Chapter 2
Silicon Nanostructures

Abstract  Functional nanomaterials play fundamental roles in the development of nanotechnology, serving as novel and powerful tools for both basic studies and practical applications. Silicon nanomaterials are an important type of nanomaterials, exhibiting unique optical, electronic, or/and mechanical properties. The fast development of silicon nanomaterials with well-defined structures and required functionalities has vastly promoted the advancement of silicon nanotechnology. Silicon nanoparticles (SiNPs) and silicon nanowires (SiNWs) are well known as the most important zero- and one-dimensional silicon nanostructures. In the past three decades, scientists have made great strides in developing a great deal of fabrication techniques to prepare SiNPs and SiNWs. In particular, solution-phase reduction, electrochemical etching and microwave-assisted synthesis, etc., have been well developed for the production of SiNPs. On the other hand, several well-studied strategies (e.g., chemical vapor deposition (CVD), oxide-assisted growth (OAG), electroless etching, etc.) are highly efficacious for the synthesis of SiNWs. In this chapter, we give an introduction to these classic synthetic methods in a detailed way, and discuss the prospect of the design and fabrication of functional silicon nanostructures.

Keywords  Silicon nanostructures · Nanotechnology · Synthetic methods · Surface modification · Silicon nanoparticles · Silicon nanowires · Silicon nanohybrids

Increasingly rapid advancement of nanotechnology has fueled a continual and urgent investigation for fabricating functional nanomaterials [1, 2]. Scientists have done elegant work on rational design of nanomaterials with well-defined structures [3–6]. To date, a variety of nanomaterials (e.g., silver/gold nanoparticles, magnetic nanoparticles, fluorescent semiconductor quantum dots, carbon nanodots/nanotubes, graphene, etc.) have been well established, greatly promoting the development of chemical, physical, and biological fields from basic research to practical applications.

Silicon material is the leading semiconductor material and dominates current industry. Silicon nanomaterials, known as one of the most important types of nanomaterials, feature a number of unique merits, such as excellent...
electronic/mechanical/optical properties, huge surface-to-volume ratios, and facile surface modification [7–10]. More importantly, the renowned biocompatibility of silicon (e.g., silicon naturally exists in human as a common trace element) leads to the promising prospect of silicon nanomaterials-based applications, including solar cells, sensors, catalysis, bioimaging, etc. To meet the increasing requirement of these applications, silicon nanomaterials with controllable structures and required functionality remain in great demand.

This chapter mainly introduces representative strategies for preparation of the most important zero- and one-dimensional silicon nanostructures, i.e., silicon nanoparticles (SiNPs) and silicon nanowires (SiNWs). Typically, several dominant synthetic methods for the preparation and surface modification of SiNPs are illustrated in Sect. 2.1. In Sect. 2.2, we introduce the classic strategies for synthesis of SiNWs, and further discuss the pros and cons of these methods. We then give a brief introduction to silicon-based nanohybrids in Sect. 2.3, and finally make a summary of this chapter in Sect. 2.4.

2.1 Fluorescent Silicon Nanoparticles

Bulk silicon with an indirect band gap basically features poor optical properties [11]. However, when the size of silicon particles is reduced to nanoscale (generally less than 5 nm), the overlap of the electron and hole wave functions is distinctly increased, leading to dramatic enhancement of recombination rates of electrons and holes. As a result, such small-sized SiNPs exhibit relatively strong fluorescence, showing the prospect of long-awaited optical applications [12, 13]. Therefore, intense studies have been intrigued to develop fluorescent SiNPs and their optics-relative applications since the first observation of porous silicon-based fluorescence [14, 15].

