Silicon Nanocrystals

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Silicon Nanocrystals and Silicon-Polymer Hybrids: Synthesis, Surface Engineering, and Applications

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Silicon nanocrystals (Si-NCs) are emerging as an attractive class of quantum dots owing to the natural abundance of silicon in the Earth's crust, their low toxicity compared to many Group II–VI and III–V based quantum dots, compatibility with the existing semiconductor industry infrastructure, and their unique optoelectronic properties. Despite these favorable qualities, Si-NCs have not received the same attention as Group II–VI and III–V quantum dots, because of their lower emission quantum yields, difficulties associated with synthesizing monodisperse particles, and oxidative instability. Recent advancements indicate the surface chemistry of Si-NCs plays a key role in determining many of their properties. This Review summarizes new reports related to engineering Si-NC surfaces, synthesis of Si-NC/polymer hybrids, and their applications in sensing, diodes, catalysis, and batteries.

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1. Introduction

Semiconductor quantum dots have emerged as a new class of luminescent materials whose emission properties can be tuned by changing the nanocrystal size,[1] shape,[2] composition,[3] and dopants.[4] Since their discovery thirty years ago, quantum dots have revolutionized the field of nanotechnology owing to their fascinating optoelectronic properties and their diverse applications have reached across the fields of physical and life sciences, engineering, and medicine. Today, semiconductor quantum dots are on the forefront of many research fields and are being investigated for applications such as solar cells,[5] LEDs,[6] catalysis,[7] bio-imaging,[8] magnetic materials,[9] sensing,[10] bioassays,[11] lasing,[12] and quantum computing,[13] among others. The most well-known quantum dots are composed of Group II–VI, IV–VI, and III–V type semiconductors. Unfortunately, these contain toxic heavy metals, such as cadmium, lead, mercury, and arsenic as well as elements whose reserves are depleting, such as indium and selenium. With increased awareness of the harmful effects of toxic heavy metals, their use in consumer products is becoming increasingly regulated as evidenced by the European Union Directive 2011/65/EU ("Restriction of the use of certain hazardous substances") that limits or bans the use of these elements. Consequently, efforts have been made to establish alternative quantum-dot materials that are nontoxic and abundant.

It is an understatement that we live in a technological world made possible by silicon (Si). While bulk Si has dominated the microelectronics industry for over half a century, it is not photoluminescent at room temperature and has limited optical applications. It was only twenty five years ago with the discovery of porous silicon (*p*-Si) by Canham,[14] that nanostructured Si began being explored and applied for its optical properties.[15] Today, a wide spectrum of methods have been reported for preparing silicon nanocrystals (Si-NCs). The most commonly used methods can be generally classified as reduction of silicon halides,[16] oxidation of metal silicides,[17] thermal disproportionation of silicon-rich oxides,[18] and decomposition of silane or disilane[19] using plasma or heat (See Scheme 1). Other methods such as magnesiothermic reduction,[20] thermal decomposition of silicon precursor in supercritical fluid,[21] and etching[22] or mechanochemical ball milling[23] of bulk silicon to prepare Si-NCs have also been reported. These procedures as well as their advantages and disadvantages were recently reviewed and will not be discussed herein.[24]

Most procedures yield Si-NCs terminated with a hydride, halogen, or oxide surface.[25] Hydride and halogen surfaces are oxidatively unstable and hydride as well as oxide terminated Si-NCs are not readily dispersed in common solvents; hence Si-NCs bearing these surfaces require further modification to passivate their surfaces and render them compatible with solvents. Conventionally, semiconductor quantum dots possess a core–shell structure where the core material is covered with a lattice-matching wide-band-gap material that confines the excitons within the core, isolates them from surface states, and increases the probability of radiative recombination.[26] Unfortunately, known methods for preparing Si-NCs do not offer ready access to similar structures. As a result, Si-NCs are typically functionalized directly with organic ligands. These surface modifications allow for the preparation of nanomaterials with a variety of functionalities and improved properties. Herein we review recent work related to tailoring Si-NC surfaces to manipulate

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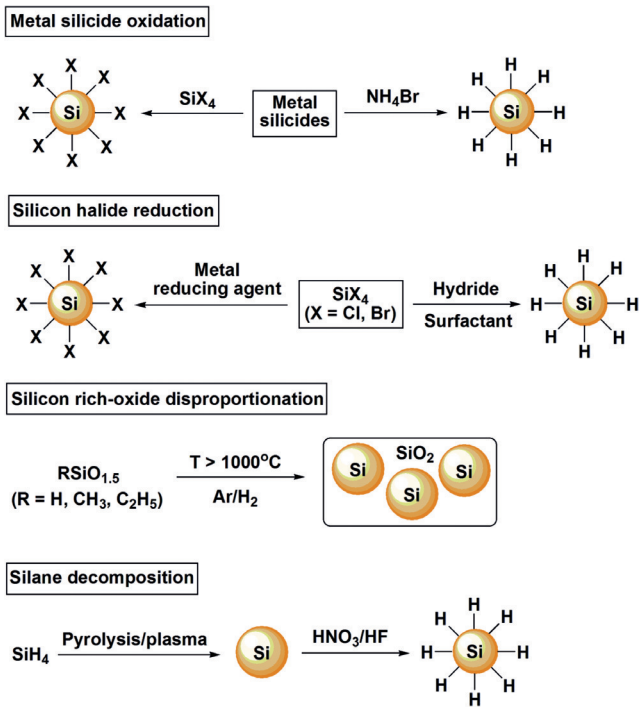

Scheme 1. General methods for preparing Si-NCs.

their dispersability, stability, photoluminescence (PL), quantum yields, and applications.

2. Monolayer Surfaces

Covalent attachment of functional monolayers onto bulk silicon surfaces began with the pioneering work of Linford and Chidsey; in their ground breaking work they investigated reactions of 1-alkenes and 1-alkynes with hydride-terminated Si(111) and Si(100) bulk surfaces.[27] In the ensuing decades, similar methodologies have been extended to porous silicon and freestanding Si-NCs.[28] Correspondingly numerous methods have been established to generate Si–C, Si–O, Si–N,[24,25] and more recently Si–S[29] linkages on NCs. Still, Si–C linked monolayers have long been considered the surface of choice. The following discussion focuses on the recent advances in reactivity of hydride and halogen surfaces on Si-NCs.

2.1. Hydrosilylation Reactions

Hydrosilylation involves the addition of a Si–H bond across multiple C–C bonds and is typically facilitated by exposure to heat,[30] light,[31] radical initiators,[32] transition-metal catalysts,[33] Lewis acids,[34] or plasmons.[35] Thermally initiated hydrosilylation is widely employed; it proceeds independent of particle size and shape, does not require a catalyst that could contaminate the product and compromise target properties, and provides efficient surface coverage. The generally accepted mechanism for this reaction involves the thermally initiated homolytic cleavage of surface Si–H bonds to provide surface silyl radicals that subsequently

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Bernhard Rieger studied chemistry at the Ludwig-Maximilians-Universität München and received his Ph.D. in 1988. After research at the University of Massachusetts at Amherst and in the plastics laboratory of BASF SE, he received his Habilitation in 1995 at the University of Tübingen. In the same year, he became Professor ordinarius at the Department of Materials and Catalysis at the University of Ulm. In 2006, he was appointed professor at Technische Universität München. Since then, he holds the WACKER-Chair of Macromolecular Chemistry and works as director of the Institute of Silicon Chemistry at TUM.

Julian Kehrle studied Chemistry at the Technische Universität München, where he received his Master's degree in 2012. Currently he is working on his Ph.D. thesis at the WACKER Chair of Macromolecular Chemistry under the supervision of Prof. Rieger. He is interested in the synthesis and the preparation of functional silicon-nanocrystal-based hybrid materials. This work is performed in cooperation with the Veinot group under the frame of the IRTG 2022.

Dr. Veinot is a professor in the Chemistry Department at the University of Alberta. His research aims to develop methods for preparing, and investigating advanced nanomaterials (NMs) and optoelectronic polymers. His team established a straightforward, scalable method that affords tailored Si nanocrystals that has become the method of choice in seven international groups. He is a former Chair of the Chemical Society of Canada Materials Chemistry Division, Associate Editor of the Canadian Journal of Chemistry, and Canadian Director of the Alberta/Technical University of Munich International Graduate School for Hybrid Functional materials.

react with terminal carbon–carbon multiple bonds. While a few rare exceptions exist,[36] reactions of this type are typically performed in neat alkene/alkyne and until recently it has long been assumed that they yielded surface-bonded monolayers. In 2014, Yang et al. conclusively demonstrated that typical thermal hydrosilylation conditions induce ligand oligomerization and that the degree of oligomerization increases with oxygen content, reaction temperature, and ligand concentration.[37] The reaction products were analyzed using NALDI (nanostructure assisted laser desorption/ionization) mass spectrometry and oligomers of up to seven repeat units could form when dodecene was employed (Figure 1 a). Consistent with these findings, Panthani et al.

