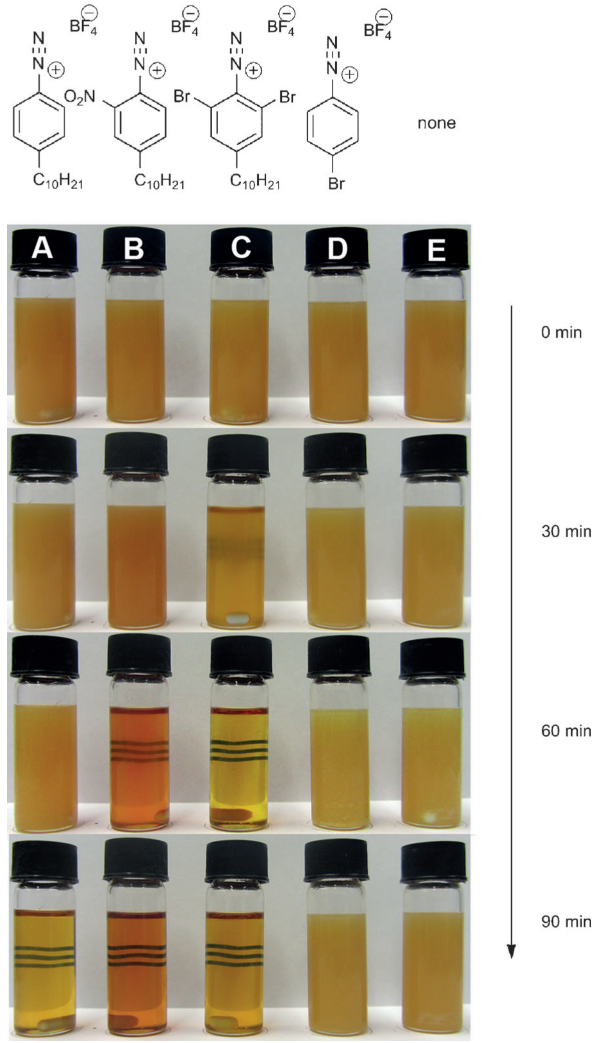

Figure 4. Functionalization of SiNCs with dodecene by using A) 4-DDB; B) 2-NO_2-4-DDB; C) 2,6-Br-4-DDB; and D) 4-BDB as radical-hydrosilylation initiators; and E) without addition of a diazonium salt.

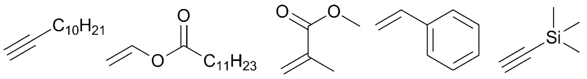

Figure 5. Alkenes and alkynes that were used for the hydrosilylation reactions from left to right: dodecyne, vinyl laurate, MMA, styrene, and ethinyl-TMS.

All given alkenes/alkynes provided stable colloidal dispersions that showed photoluminescence with a maximum at approximately 700 nm. The FTIR spectra of the functionalized SiNCs are given in Figure 6 and show the expected bands arising from the surface groups in question, as well as trace Si–H and Si–O bands.

The functionalized SiNCs were further analyzed by using dynamic light scattering (DLS) method. Table 1 lists the hydrodynamic radii of the SiNCs. The values are in accordance with the size of the SiNCs and literature results.[11]

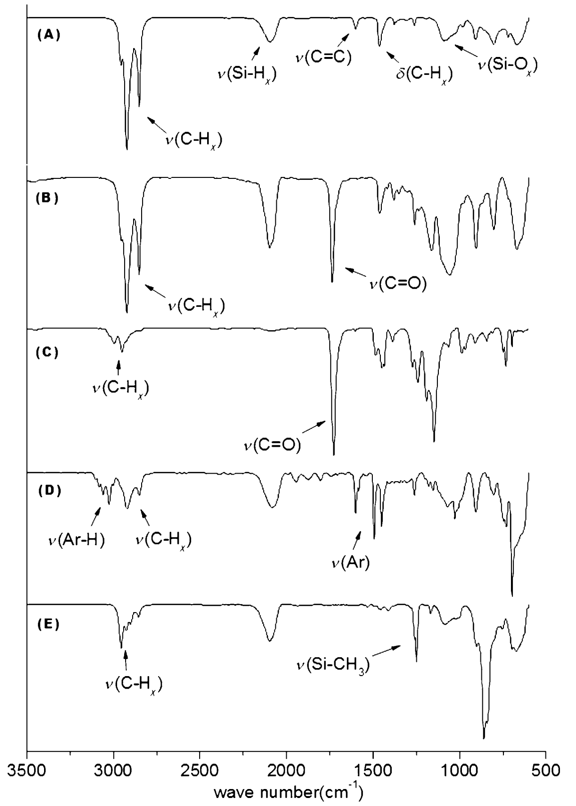

Figure 6. FTIR spectra of the hydrosilylated SiNCs with A) dodecyne; B) vinyl laurate; C) MMA; D) styrene; and E) ethinyl-TMS.

Table 1. Hydrodynamic radii with polydispersities of the functionalized SiNCs by diazonium salt initiated hydrosilylation determined with DLS.

Reagent	Hydrodynamic radius [nm]	Polydispersity [%]
dodecene	3.8	30.3
dodecyne	4.4	32.3
ethinyl-TMS	3.6	38.9
vinyl laurate	3.5	38.4
MMA	2.5	70.2
styrene	5.3	62.6

In summary, we have shown that SiNCs can be functionalized with aryl groups by direct reductive grafting of diazonium salts. However, the coverage of the SiNCs is incomplete, and oxidation is a strongly occurring side reaction. More effective is the application of diazonium salts as radical initiators for hydrosilylation reactions. For this purpose, new toluene-soluble diazonium salts were synthesized. Those with electron-withdrawing groups, such as 2,6-bromo-4-decyl-diazobenzene tetrafluoroborate, have shown to be the most reactive. Several alkenes and alkynes were hydrosilylated on the SiNCs using this method. In all cases, photoluminescent stable colloidal SiNC dispersions were obtained within reaction times of a few hours. Most importantly, we have demonstrated that the application of diazonium salts offers a new, mild, and fast way to initiate hydrosilylation reactions on SiNCs and opens the door to convenient and predictable surface modification.

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Keywords: diazo compounds · hydrosilylation · silicon nanocrystals · surface grafting

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