In recent two decades, many synthetic strategies (e.g., solution-phase reduction [16, 17], microemulsion [18, 19], sonochemical synthesis [20], mechanochemical synthesis [21], laser ablation [22], plasma-assisted aerosol precipitation [23–25], electrochemical etching [26–30], and microwave-assisted synthesis [31–34], etc.) have been developed for the preparation of SiNPs. For the solution-phase reduction synthesis proposed by Kauzlarich and coworkers, silicon halides (e.g., SiCl4) are reduced in organic solution (e.g., ethylene glycol dimethyl ether) to produce silicon nanocrystalline under mild conditions [16]. Moreover, surface of the prepared SiNPs is readily modified, offering possibility to modify the SiNPs to meet various requirements [16]. Plasma-assisted aerosol precipitation is considered as another established method for production of SiNPs with high efficiency and yield [23–25]. In this synthetic strategy, luminescent SiNPs between 2 and 8 nm can be rapidly synthesized via a single-step non-thermal plasma process [24]. In 2009, Lee and coworkers developed a polyoxometalate (POMs)-assisted electrochemical etching method for synthesizing multi-color luminescent SiNPs [27]. In this system, graphite and silicon wafer serve as anode and cathode in an electrochemical
cell, respectively; besides, H$_3$PMo$_{12}$O$_{40}$ (POM) and H$_2$O$_2$ (POM + H$_2$O$_2$ = HPOM) are used as catalysts (Fig. 2.1a). Notably, the sizes of SiNPs are readily controllable via adjustment of current density, vastly facilitating the production of multi-color luminescent SiNPs with different sizes (Fig. 2.1b). Figure 2.1c displays SiNPs with sizes ranging from ~1 to ~4 nm, which feature wide-ranging emission spectra covering 450–740 nm. It is worthwhile to point out, in comparison to strong fluorescence of direct-band-gap semiconductors (e.g., CdTe and CdTe/CdS/ZnS QDs with high quantum yield (QY) of 60–80 %, [6, 7]), most of the prepared fluorescent SiNPs show relatively low QY (often lower than 20 %), which is possibly due to surface oxidation [35–39]. In 2006, Kortshagen et al. developed a plasma-assisted synthesis method to efficiently protect surface oxidation of SiNPs, yielding the highly luminescent SiNPs with a high QY value larger than 60 % [23]. Very recently, Li, He and coworkers reported a class of SiNPs with ultrabright photoluminescence, whose quantum yield was remarkably as high as 75 %. Specifically, the SiNPs were synthesized by the solution-reduction method, followed by modifying with diphenylamine (di) and carbazole (ca). After such a surface modification, the optical properties of SiNPs were significantly changed, e.g., the maximum emission peak of carbazole-modified SiNPs (ca-SiNPs) shifted from 405 to 480 nm, and more significantly, the photoluminescence quantum yield (PLQY) was remarkably enhanced up to 75 % [40].
It is worth pointing out that, SiNPs prepared via the above-mentioned methods often possess poor aqueous dispersibility since their surface is covered by hydrophobic ligands, which severely hampers their biological and biomedical applications [41, 42]. Tremendous efforts have been made to improve aqueous dispersibility of the hydrophobic SiNPs and develop new synthetic strategies for direct preparation of hydrophilic SiNPs. In the former case, several kind of hydrophilic species (e.g., acrylic acid and allylamine) are employed to modify SiNPs surface, effectively improving the water dispersibility of the SiNPs [43–45]. For example, in 2004, Ruckenstein et al. grafted the red-emitting SiNPs with hydrophilic poly(acrylic acid) under UV irradiation, producing poly(acrylic acid)-modified SiNPs with good aqueous dispersibility [43]. Thereafter, Tilley and coworkers reported the synthesis of blue-emitting SiNPs with good aqueous dispersibility due to surface-covered water-soluble allylamine molecules [18, 45]. Swihart’s group functionalized multi-color fluorescent SiNPs with acrylic acid to render them hydrophilic [44]. While these resultant SiNPs are water-dispersible, their fluorescence is often severely quenched when pH changed, which is not suitable for applications in complicated biological environments.