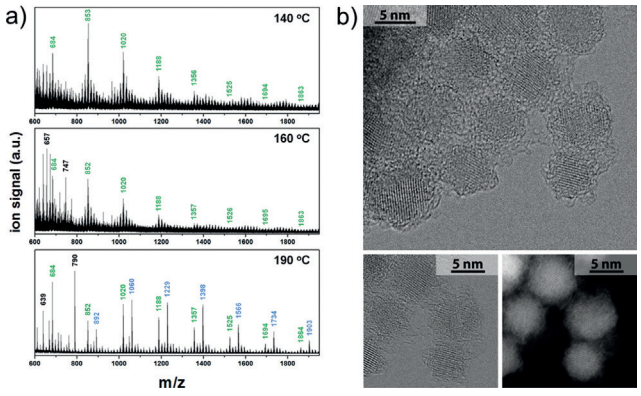
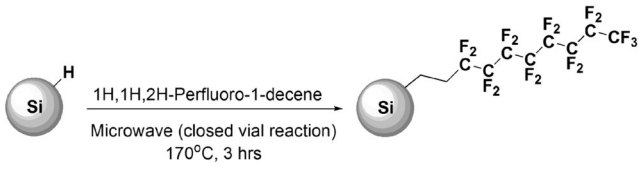


Figure 1. a) NALDI mass spectra of dodecyl-functionalized Si-NCs at the indicated temperatures. b) Bright field (top, bottom left) and dark field (bottom right) STEM images of alkyl-passivated Si-NCs on the edge of a graphene support. Reproduced and adapted with permission from the American Chemical Society.[37,38]

published TEM images of alkyl-stabilized Si-NCs obtained from thermal hydrosilylation. Their images were obtained using graphene supports and show what appear to be ligands around the NC surface (Figure 1 b).[38] It is reasonable that ligand oligomerization contributes to the robustness, increased stability, and PL quantum yields[39] of thermally hydrosilylated Si-NC surfaces, however these long electrically insulating alkyl chains also present a potential challenge to the eventual application of Si-NCs in optoelectronic devices.

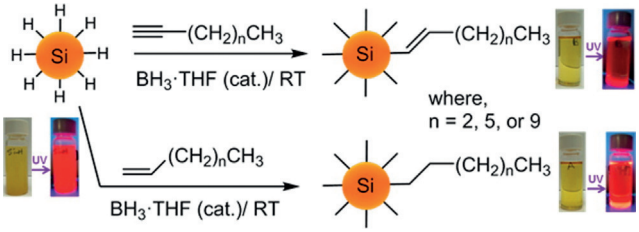
Qian et al. tethered fluoro-substituted alkenes onto Si-NC surfaces in attempts to enhance the oxidative stability.[40] Perfluorodecyl groups were grafted onto Si-NC surfaces upon heating in a microwave reactor (Scheme 2). The researchers propose this approach is a facile and "green" method for modifying Si-NC surfaces. They also propose an



Scheme 2. A summary of the synthesis of perfluorodecyl-functionalized Si-NCs. Adapted with permission from the American Chemical Society.[40]

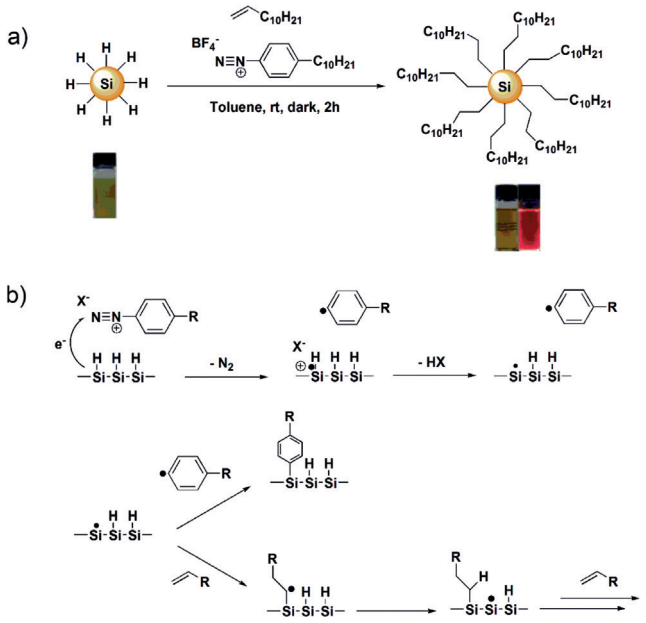
associated increase in absolute PL quantum yield resulting from the low frequency of carbon–fluorine stretching modes that minimize non-radiative relaxation pathways. In addition they noted enhanced oxidative and PL stability in perfluorodecyl functionalized Si-NCs compared to the dodecyl surface ligand upon exposure to humidity. Similar work from the same group also indicated that introducing heteroatoms (i.e., C–X bonds; X = S or F) into the surface-bonded alkyl or aryl moieties lead to enhanced absolute photoluminescence quantum yields presumably because of the associated lowering of the C–X bond vibration frequency.[41]

While a very small number of exceptions exist,[42] thermal hydrosilylation requires high reaction temperatures, and as a result only high-boiling alkenes and alkynes can be conveniently grafted onto Si-NC surfaces. Photochemically induced hydrosilylation provides a seemingly obvious alternative. However, its utility is limited by size-dependent reactivity, intolerance to chemical functionality, and long reaction times.[43] Other room-temperature hydrosilylation routes make use of transition-metal catalysts, but these additives can compromise Si-NC properties (e.g., PL quenching) and removing the residual catalyst is difficult.[44] Recently, Purkait et al. modified Si-NC surface chemistry at room-temperature via borane-catalyzed hydrosilylation.[45] They functionalized Si-NCs with a variety of terminal alkenes and alkynes (Scheme 3), realizing up to 96 % surface coverage.



Scheme 3. Borane-catalyzed hydrosilylation of Si-NC surfaces with terminal alkenes and alkynes. Reproduced and adapted with permission from the American Chemical Society.[45]

Höhlein et al. also reported a room-temperature route to Si-NC surface hydrosilylation initiated by diazonium salts (Scheme 4).[46] While diazonium salts have been used to directly graft aryl groups onto silicon surfaces,[47] their use as radical initiators has only been shown for porous silicon.[48] The researchers also investigated the influence of substituents on the efficacy of the reaction and found that those with electron-withdrawing groups provided the highest surface coverage. Diazonium-salt-initiated hydrosilylation was also tolerant of various functional groups and afforded attachment of hydrocarbon alkenes and alkynes, vinyl laurate, methyl methacrylate, ethynyltrimethylsilane, and chlorodimethyl-(vinyl)silane. In another study, the same researchers demonstrated that chlorodimethyl(vinyl)silane functionalized Si-NCs could be further modified upon reaction with alcohols, silanols, and organolithium reagents.[49]



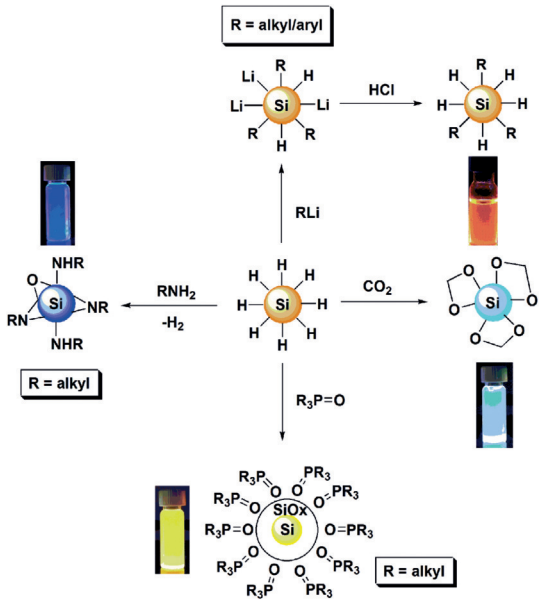
Scheme 4. a) Modification of Si-NCs with alkenes via diazonium-salt-induced hydrosilylation. b) Proposed mechanism for diazonium-salt reactivity with silicon hydride surfaces. Reproduced and adapted with permission from John Wiley and Sons.[46]

2.2. Alternative Reactions on the Silicon Hydride Surface

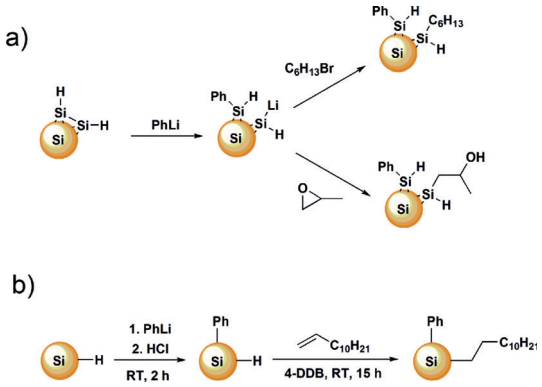
While hydrosilylation remains the leading approach toward Si-NC surface functionalization, attempts to circumvent its limitations have seen exploration of the reactivity of Si–H surfaces. Some recently reported reactions are summarized in Scheme 5. While hydrosilylation leads to optical properties dominated by band-gap emission, investigations to date suggest that most alternative functionalization pathways yield materials that emit from defect/surface states.

We have shown hydride-terminated Si-NCs react directly with amines to afford Si-N covalent linkages.[50] The surface passivation resulting from this reaction is incomplete and significant oxidation is observed. The incorporation of nitrogen and oxygen moieties onto the surface leads to particle-size-independent surface-species-based blue photoluminescence.[51,52] Hydride terminated Si-NCs also react with CO_2 at high pressures (i.e., 10 bar) and temperatures above 100 °C, yielding an acetal surface that provides blue-green photoluminescence.[53] At longer reaction times the surface acetal groups decompose forming formaldehyde and oxidized particles that precipitate from the reaction mixture. Analogous to molecular silanes, hydride-terminated Si-NCs react with phosphine oxides forming the corresponding tri-substituted phosphine.[53] Under ambient conditions, the reduced phosphines are oxidized to the corresponding phosphine oxide and stabilize oxide-coated Si-NCs in organic solvents. The optical properties of these phosphine-oxide-stabilized oxide-coated Si-NCs are complex; studies indicate band gap and defect states play a role in determining the emission maxima. The relative PL quantum yields obtained for Si-NCs derived from reactions of hydride-terminated Si-NCs with amines, CO_2, and phosphine oxides are higher relative to those obtained for hydrosilylated Si-NCs.[53] However, in contrast to Si-NCs exhibiting band-gap-based PL, those emitting from surface states appeared to photobleach (Figure 2).