To improve pH stability of the SiNPs, He et al. and Swihart et al. independently reported polymer-coated or micelle-encapsulated water-dispersible SiNPs featuring robust pH stability [29, 30, 46]. Typically, the micelle-encapsulated SiNPs maintained stable fluorescence in acidic-to-basic pH environments (pH 2–12). However, the QY value of such micelle-encapsulated SiNPs reduced to 2–4 % from ~17 % of pure SiNPs, since SiNPs surface was deteriorated during micelle encapsulation procedure [46]. In the case of polymer-coated SiNPs, different SiNPs were linked together by polymer chains under light irradiation, producing silicon nanospheres (SiNSs) containing tens to hundreds of SiNPs [29]. Figure 2.2a presents typical TEM images showing that the prepared nanospheres exhibit spherical structure with controllable diameters of approximately 59, 121, and 207 nm. The high-resolution TEM images (Fig. 2.2b) reveal the SiNP inside the nanosphere have the characteristic silicon nanocrystal lattice and high crystallinity. Notably, the authors demonstrated that the optical properties of the nanospheres were improved (Fig. 2.2c), whose quantum yield reached 20–25 %. On the basis of which, the same authors further introduced a kind of water-dispersed oxidized SiNSs (O-SiNSs) via thermal oxidation of the precursor SiNSs [30]. Significantly, in addition to strong fluorescence, the prepared O-SiNSs was ultrahighly stable under high-power UN irradiation (Fig. 2.2d) and in acidic-to-basic environments covering pHs 2–12 (Fig. 2.2e).

It is worth pointing out that, despite distinctly improved pH stability, the polymer-coated or micelle-encapsulated SiNPs are relatively not suitable for bioapplication due to relatively large sizes (50–200 nm) [29, 30, 46] (recent reports reveal that small-sized (<10 nm) nanoparticles are more readily to be excluded via renal clearance [47, 48]). Consequently, small-sized, fluorescent, and water-dispersible SiNPs are required for broad bioapplications. Recently, He’s group presented a microwave-assisted one-pot method for synthesizing water-dispersible SiNPs using SiNWs and glutaric acid as reaction precursors [31]. In
this strategy, microwave dielectric heating was utilized to take advantage of its rapid temperature elevation, homogenous heating and high reaction selectivity. Notably, the prepared SiNPs featured excellent aqueous dispersibility, small sizes (\(\sim 4\) nm), robust pH- (pHs 1–10) and photo-stability, and strong fluorescence (\(\sim 15–20\) %) (Fig. 2.3). Thereafter, they further employed hydrophilic proteins (e.g., goat anti-mouse immunoglobulin) as novel ligands to prepare fluorescent SiNPs [33]. Significantly, the prepared SiNPs simultaneously possessed good aqueous dispersibility and biospecific properties owning to plenty of surface-covered protein ligands. Therefore, the as-prepared fluorescent SiNPs with biospecific properties was efficacious for immunofluorescent cellular targeting.

For all the above “top-down” strategies, two independent procedures are often required, that is, hydrophobic SiNPs are first prepared using large-size silicon source (e.g., crystalline Si particles, SiOx powders, bulk silicon, or SiNWs, etc.), followed by surface modification with hydrophilic ligands, which nevertheless involves relatively complicated and time-consuming procedures and sometimes degrades the optical properties of SiNPs. More recently, He, Lee, and coworkers developed a facile “bottom-up” strategy for preparing fluorescent water-dispersible SiNPs by using silicon-based organic molecules (e.g., 3-(aminopropyl) trimethoxysilane, \(C_6H_{17}NO_3Si\)) as the reaction precursor (Fig. 2.4) [34]. The highly luminescent (PLQY: 20–25 %), water-dispersible and ultrasmall (diameter: 2.1 Fluorescent Silicon Nanoparticles 23

Fig. 2.2 a TEM images of three kinds of SiNWs with sizes of \(\sim 60\) nm (left), 120 nm (middle), and 200 nm (right). b HRTEM image of a single SiNP inside the prepared SiNSs. c Comparison of Fluorescent intensities of the resultant SiNSs and pure SiNPs. a–c Reproduced from ref. [29] by permission of John Wiley & Sons Inc. d Temporal evolution of photoluminescence intensity of FITC, II/VI QDs, the prepared SiNSs, and O-SiNSs under long-term UV irradiation or e various pH values. d–e Reprinted with permission from Ref. [30]. Copyright 2009 American Chemical Society
2.2 Silicon Nanowires

SiNWs are regarded as the most important one-dimensional silicon nanostructure, and have obtained giant attentions thus far [49, 50]. Through the past 50-year development, significant progress has been achieved to fabricate SiNWs with controlled morphologies and properties.