Höhlein et al. further demonstrated that hydride-terminated Si-NCs react directly with organolithium reagents via cleavage of surface Si–Si bonds to form Si–Li and Si–R surface species (Scheme 6a).[54] The reaction proceeds at room temperature and the Si–H bonds can be further functionalized to yield mixed monolayers (Scheme 6b).



Scheme 5. Reactivity of Si-H terminated Si-NCs with organolithium reagents, carbon dioxide, alkylamines, and alkylphosphine oxides. Reproduced and adapted with permission from John Wiley and Sons and The American Chemical Society.[53,54]



Scheme 6. a) Reaction of Si-NCs with phenyllithium and subsequent reactivity of Si-Li groups and b) reaction of Si-NCs with phenyllithium and subsequent reactivity of Si-H groups yielding mixed-surface Si-NCs. Reproduced and adapted with permission from John Wiley and Sons.[54]

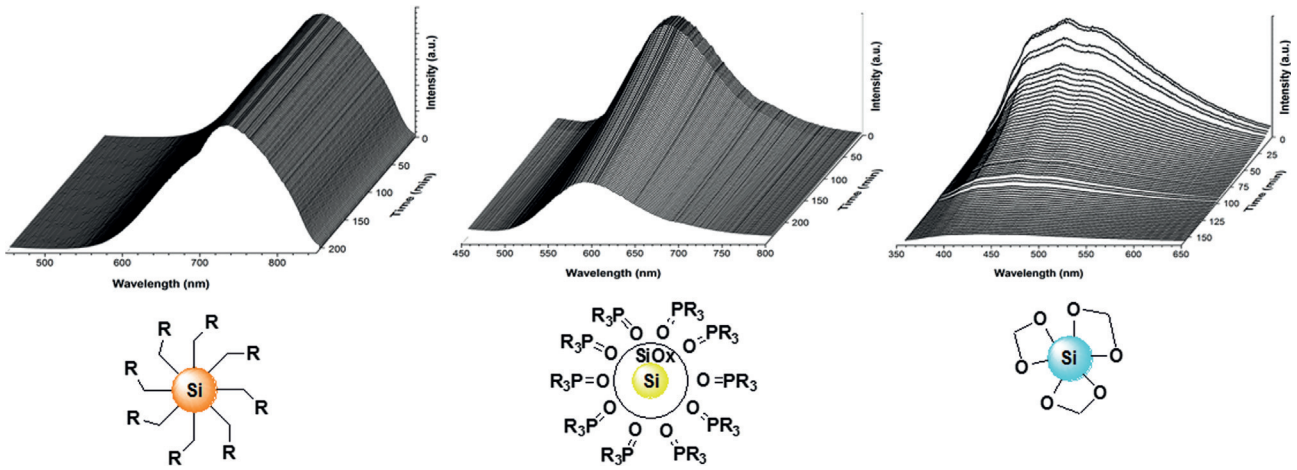


Figure 2. Photostability of Si-NCs stabilized with dodecyl, trioctylphosphine oxide, and acetal functional groups. The Si-NC solutions were continuously illuminated for over 150 min. Reproduced and adapted with permission from The American Chemical Society.[53]

2.3. Halogenated Silicon Surfaces

Most solution-phase methods for preparing chloride- or bromide-terminated Si-NCs never see the halogen-terminated particles isolated; they are typically derivatized in situ. The versatile reactivity of Si–X (X = Cl, Br) surfaces has seen these particles derivatized using numerous approaches including reactions with Grignard and organolithium reagents, amines, alcohols, silanols. This body of work has been reviewed elsewhere.[24,25]

Of particular interest, Wheeler et al. prepared chloride-terminated Si-NCs via decomposition of $SiCl_4$ in the presence of H_2 in a non-thermal plasma reactor and stabilized the Si–bond with hard donor molecules via hypervalent interactions (Figure 3).[55] ATR-FTIR analysis revealed shifts in the

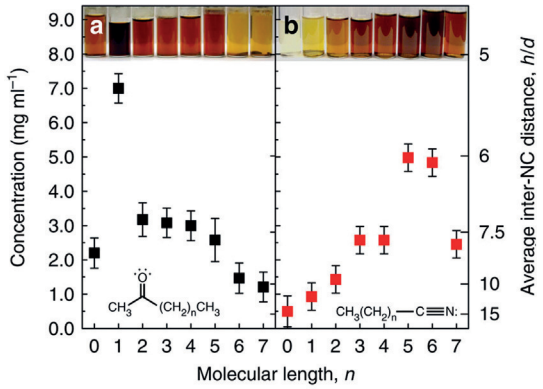


Figure 3. Concentration of chloride terminated Si-NCs as a function of molecular length *n* of the stabilizing group a) *n*-alkanone and b) *n*-alkanenitriles. Reproduced and adapted with permission from Nature publishing group.[55]

stretching modes of carbonyl, nitrile, and Si–Cl bonds consistent with interactions between Si-NC and donor molecules (Figure 4). The stability of the colloidal NC suspensions depended upon the donor strength; interestingly,

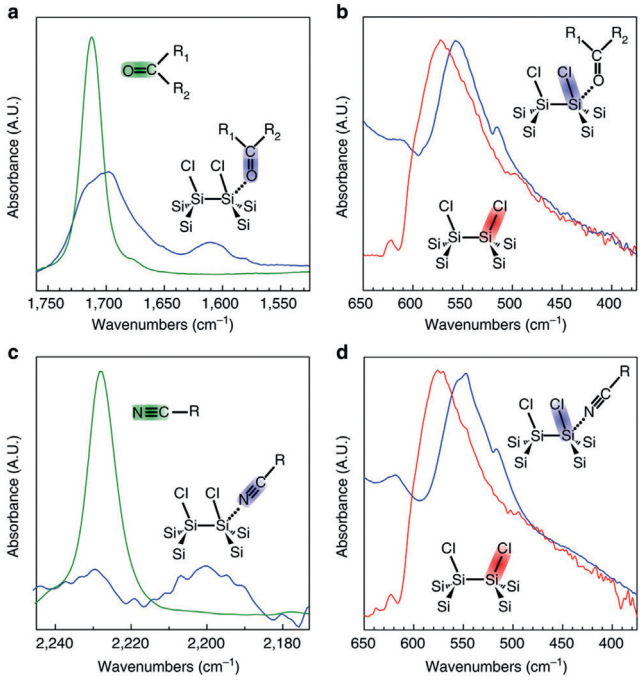


Figure 4. ATR-FTIR spectra depicting hypervalent interactions between ketones and nitriles with chloride-terminated Si-NCs. Reproduced and adapted with permission from Nature publishing group.[55]

the surface-bonded groups were labile—an unprecedented discovery for Si surfaces.

While halogen termination of Si-NCs has been achieved in situ, few reports outlining the deliberate halogenation of Si-NCs have appeared. Chlorination/alkylation on bulk Si-(111) and Si(100) surfaces was first reported by Bansal et al. and gives a well-ordered, chemically passivated surface.[56] Chlorination is achieved by treating atomically flat bulk Si surfaces with PCl_5 at temperatures higher than 90 °C in the presence of benzoyl peroxide. We investigated similar reactivity with hydride-terminated Si-NCs.[57] In the case of the Si-NC system PCl_5 chlorination proceeded at room temperature without a radical initiator (Figure 5a). A complication of this

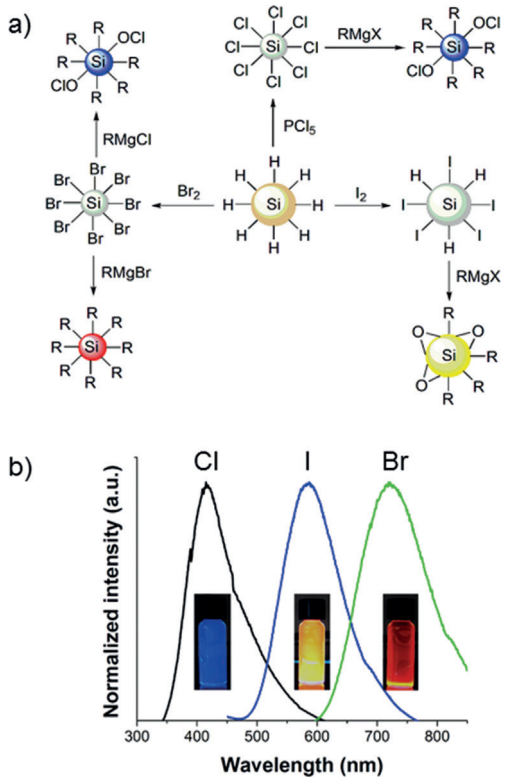


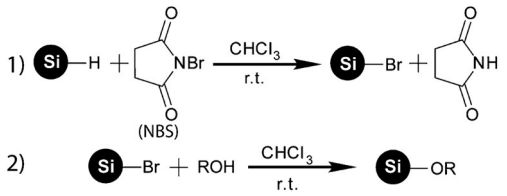
Figure 5. a) Schematic representation of halogenation and alkylation of hydride terminated Si-NCs and b) PL spectra of alkylated Si-NCs derived from halogenated surfaces. Reproduced and adapted with permission from the American Chemical Society.[58]

approach is that PCl_5 etches the Si-NC surface at elevated temperatures and can lead to complete dissolution of the particles.[58] Similarly, bromination can be achieved upon reaction of hydride-terminated Si-NCs with elemental bromine at room temperature. Anisotropic etching of the Si-NCs was also observed for this reaction, albeit faster than that noted for PCl_5. Iodination can be achieved upon reaction of elemental iodine with hydride-terminated Si-NCs, however this procedure does not lead to complete modification. The formation of Si–X (X = Cl, Br and I) was confirmed using Raman and X-ray photoelectron spectroscopy.