As early as 1957, Treuting et al. reported the first preparation of Si whiskers with \( <111> \) orientation, or filamentary Si crystals with macroscopic dimensions [51]. Thereafter, Wagner and Ellis performed the illuminating work and established the vapor-liquid-solid (VLS) mechanism of the Si whisker growth [52]. These pioneer studies open exciting avenues for fabrication of SiNWs. The second
phase in silicon-wire studies were launched in the mid 1990s triggered by development in microelectronics. In 1998, Lieber’s [53] and Lee’s groups [54] independently reported the strategy of VLS growth assisted by laser ablation, which is especially suitable for large-quantity preparation of single-crystal SiNWs with controllable diameters and lengths (diameter: 6–20 nm, lengths: 1–30 μm). In general, the VLS process involves four steps as follows (Fig. 2.5) [55], silicon precursor is first decomposed using metal catalysts. The liquid alloy made of silicon and metal is formed in the second step. Afterwards, the resultant silicon-metal alloy is diffused with silicon. In the final step, Si supersaturation leads to

Fig. 2.4 a Schematic mode of the “bottom-up” strategy. b TEM/HRTEM, c size distribution, and d absorption and photoluminescence (UV–PL) spectra of the SiNPs prepared through microwave-assisted strategy. Inset in (b) presents the enlarged HRTEM image of a single SiNP. e Temporal evolution of fluorescence intensity of FITC, CdTe and CdSe/ZnS QDs, and the as-prepared SiNPs under long-term UV irradiation. f Photos of reaction precursors and the prepared SiNPs aqueous solution irradiated by UV light (left) or ambient light (right). g–k Pictures of fours aqueous samples (i.e., FITC, CdTe and CdSe/ZnS QDs, and SiNPs), persistently irradiated by UV lamp (365 nm, 450 W) for 180 min. Reprinted with permission from Ref. [34]. Copyright 2013 American Chemical Society
nucleation at the liquid/solid interface and production of SiNWs. Since then, a number of approaches have been developed to synthesize SiNPs, which can be categorized as two typical types of growth, that is, the bottom-up or top-down growth of SiNWs. For the former strategy, SiNWs growth is triggered by an assembly process joining ultrasmall Si atoms, such as metal-catalyzed VLS growth [52, 56, 57], oxide-assisted growth (OAG) [49, 58], supercritical-fluid-based and solution-based growth [59–62], laser ablation [63, 64], and thermal evaporation with catalyst [65, 66]. In contrary, for the top-down approaches (e.g., electron beam lithography (EBL), reaction ion etching (RIE), and metal-catalyzed electroless etching, etc.), large-sized bulk silicon precursor is employed for synthesizing SiNWs via lithography and etching [67–72]. Several representative strategies will be introduced in detail in the following pages.

2.2.1 Chemical Vapor Deposition

Chemical vapor deposition (CVD) is another established strategy especially suitable for preparing vertically aligned SiNWs with high aspect ratio. Metal catalyst (e.g., gold) and gaseous silicon reactants (e.g., silane, SiH₄, disilane, Si₂H₆, silicon dichloride, SiH₂Cl₂, or silicon tetrachloride, SiCl₄, etc.) are generally used in the CVD growth. Different reaction temperatures are required to produce SiNWs when the silicon precursors are varied because of their distinct chemical stability. For example, the temperature ranging from 800 to 1000 °C is often required for SiNWs growth by using SiCl₄ as silicon precursor. In terms of silane-based silicon precursor, the growth temperature reduces to 400–600 °C [73, 74].