Halogen exchange was observed between bromide-terminated Si-NCs and RMgCl reagents. Alkyl-functionalized Si-NCs obtained from chloride, bromide, and iodide surfaces exhibited blue, red, and yellow-orange photoluminescence, respectively (Figure 5b). While the red photoluminescence originated from a transition across the band gap (confirmed through long-lived excited states), the blue and yellow-orange photoluminescence appear to originate from surface defects and had nanosecond lifetimes.

Bell et al. reported room temperature bromination of hydride terminated Si-NCs using N-bromosuccinimide (Scheme 7).[59] NCs functionalized in this way were subsequently modified upon exposure to alcohols to yield red photoluminescent Si-NCs.

Residual chorine-based impurities can influence Si-NC optical properties. Often, blue photoluminescence is reported for particles derived from chloride surfaces. We have demonstrated that oxychloride moieties can induce surface-state-based blue emission that is independent of particle size.[58] In contrast, well-passivated Si-NC alkyl surfaces derived from bromide termination show size-dependent photoluminescence from band-gap emission.



Scheme 7. Bromination of hydride terminated Si-NCs with N-bromosuccinimide and its subsequent alkoxylation. Reproduced and adapted with permission from the Royal Chemical Society.[59]

Recently, numerous groups have explored the chloride surface of Si-NCs as a reactive platform for attaching substituted amines. Li et al. and Wang et al. demonstrated that attaching aryl amines bearing different substituents can influence the Si-NC photoluminescence maximum (Figure 6).[60,61] The origin of this luminescence remains in question, however solvatochromism demonstrated by our group is consistent with the emission arising from a charge-transfer state involving silicon oxynitrides. The PL from aminated surfaces are short-lived with excited-state lifetimes (ca. 5 ns) and exhibit very high quantum yields (ca. 75%).

Zhai et al. used chloride terminated Si-NCs for straightforward attachment of D-mannose and L-alanine to yield luminescent water-soluble particles (Figure 7).[62] This route provides a general method for attaching sugars and amino acids to Si-NCs. Uptake and PL emission of mannose- and alanine-functionalized Si-NCs in MCF-7 cells was also shown.

3. Si-NC/Polymer Hybrid Materials

Hybrids of functional polymers and semiconductor nanocrystals are attractive because the properties of the individual components may be tuned independently. Combining these complementary materials into a hybrid offers new systems that possess the properties of the components, as well as hybrid characteristics arising from the synergistic interactions between the nanomaterial and polymer. A variety of approaches for assembling polymers and quantum dots of binary (e.g., CdSe, InP, PbTe),[63] ternary (e.g., $CuInSe_2$, $CuInS_2$),[64] and quaternary (e.g., $Cu_2ZnSnSe_4$)[65] compound semiconductors have been established. In contrast, Si-NC/polymer hybrids remain in the early stages of development, partly because of limited availability of well-defined Si-NCs.

Physical blending of components provides a straightforward approach toward obtaining hybrids. This approach was employed by Liu et al., who combined hydride terminated Si-NCs with regio-regular poly-3-hexylthiophene (P3HT, a common and useful optoelectronic polymer) and explored the composite in prototype photovoltaic devices.[66] While promising, this procedure was plagued by particle aggregation that lead to non-uniform films and comparatively poor prototype device performance. To improve material homo-

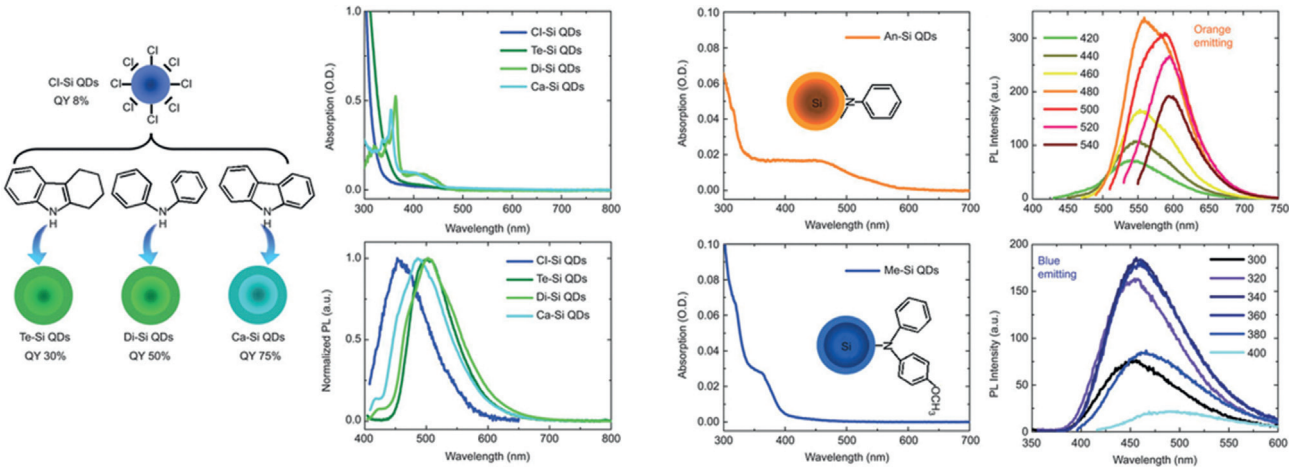


Figure 6. Absorption and emission spectra of Si-NCs functionalized with substituted amines. Reproduced and adapted with permission from the Nature publishing group.[61]

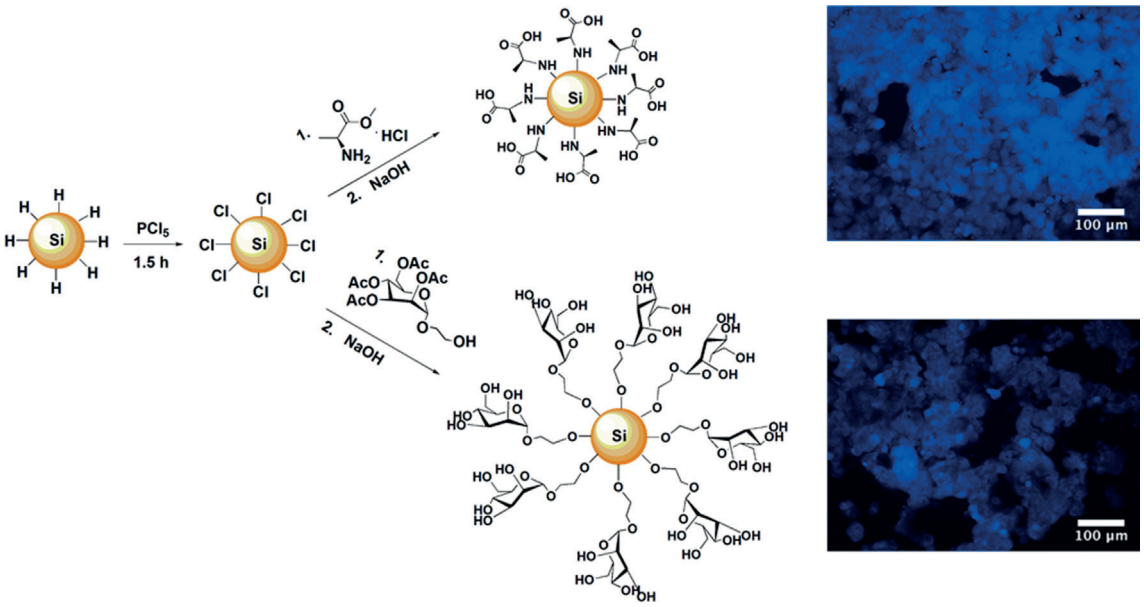


Figure 7. Synthesis of alanine and mannose functionalized Si-NCs and fluorescence images of MCF-7 cells incubated with Si-NCs bearing the corresponding functional groups. Adapted with permission from the Royal Chemical Society.[62]

geneity Mitra et al. employed an atmospheric-pressure microplasma technique to coat Si-NCs with PEDOT:PSS polymer (Figure 8a).[67] This provided a uniform polymer coating on the NCs and improved their stability, solvent dispersability (Figure 8b), and photoluminescence.

Drawing on work related to compound semiconductor quantum dots, Hessel et al. exploited non-covalent interactions; they reported preparation of Si-NC/poly(maleic anhydride) hybrids (Figure 9a).[68] Encapsulating alkyl terminated Si-NCs within this amphiphilic polymer shell made the particles water dispersible and suitable for in vivo biological imaging applications. They also demonstrated that the hybrid was luminescent (Figure 9b), stable over large pH ranges and ionic strengths, large enough to bypass the renal system, and small enough to remain in the circulatory system for extended periods. These properties made these hybrid nanomaterials attractive for biological applications.

While noncovalent interactions are clearly useful in the assembly of nanomaterial/polymer hybrids, these comparatively weak interactions can bring challenges associated with their long-term stability. Forming covalent linkages between the Si-NC and polymers provides one method for improving homogeneity, charge transport, and long-term stability. Yang et al. reported the "one-pot" synthesis of a Si-NC/polystyrene hybrid (Figure 10a) that is chemically resistant, photoluminescent, homogeneous, and solution processable.[69] The hybrid is believed to form by the thermally induced auto-initiated polymerization of styrene. Styrene radicals can abstract hydride from the Si surface leaving behind a silyl radical that reacts with free styrene molecules to yield

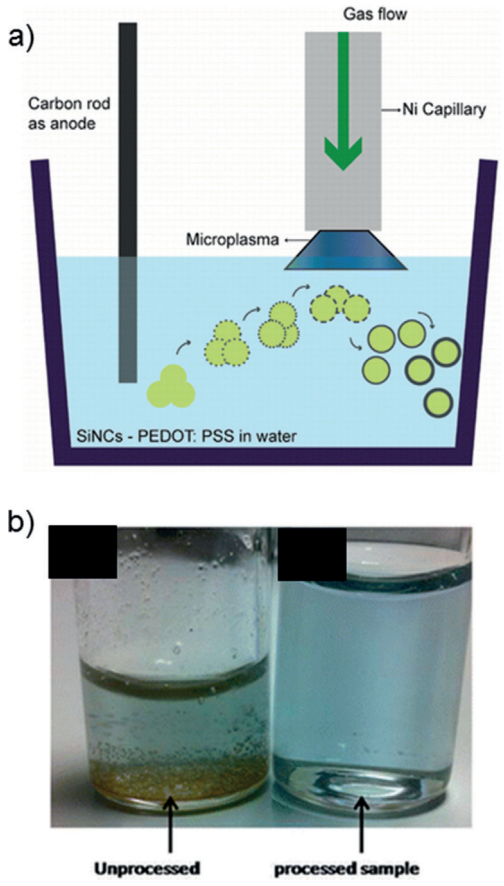


Figure 8. a) Schematic representation of the microplasma apparatus used to coat Si-NCs with PEDOT:PSS and b) photographs of Si-NCs in water-polymer solution before and after microplasma processing. Reproduced and adapted with permission from the American Chemical Society.[67]

polystyrene-functionalized Si-NCs. The researchers fabricated freestanding luminescent films, microfibers, and coated optical fibers using the Si-NC/polystyrene hybrid (Figure 10 b–d). Dung et al. showed a similarly prepared Si-NC/polystyrene hybrid was stable to 250 °C and was a useful charge-trapping material in prototype metal-insulator-semiconductor devices and thin-film field-effect transistors.[70] Choi et al. synthesized Si-NC/polystyrene hybrids with varying proportions of the NC and polymer components.[71] The refractive index of spin-coated films increased with the Si-NC concentration.

While simple hydrocarbon-based polymers (i.e., polystyrene) can be attached to the Si-NC surfaces using straightforward hydrosilylation, alternative grafting methods are required to access other functional polymers. Our group recently established a multistep surface-initiated group-transfer polymerization (SI-GTP) procedure for modifying Si-NCs. Polydiethylvinylphosphonate (PDEVP) embedded Si-NCs were synthesized as outlined in Scheme 8.[72] Initially the surfaces of hydride-terminated Si-NCs were modified with ethyleneglycol dimethacrylate (EGDM) using photoinduced hydrosilylation. This new surface served as an anchor for the catalyst (i.e., $Cp_2YCH_2Si(CH_3)_3$; Cp = cyclopentadienyl) that readily polymerizes diethylvinylphosphonate to yield Si-NCs embedded within PDEVP. The resulting material is soluble in water and luminescent (Figure 11 a). Importantly, the lower critical solution temperature (LCST) characteristic of the PDEVP was retained in the new hybrid (Figure 11 b,c).

Sato et al. reported the synthesis of luminescent, flexible, extendible, and transparent Si-NC/silicone polymer hybrids.[73] Silicone elastomer was directly bonded to the Si-NC surface via siloxane linkages. The luminescent properties of the hybrids were altered by changing the Si-NC size (Figure 12 a). This hybrid was molded to form a variety of shapes (Figure 12 b) and was photostable under a variety of conditions (e.g., pH, solvent polarity, and mechanical stress).

Höhlein et al. reported an alternative method for interfacing polymers with Si-NCs. They demonstrated surface-initiated reversible addition-fragmentation chain transfer (RAFT) polymerization on Si-NC surfaces with styrene, methyl methacrylate, hexyl acrylate, *N*-isopropylacrylamide, and 4-vinylbenzyl chloride to yield luminescent NC/polymer hybrids.[74] Initially hydride terminated Si-NCs were function-

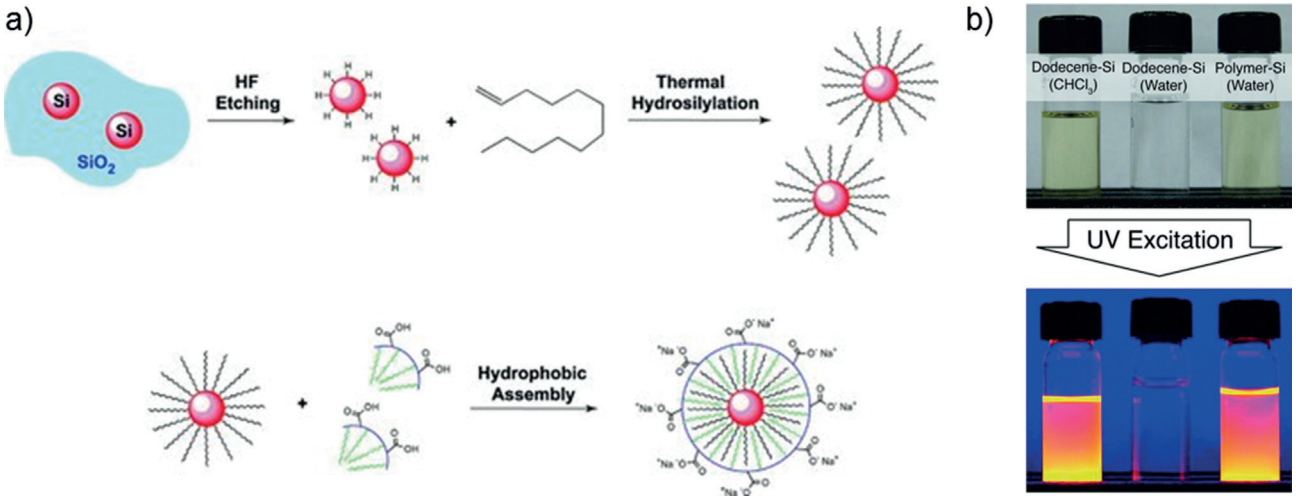


Figure 9. a) Preparation of a Si-NC/poly(maleic anhydride)-based hybrid. b) Photographs of vials containing Si-NC solutions under ambient light and when illuminated by UV (350 nm) light. Reproduced and adapted with permission from John Wiley and Sons.[68]

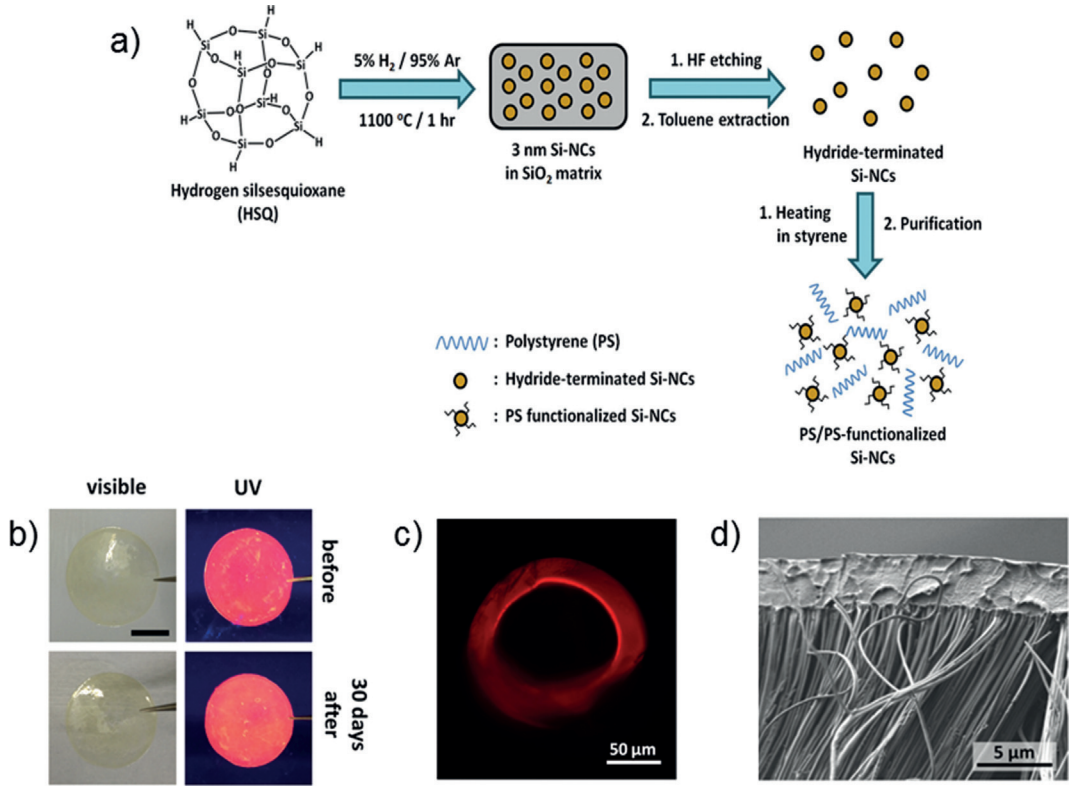
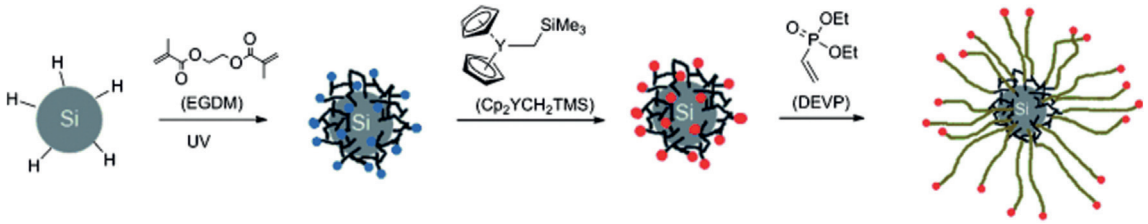