In 2004, Lieber and coworkers employed gold nanoclusters and silane (SiH₄), serving as catalysts and precursors, respectively, to produce ~3 nm SiNWs with
undetectable amorphous oxide [75]. In this case, hydrogen was utilized since it could passivate the nanowire surface and reduce surface roughness. In 2005, Yang and coworkers used SiCl$_4$ and gold colloids as the precursor and catalyst, respectively, for SiNWs growth under 800–850 °C in the VLS-CVD process [76]. In this method, the gold colloids were capable of defining the size and position of the SiNWs. Notably, the oxide layer on the Si surface could be readily removed by gaseous HCl, which was the byproduct SiCl$_4$ decomposition in H$_2$, facilitating homoepitaxial growth of SiNWs and production of the SiNWs with clean Si crystal surface. As mentioned above, gold is employed as the most frequently used metal catalyst in the VLS growth, unavoidably leading to gold contamination in the prepared SiNWs [77]. The presence of metallic contaminations may often induce deep-level electronic states of the silicon band gap and degradation of the minority-carrier lifetime, which is adverse to photovoltaic applications. To address this issue, other kinds of metals (e.g., Cu, Al, and Pt, etc.) have been employed as alternative catalysts for synthesizing SiNWs [78–83].

In 2007, using Cu and SiCl$_4$ as catalyst and Si as precursor, respectively, Atwater and coworkers grew large-area (>1 cm$^2$) SiNWs (diameter: ~1.5 μm, lengths: >75 μm) arrays with vertical orientation [79]. Note that a patterned oxide buffer layer was used in this work to avoid migration of catalysts during the synthetic process, which was favorable for controlling size, position, and uniformity of the SiNWs arrays (Fig. 2.6a). Wang et al. demonstrated that Al could be used as another kind of available catalyst for VLS SiNWs growth, due to similar binary phase diagram of Al-Si [82]. They further revealed that the growth process was probably via CVD-vapor-solid-solid (VSS) mechanism rather than CVD-VLS, because the eutectic temperature of aluminum-silicon binary phase diagram (577 °C) is considerably higher than that employed in the reported method. Moreover, the wires tended to be tapered by using Al as the catalyst. However, the tendency of tapering was found to be reduced by lowering the growth temperature (Fig. 2.6b, c).
2.2.2 Oxide-Assisted Growth

The OAG method is widely regarded as another popular strategy for fabricating SiNWs. Compared to the metal catalysts-assisted VLS method, oxides are employed in the OAG methods to induce the nucleation and growth of nanowires, producing the SiNWs free of metal contamination. In addition, the OAG method is highly efficacious for producing small-sized SiNWs in large quantities. Moreover, a variety of well-defined silicon structures (e.g., rods, chains, and ribbons, etc.) are readily fabricated using the OAG method [58]. Notwithstanding, the VLS method is more suitable for synthesizing SiNWs with controllable diameters and growth alignment via adjusting sizes and distribution of metal seeds [53, 54, 58, 65, 66]. Consequently, VLS and OAG methods with different shortcomings and advantages are well complementary to each other, and serve as both well-established strategies for synthesis of high-quality SiNWs.

In 1999, Lee and coworkers synthesized bulk-quantity SiNWs by thermal evaporation of a powder mixture of silicon and SiO$_2$ [84], in which SiNW nucleus containing a polycrystalline Si core was formed at the initial nucleation stage (Fig. 2.7). In their following study, they further fabricated the ultrasmall (diameter: ~1 nm) SiNWs via the optimized OAG approach [49], whose surfaces were terminated with hydrogen by a hydrofluoric acid dip. They also observed Si(111) facet and SiH$_2$ on Si(001) facet in the prepared SiNWs sample via scanning tunneling microscopy (STM) characterization. Besides, the authors found that, in comparison to regular silicon wafer whose surface was easily to be oxidized, the
surface of as-prepared SiNWs seemed to be more resistant to oxidation. They further revealed that the electronic energy gaps decreased with increasing SiNW diameter from 3.5 electron volts for 1.3 nm to 1.1 electron volts for 7 nm [49].

2.2.3 Metal-Catalyzed Electroless Etching

Top-down SiNWs growth has recently emerged as an attractive method for preparing SiNWs with desirable flexibility and precision, which is capable of massive and facile production of SiNWs in a low-cost manner.