Figure 10. a) Synthesis of Si-NC/polystyrene hybrid; b) chemical stability of free-standing Si-NC/polystyrene thin film in saturated NaOH solution; c) PL image of optical fiber coated with Si-NC/polystyrene and d) SEM image of Si-NC/polystyrene microfibers after removal of the porous alumina template. Reproduced and adapted with permission from John Wiley and Sons.[69]



Scheme 8. Synthesis of PDEVP-functionalized Si-NCs. Reproduced and adapted with permission from John Wiley and Sons.[72]

alized with chloro(vinyl)dimethylsilane, which was further modified with 6-hydroxylhexyl 3-(methylthio)-2-phenyl-3-thioxopropanoate (HMT). Polymerization was performed upon addition of a monomer and ethyl-3-(methylthio)-2-phenyl-3-thioxopropanoate (EMPT) mixture to the Si-NC/HMT system (Scheme 9). The process exploited living polymerization and yielded particles with narrow size distributions. The polymer grafted Si-NCs showed higher stability in KOH solution compared to equivalent alkyl functionalized nanoparticles.

4. Applications

Si-NCs have garnered much interest as potential competitors and replacements for conventional Group II–VI and III–V quantum dots. Si-NCs also offer the added advantage of being compatible with common electronics platforms and have low toxicity.[75] Hence, they are attractive materials for electronics and biological applications. Recently, Reviews related to the prototype investigations of Si-NCs in biological, magnetic resonance imaging, and photovoltaic applications have appeared and these topics will not be discussed herein.[24,76–79] Si-NCs have also been investigated as active materials in battery electrodes, sensors, and diodes, as well as catalysts. The following Section provides a perspective on these uses of Si-NCs.

PL-based sensors are attractive because of their high sensitivity, rapid response, portability, limited infrastructure requirements, and low cost.[80] Quantum dots are preferred luminophores because of their stable, tunable emission properties. Cd-based quantum dots were demonstrated as PL sensors to detect nitroaromatic explosives.[81] Our group developed disposable, paper-based sensors using dodecyl-functionalized Si-NCs to detect a series of nitroaromatic, nitroamine, and nitrate ester containing explosives.[82] The

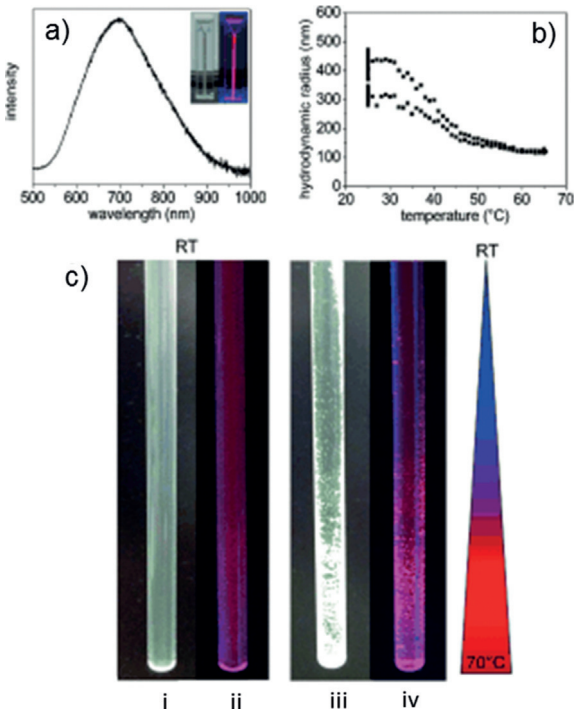


Figure 11. a) PL spectrum of PDEVP grafted Si-NCs at $\lambda_{ex} = 365$ nm (inset: PDEVP/Si-NC solutions under ambient light and UV illumination); b) dynamic light scattering (DLS) measurement of the LCST effect of PDEVP grafted Si-NCs in water and c) dispersion of PDEVP grafted Si-NCs in water at room temperature (i–ii) and after heating the bottom part of the tube to 70 °C for several hours (iii–iv). Reproduced and adapted with permission from John Wiley and Sons.[72]

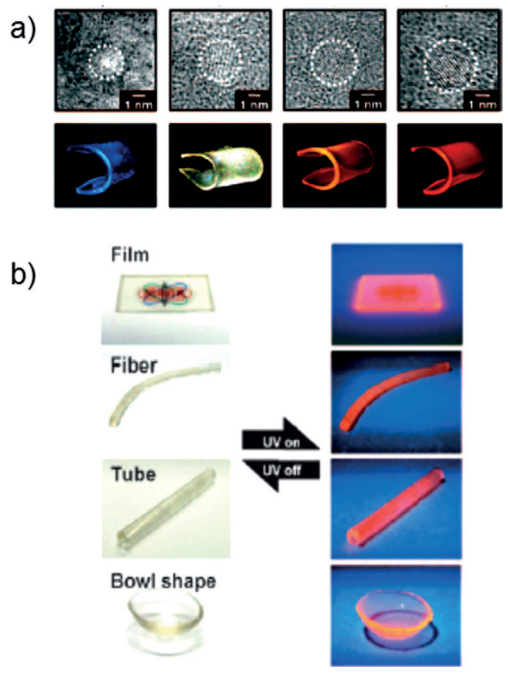
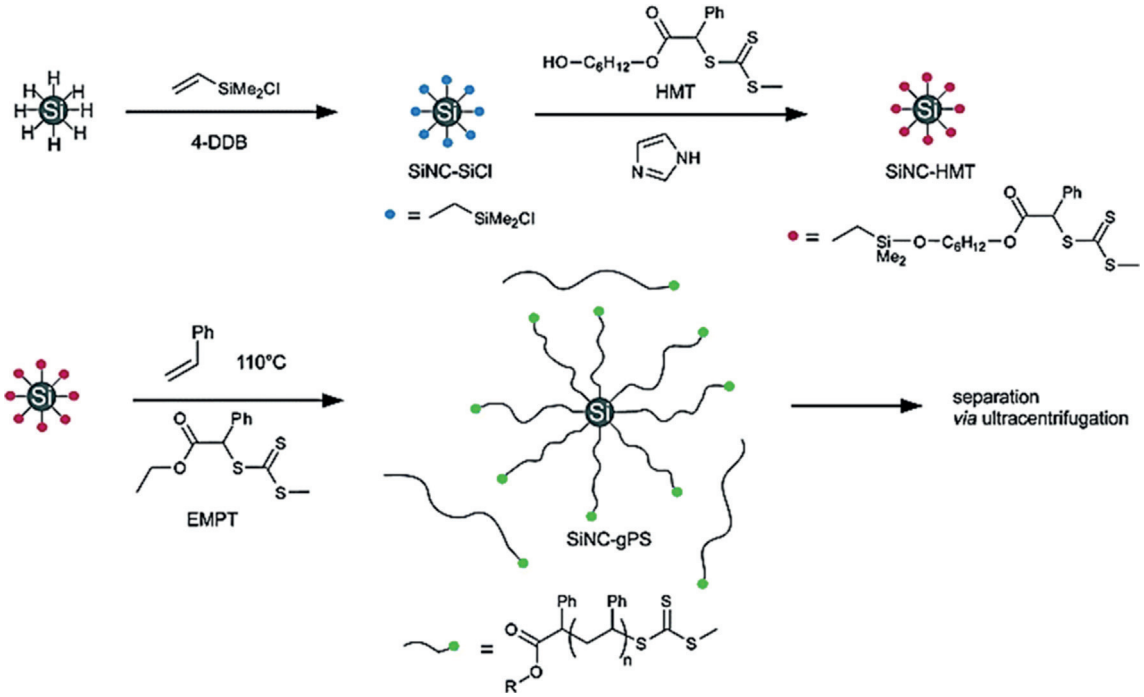


Figure 12. a) TEM micrographs and photographs of Si-NC/silicone elastomer hybrid material emitting different colors under UV illumination and b) images of Si-NC/silicone elastomer drawn into various shapes, viewed under ambient and UV light. Reproduced and adapted with permission from John Wiley and Sons.[73]

paper-based sensor was prepared by dip-coating filter paper in a concentrated toluene solution of Si-NCs. Quenching of the PL of the resulting NC impregnated paper sensors upon exposure to solutions of mononitrotoluene (MNT), dinitrotoluene (DNT), trinitrotoluene (TNT), 1,3,5-trinitroperhy-



Scheme 9. Surface-initiated RAFT polymerization to yield polystyrene-functionalized Si-NCs. Reproduced and adapted with permission from the Royal Chemical Society.[74]

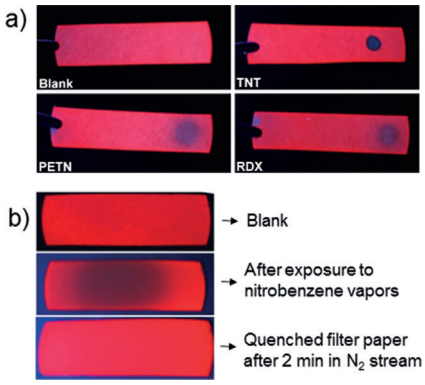
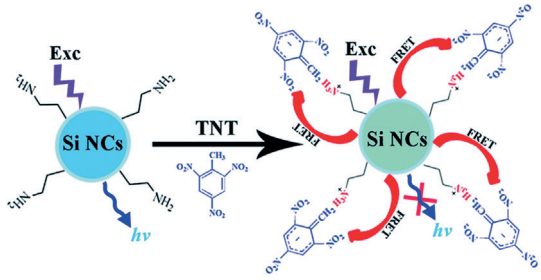


Figure 13. a) Photographs of paper-based sensors under UV illumination upon exposure to the explosives indicated. b) Reversible quenching of Si-NC PL in presence of nitrobenzene vapors. Reproduced and adapted with permission from the Royal Chemical Society.[82]

dro-1,3,5-triazine (RDX), and pentaerythritol tetranitrate (PETN) could be detected visually (Figure 13a). The PL was also quenched upon exposure to solid nitroaromatic residues or nitroaromatic vapors. The quenching was reversible for volatile compounds (Figure 13b). Investigations indicate the quenching of PL arises from electron transfer from the Si-NC to the π^* orbitals of the nitro-containing compounds. These paper-based sensors allowed detection of nitroaromatics at nanogram levels in the solid and vapor phases.

Ban et al. prepared water-dispersible amino-capped Si-NCs as PL probes for the detection of TNT in aqueous media.[83] In the absence of conclusive evidence, they proposed that TNT formed a complex with surface amine groups through strong donor/acceptor interactions and that the resulting TNT/amine complex quenched the Si-NC PL via Förster resonance energy transfer (FRET; Scheme 10). They



Scheme 10. Schematic representation of luminescence quenching by TNT of amine capped Si-NCs via the FRET mechanism. Reproduced and adapted with permission from the Royal Chemical Society.[83]

further proposed that the quenching efficiencies depended on the binding affinities of nitro-analytes on the Si-NC surface and the electron-accepting ability of the nitro-containing compounds. Similarly, Zhang et al. showed selective dopamine detection using luminescent Si-NCs in aqueous medium at very low concentrations of the analyte dopamine (ca. nM).[84] They also showed that other common molecules in a living system did not interfere with dopamine making the method selective (Figure 14).

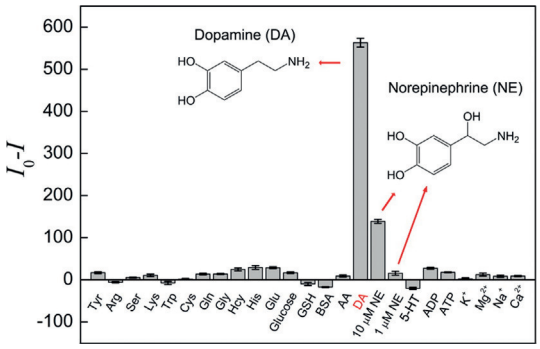


Figure 14. Fluorescence responses of Si-NCs in the presence of various analytes. Reproduced and adapted with permission from the American Chemical Society.[84]

Properties such as tunable luminescence and straightforward fabrication, among others, make quantum dots attractive emissive materials for light-emitting diode (LED) applications. Generally, the quantum dots are placed between layers of organic polymers that serve as charge-transport media. Hybrid nanocrystal–organic LEDs of this type have been fabricated using Si-NCs. A typical device structure is shown in Figure 15.

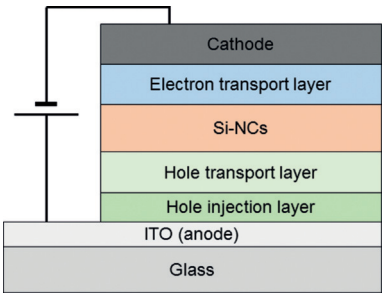


Figure 15. Typical device architecture of a hybrid Si-NC organic LED.

Cheng et al. reported infrared electroluminescence at 868 nm from a hybrid Si-NC/organic LED with an external quantum efficiency of 0.6%.[85] The Si-NCs were prepared by decomposition of silane gas using non-thermal plasma and were functionalized with dodecyl groups. The researchers observed a direct correlation between emissive-layer (i.e. the Si-NC layer) thickness and external quantum efficiencies of the device. The same research group later reported hybrid NC/organic LEDs consisting of 3 and 5 nm dodecyl functionalized Si-NCs that showed external quantum efficiencies up to 8.6%.[86] They attributed the increase in the efficiencies to an increase in the energy gap of hole- and electron-transport layers that provided better confinement of both charge carriers and excitons in the NC emissive layer.

Similarly, Maier-Flaig et al. reported red/orange electroluminescence from hybrid Si-NC/organic LEDs consisting of allylbenzene-functionalized Si-NCs up to maximum external quantum efficiencies of 1.1%; they propose that Si-NC size polydispersity leads to rapid degradation of the LEDs causing short circuits.[87] They also observed inhomogeneous emissions across the device that were reasonably attributed to

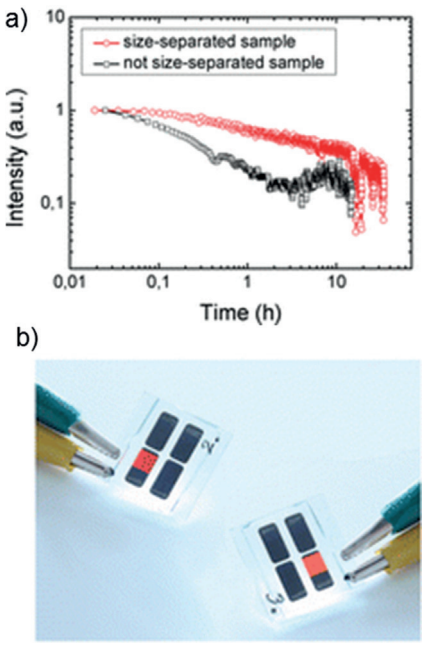


Figure 16. a) Electroluminescence intensity of polydisperse and size-separated Si-NCs over time at a constant current of 1.6 mA cm^{-2} and b) photographs of hybrid Si-NC/organic LEDs showing red and orange electroluminescence. Reproduced and adapted with permission from the American Chemical Society.[87]

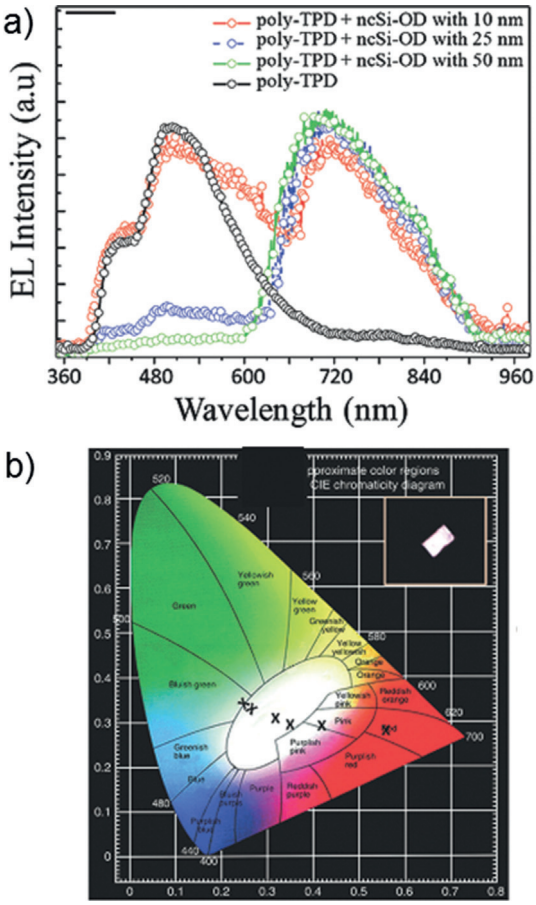


Figure 17. a) Electroluminescence spectra with and without the Si-NCs at various thicknesses and b) CIE diagram showing the chromaticity coordinates of various devices (inset: Photograph of a white LED). Reproduced and adapted with permission from John Wiley and Sons.[88]

impurities and defects arising from particles of various sizes. Upon purification of Si-NCs using size-selective precipitation, the researchers fabricated brighter, more stable (Figure 16a) and homogeneously emissive devices (Figure 16b).

Ghosh et al. reported white-light emission from hybrid Si-NC/organic LEDs by combining emission from Si-NCs and a luminescent polymer in the device active layer.[88] The researchers combined the red emission from octadecyl functionalized Si-NCs and blue-green emission from poly-TPD to yield white light (Figure 17) with external quantum efficiencies ranging from 0.033–0.36%.

Lin et al. recently demonstrated the fabrication of Si-NC-based photodiodes.[89] Thin films of allyl disulfide functionalized Si-NCs showed enhanced conductivity compared to alkyl-functionalized particles. They proposed the lone-pair electrons on the disulfide structural unit facilitated the charge transport process. Photodiodes were fabricated from the Si-NC ink by spin coating on ITO glass. An electron-blocking layer (PEDOT:PSS) was added between the ITO and Si-NC layers to improve the charge separation in the device (Figure 18a). The device showed UV responsivity (Figure 18b) with a peak photoresponse of 0.02 AW^{-1}, thus making it applicable for UV detection.