In 2002, Peng and coworkers introduced a HF-etching-assisted nanoelectrochemical strategy to synthesize wafer-scale aligned SiNWs [69], and further investigated the mechanisms in their following studies [85–88]. The fabrication process is typically divided into two steps: metal catalyst film is first deposited on silicon wafer via electroless metal deposition. Afterwards, the resultant silicon wafer is etched using aqueous HF solution containing oxidizing agents (e.g., H2O2, Fe(NO3)3, or HNO3, etc.). This metal-catalyzed electroless etching process is basically based on noble metal catalysts-assisted selective oxidization of Si, followed by oxidizing HF solution-induced exclusive etching of silicon at the metal-silicon interface, and eventually yields the SiNWs of controllable lengths (Fig. 2.8) [69–71, 89, 90]. It is worthwhile to point out that this HF-etching method is superbly suited to mild, facile and low-cost fabrication of SiNWs at room temperature and atmospheric pressure, without requiring expensive instruments and reagents.

2.3 Silicon Nanohybrid

Hybrid nanomaterials (nanohybrids) that combine with various types of nanostructures (e.g., nanoparticles, nanowires, and nanotubes) have recently gained great attentions [91–95]. Notably, rational design of the architecture would endow the nanohybrids with desirable features, facilitating investigation of the relationship between nanostructures and electronic/optical/magnetic properties [91–93]. Moreover, to meet the increasing demands of various applications, nanohybrids with multifunctional properties have been fabricated by combinations of various functional nanostructures. In recent years, silicon-based nanohybrids made of metal NPs (e.g., AuNPs, AgNPs, PtNPs, and CdTe QDs, etc.)-decorated SiNWs or SiNPs doped with magnetic materials (e.g., Mn, Fe, Fe2O3, Fe3O4) have been well developed and utilized for solar cells, catalysts, chemical/biological sensors, cancer therapy, and bioimaging, etc. [10, 96–109].

Basically, noble metal (Pt, Au, and Ag) ions can be facilely reduced by surface-covered Si-H bonds of SiNWs, yielding Pt/Au/Ag NPs-decorated SiNWs. Such resultant metallic nanoparticles decorated-SiNWs have been extensively explored
for myriad applications (e.g., surface-enhanced Raman scattering (SERS), catalysis, solar cell, and cancer therapy) due to their unique photo/electronic/catalytic properties. For example, in 2011, He and coworkers developed a well-defined SERS platform for DNA detection by using SiNWs decorated with AgNPs (AgNPs@SiNWs). The AgNPs@SiNWs nanohybrid-based biosensor achieved the detection of DNA with a remarkably low concentration (∼1 fM) due to their very high SERS enhancement factor (up to ∼10^10) [100]. Lee and coworkers employed PtNPs-decorated SiNW arrays for fabricating photoelectrochemical solar cells, yielding distinctly improved photoconversion efficiency with high energy conversion efficiency (8.14 %) (Fig. 2.9a, b) [97]. In 2011, He et al. presented a kind of highly fluorescent (QY: ∼30 %) SiNWs coated with multi-color QDs, capable of cell imaging in long-term manner to take advantage of the excellent anti-photobleaching property of the resultant QDs-decorated SiNWs (Fig. 2.9c, d) [101]. More recently, Su et al. decorated AuNPs on SiNWs surface, and further demonstrated that the prepared AuNPs-decorated SiNWs could produce sufficient heat under near-infrared (NIR) irradiation [103]. In this case, the SiNWs had high

---

**Fig. 2.8** Schematics of Ag particle movement in bulk Si induced by catalysts: a A hydrated proton gradient across the Ag particle leads to self-electrophoresis-driven motion. b Self-electrophoresis-driven motion of Ag particles. c Silicon nanostructures are formed due to tunneling motion of Ag particles in a silicon substrate. Reproduced from Ref. [71] with permission from John Wiley & Sons Inc.
absorption at NIR region and converted NIR light into heat, whereas AuNPs coated on surface of SiNWs significantly improve the conversion of light to heat. As a result, such SiNWs-based nanohybrids, served as novel hyperthermia nanoagents, were efficacious for treatment of tumor cells. More examples of silicon nanohybrids-based applications will be introduced in following Chapters (i.e., Chaps. 3, 4 and 5) in a detailed way.