The same research group also showed that Si nanoparticles can aid in hydrogen generation from water in the absence of any external stimulants (e.g., light, heat, or electricity). Si nanoparticles (ca. 10 nm) generated hydrogen gas at an accelerated rate by splitting water:[90] the rate was found to be 1000 times faster than bulk Si, 150 times that of 100 nm Si particles, and six times faster than metal formulations, thus making it a potential material for hydrogen generation. Peng et al. showed that Si-NCs prepared via the high-energy ball milling process can be used to catalyze the reduction of carbon dioxide.[91] Under illumination, Si-NCs with no surface groups photochemically reduced CO_2 to formaldehyde. However, no reduction products were observed with alkyl-passivated Si-NCs. El-Demellawi et al. demonstrated that Si-NCs can catalyze the dehydrogenation of secondary alcohols to yield ketones and hydrogen.[92] The reactions proceeded at room temperature, without energy input. These observations are of great practical importance because these solvents are routinely used to store and process Si-NCs. Our group demonstrated, that chloride-terminated Si-NCs can catalyze the polymerization of hexylthiophene Grignard reagents to form P3HT (Figure 19).[93] Chloride termination was achieved by reacting hydride terminated Si-NCs with PCl_5 (Figure 5). Polymerization was achieved at room temperature by addition of the Grignard reagent to the chloride-terminated Si-NCs and is believed to proceed similar to Lewis acid mediated polymerization reactions.

Nanostructured Si has gained a lot of attention as a high-capacity anode material for Li-ion batteries. Si exhibits a low working potential and high theoretical charge capacity (4200 mAh g^{-1}), but suffers from structural damage during

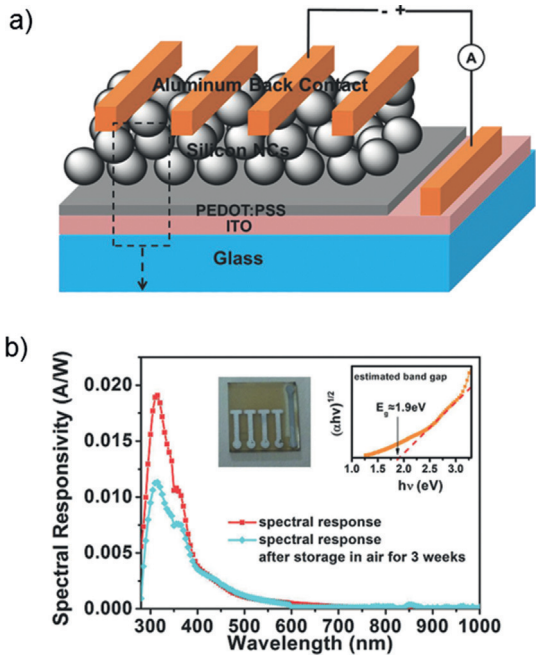


Figure 18. a) Device architecture of a Si-NC based photodiode and b) spectral responsivity of the device to illumination. (Inset: photograph of the Si-NC photodiode and band gap estimation using the Tauc method). Reproduced and adapted with permission from John Wiley and Sons.[89]

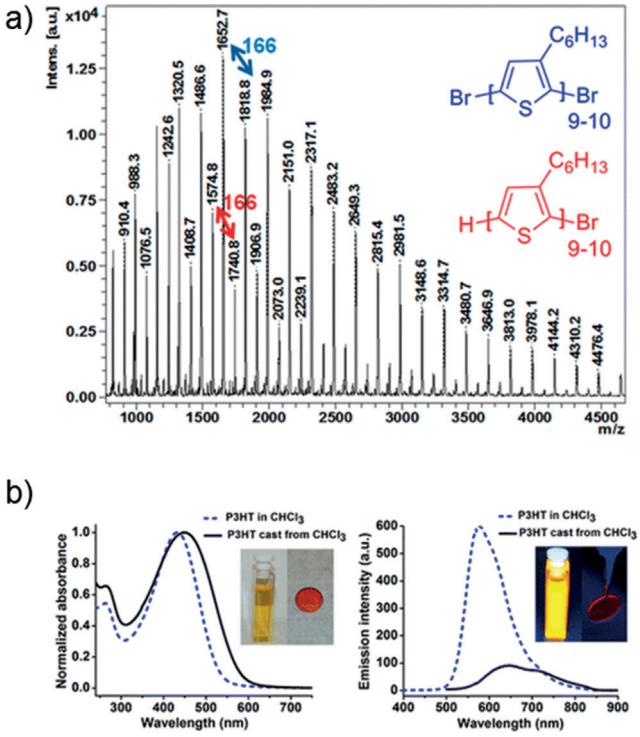
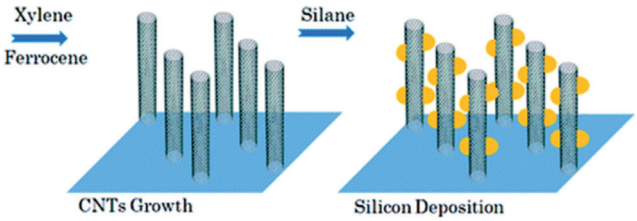


Figure 19. a) MALDI-TOF mass spectrum of P3HT obtained in the presence of chloride terminated Si-NCs and b) UV/Vis absorption (left) and emission (right) spectra of P3HT. Inset: P3HT in chloroform and as a solid film under ambient light (left) and UV illumination (right). Reproduced and adapted with permission from the American Chemical Society.[93]

cycling due to large volume changes (up to 400%).[94] Si-NCs decrease degradation issues because of their increased surface to volume ratio. Kim et al. demonstrated that battery performance is significantly influenced by Si-NC size.[95] They prepared 5, 10, and 20 nm Si-NCs by reduction of $SiCl_4$ in the presence of different surfactants. While smaller Si-NCs exhibited higher charge capacity (ca. 3000 mAh g^{-1} over 40 cycles) compared to larger particles (20 nm), they suffered from lower Coulombic efficiency and capacity retention. However, this obstacle was addressed by encapsulating the smaller Si-NCs within a carbon shell. The researchers concluded that the critical Si-NC size for an efficient battery anode-material was 10 nm. Si nanomaterials have been combined with carbon composites to create hybrids that can overcome common Si-based shortcomings, such as structural degradation, electrical isolation, and formation of an unstable interface.[96] Among the carbon materials employed, graphene is attractive because it can improve carrier transport and mitigates volume changes associated with Li ion uptake.[97] Recently, Ko et al. reported a hybrid material consisting of 5–10 nm amorphous Si nanoparticles and graphene for Li-ion batteries.[98] The material exhibited exquisite elastic properties during the volume change, a capacity of up to 2858 mAh g^{-1}, 92.5% Coulombic efficiency, and good cycling stability. Wang et al. prepared a Si-NC/carbon nanotube hybrid upon decomposition of silane gas on vertically aligned carbon nanotubes (Scheme 11).[99] These structures exhibited a highly reversible capacity of 2000 mAh g^{-1} over 25 cycles.



Scheme 11. Schematic of the formation of Si-NC/carbon nanotube hybrids for Li-ion battery application. Reproduced and adapted with permission from the American Chemical Society.[99]

Liu et al. designed a "yolk–shell" type of Li-ion anode material by introducing a void space between the Si nanoparticle and carbon layer.[100] The void space compensates for expansion of the Si particle without the disruption of the carbon shell or the interface. Such structures showed capacity up to 2833 mAh g^{-1}, high cycle life (ca. 1000), and Coulombic efficiencies of 99.8%. Other reports on Si nanomaterials based Li-ion battery anodes have been reviewed and are not detailed here.[101]

5. Conclusions and Outlook

In this Review, we have outlined recent important developments related to Si-NC surface chemistry and their

influence on stability, solubility, mechanical, and optoelectronic properties. While hydrosilylation has long been the "go to" reaction for derivatizing Si-NC surfaces, new insights, such as surface-initiated oligomerization, slower reactivity of photochemical hydrosilylation, and borane-catalyzed hydrosilylation, have recently been demonstrated. In addition, new reactivity has emerged for Si hydride and Si halogen surfaces that enable the attachment of ligands with versatile functional groups and enable reactions at lower temperatures. Si-NC/polymer hybrid materials have also been prepared that show synergistic properties, the processable polymers allows the materials to be formed into various morphologies. Polymerization is carried out on the Si-NC surface using radical initiators, RAFT, or surface-initiated group-transfer polymerization methods. Incorporation of polymers onto Si-NC surfaces further expands the field of accessible functional materials. Tunable surface chemistry enables Si-NCs and the hybrids to be further employed in diodes, sensors, catalysis, bioimaging, and photovoltaics, among others.

Readily available, sustainable, and non-toxic, Si-NCs are amenable to commercial-scale applications. While not as well-known as their compound semiconductor counterparts, Si-NCs offer a host of exciting opportunities for both pure and applied research. While proof-of-concept devices highlighting this promise have been fabricated, significant technical advances are required before these materials can be commercialized. Many questions remain unaddressed, including: How to achieve completely oxide free Si-NC surfaces with smaller ligands? How can LED external quantum efficiencies be increased in Si-NC-based devices? What specific emitting species and electronic transitions lead to surface-defect-based emissions? Silicon may be the "grand-old semiconductor", however, it is a relative newcomer to the field of quantum dots and it offers numerous new opportunities to researchers in many fields.

Abbreviations

ATR-FTIR	attenuated total reflectance Fourier transfer infrared spectroscopy
a.u.	arbitrary units
CIE	International Commission on Illumination (Commission Internationale de l'Éclairage)
DNT	dinitrotoluene
ITO	indium tin oxide
LED	light-emitting diode
MALDI	Matrix assisted laserdesorption/ionization
MNT	mononitrotoluene
NALDI	nanostructure assisted laser desorption/ionization
NC	nanocrystal
P3HT	poly-3-hexyl thiophene
PEDOT:PSS	poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate)
PETN	Pentaerythritol tetranitrate
PL	photoluminescence
Poly-TPD	Poly(4-butylphenyl diphenylamine)
p-Si	porous silicon
PV	photovoltaic
RAFT	reversible addition fragment transfer polymerization
RDX	1,3,5-Trinitroperhydro-1,3,5-triazine
SI-GTP	surface-initiated group-transfer polymerization
Si	silicon
TNT	trinitrotoluene

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