In another aspect, by adding paramagnetism to fluorescent SiNPs, researchers can realize concurrent optical and magnetic (e.g., magnetic resonance imaging (MRI)) detection. Magnetic impurity doping is known as an available approach for offering semiconductor with magnetic properties [110]. In contrast to their single-component counterparts, the resultant doped nanomaterials feature enhanced and multiple functionalities [111]. In 2007, Kauzlarich and coworkers synthesized Mn-doped SiNPs with fluorescent and magnetic properties [105]. In their study, Mn doped Zintl salts (NaSi$_{1-x}$Mn$_x$, $x = 0.05, 0.1, 0.15$) were reacted with NH$_4$Br to produce H-terminated nanohybrid. Later, the same group developed another approach to produce fluorescent and paramagnetic Mn-doped SiNPs ($Si_{3n}$NPs) [107]. In this case, the precursor Mn-doped sodium silicide was first obtained, followed by the reaction with NH$_4$Br and N,N-dimethylformamide (DMF) to prepare the hydrophobic $Si_{3n}$NPs. Finally, the allylamine was added to the reaction mixture to obtain water-soluble $Si_{3n}$NPs. In 2012, they further
demonstrated the preparation of allylamine-terminated Fe-doped SiNPs featuring strong fluorescence (QY: \( \sim 10\% \)) and significant \( T_2 \) contrast, which was suitable for simultaneous fluorescent and magnetic imaging [109].

Another alternative means for fabricating SiNPs with magnetic properties is to encapsulate SiNPs with magnetic NPs, providing higher magnetization with less effect on the luminescence. In 2011, Fukata and coworkers designed the nano-hybrids that combined silicon and magnetic iron oxides (e.g., Fe\(_3\)O\(_4\) (\( \gamma \)-Fe\(_2\)O\(_3\)) with size-dependent optical and magnetic behaviors (Fig. 2.10) [108]. For example, the as-prepared nanohybrids with the mean size of 3.0 nm exhibited super-paramagnetic behavior and green fluorescence, but showed ferromagnetic behavior without fluorescence when the mean diameter was larger than 5.0 nm.

![TEM images of the pure SiNPs (a) and SiNPs doped with Fe different contents of 5.3 % (b), 8.3 % (c), and 15.3 % (d).Insets in a–d show HRTEM and energy dispersive X-ray (EDX) spectra of the mentioned four samples. Reprinted with permission from Ref. [108]. Copyright 2011 American Chemical Society](image-url)
2.4 Conclusions

In this chapter, we first summarized the representative achievements in the synthesis of fluorescent SiNPs. Several important synthetic strategies (e.g., solution-phase reduction synthesis strategy, electrochemical etching approach, microwave-assisted method, etc.) were reviewed in details. On the basis of which, we further discussed the surface modification of SiNPs and relationship between optical and surface properties of SiNPs. Typically, quantum yield of SiNPs can be distinctly enhanced via proper surface modification (e.g., introducing novel surface ligands). Moreover, we suggested “bottom-up” methods as the highly promising route for large-scale preparation of highly luminescent SiNPs. In the second section, we gave a detailed introduction to three classic methods for synthesizing SiNWs, i.e., CVD, OAG, and electroless etching. We further analyzed advantages and shortcomings of these methods from the viewpoints of synthetic procedures, growth mechanism, catalysts, production cost, etc. We also briefly introduced typical kinds of silicon-based nanohybrids (e.g., metal nanoparticles-decorated SiNWs and magnetic materials-doped SiNPs). These high-quality silicon nanomaterials and their nanohybrids featuring unique optical/electronic/thermal properties afford exciting and new possibilities for myriad biological and biomedical, electronical, catalytic, and energetic applications.

References

Silicon Nano-biotechnology
He, Y.; Su, Y.
2014, VIII, 109 p. 47 illus., 26 illus. in color., Softcover
ISBN: 978-3-642-54667-9