Published in final edited form as:

Mikrochim Acta. 2014 November 1; 181(15-16): 1759–1780.

Silica Nanowires: Growth, Integration, and Sensing Applications

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Abstract

This review (with 129 refs.) gives an overview on how the integration of silica nanowires (NWs) into micro-scale devices has resulted, in recent years, in simple yet robust nano-instrumentation with improved performance in targeted application areas such as sensing. This has been achieved by the use of appropriate techniques such as di-electrophoresis and direct vapor-liquid-growth phenomena, to restrict the growth of NWs to site-specific locations. This also has eliminated the need for post-growth processing and enables nanostructures to be placed on pre-patterned substrates. Various kinds of NWs have been investigated to determine how their physical and chemical properties can be tuned for integration into sensing structures. NWs integrated onto interdigitated micro-electrodes have been applied to the determination of gases and biomarkers. The technique of directly growing NWs eliminates the need for their physical transfer and thus preserves their structure and performance, and further reduces the costs of fabrication. The biocompatibility of NWs also has been studied with respect to possible biological applications. This review addresses the challenges in growth and integration of NWs to understand related mechanism on biological contact or gas exposure and sensing performance for personalized health and environmental monitoring.

Keywords

Nanowires; Silica Nanowires Growth & Integration; Silica Nanowires for Sensing Applications

Introduction

For years nanostructures have emerged as a source of new innovation at domestic and industrial level. Their physical properties such as length, width, and high-aspect structures provide the potential for applications in an arena of situations [1]. More so their physical

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structure also lends them to be chemically altered for applications involving biological and chemical applications. Nanostructures are becoming prevalent in our everyday lives (e.g. healthcare and cosmetic products) [2]. For these to become more widely available commercially, current technology and nanotechnology must be merged in a way that uses the best of both to improve everyday life [3]. However to address the challenges of integration such devices must be explored and understood. Researchers have been working for years to discover and develop ways of using nanostructures to better serve human needs in industries such as health care [4], defence [5], and environmental monitoring [6]. With these advancements, the advent of nanostructure influences in our daily lives will be a reality soon. Innovations and ideas have to be vetted thoroughly to insure that theoretical calculations and hypothesis are practical to integrate into society [7]. To be practical, ideas/innovations will need to be marketable, mass manufacturable and commercialized for consumer purchase. To achieve these goals work should be pursued with the focus on integrating nanostructures into existing detection platforms and devices [8–12].

Over the past decade, 1D nanostructure such as nanowires (NWs), nanotubes, nanorods, and nanosprings have attracted researchers due to their potential applications in drug delivery carriers, sensors, and opto-electronic devices [13]. The ability to synthesize large quantities of 1D nanostructure with uniform properties and through a repeatable process is in demand for technological prospects [14]. In this context, NWs seem an interesting option which offers facile and improved electrical and thermal transport in size-confined systems with the understanding of physics at the nano-scale [9,15]. NWs are on the precipice of being introduced into technology for device development to help mankind [16,17]. These devices will provide services that will allow for more accurate testing of human and biological materials. For this transition from lab only phase into the market for profitability and human use, nanostructures must be produced in packaged format that allows their repeatable use in atmosphere not as selectively controlled as in laboratory. Fig. 1 illustrates various oriented grown NWs with improved and tuneable properties.

Recently, NWs are foreseen as the future of many technological applications such as energy harvesting, opto-electronic, and sensing systems. This is due to their high surface to volume ratios, which provide additional effective area and can lead to an increase in device performance and sensitivities. NWs based sensors detect signals by reacting with the target material and translating the reaction into a measurable response such as impedance, voltage, or current [15,22]. As these NWs will be critical building blocks of future nanosystems, the ability to produce them at desired locations, in a controlled manner on any substrate is of great importance [1]. The primary challenge of producing these types of sensors is maintaining the functionality of the sensing material i.e., NWs after final placement on a testing substrate, such as a bio-platform.

NWs are defined as nanostructures that can be composed of both metallic and nonmetallic elements with nanometer sized diameters and micron long lengths. These NWs are robust and have physical strength on the order of 1 million psi; this strength is directly attributed to their crystalline structure and high aspect ratio dimensions. NWs were originally called nano-whiskers due to their whisker-like appearance. For example, Silicon (Si) [23–25,22,26], Au [27,28], Ag [29,30], Ni [31], ZnO [32,33], CuO [34], SnO₂ [35] etc., NWs

have been explored over the past decade due to their unique 1D morphology and electrical, mechanical, optical, magnetic, and thermal properties. The oriented growth and integration of NWs in micro devices has been explored (Figure 1). However, Si NWs are broadly explored for devices application such as nano-scaled flexible large area electronics, photovoltaic, battery and sensors. Beside this, an indirect band gap of silicon NWs limits application as an optically active material for functional optoelectronics [36]. Thus, the fabrication and growth of electrically and optically active porous NWs is required which may explore opportunities for next generation devices [37]. However, limited surface charge and difficulties in surface modification limit Si NWs application in device development. These obstructions raise the scientific and technological demand of (Silica) nanostructures, which have been grown in desired orientation and used for potential applications. Silica nanostructures due to surface modification and functionalization have attracted for applications. A wide range of nano-morphology and aspect ratios can be achieved to control surface area of architecture which increases the number of sites for the conjugation of biomolecules and gases. In biomedical application, florescent tagged silica nanostructures can be tracked in-vivo to selected body organ on application of external field. It was noticed that aspect ratio of 1 D silica nanostructures crucial for the selection in particular application. For example, silica nanostructures with aspect ratio of 1 possesses a tendency to form clumps, whereas silica NWs with aspect ratio > 1 do not [38]. These silent features of silica NWs offer a higher degree of functional control for sensing applications.

Silica is one of abundant and bio-compatible material and extensively used for various applications. Reports on natural silica in many shape, size, and morphologies have inspired researchers to scale down silica from bulk to sub-micron to nano-meter range for applications [39–41]. Fig. 2 illustrates various natural silica nanostructures.

Since the discovery of silica NWs, efforts have been made to optimize synthesis parameters, and explore novel chemistries/strategies to control size, length, and orientation for applications and device development. The optical, electrical, molecular and magnetic properties of these NWs found to be dependent on synthesis route, used precursor, dimensions (length and diameter), and doping of other materials or nanocomposite fabrication. Reports describe that silica NWs contains various defects, such as non-bridging oxygen atoms, dangling bonds, strain bonds and oxygen vacancies, and the silica matrix is nonstoichiometric (SiO_x instead of Silica) [44]. These features presented silica NWs as a potential candidate for gas and biosensing. Fig. 3 is an attempt to show investigated various form of silica NWs. In this review, our aim is to bring the attention of researchers towards silica NWs due to their tuneable aspect ratios, their dependent optical, photonic, and electronic properties with excellent biocompatibility for sensing application. The chemistries and methodologies adopted for oriented growth of silica NWs along with their integration for device application are described in next section.

Growth of silica NWs

Silica NWSs were first reported 1964 by Wagner and Ellis using the vapor liquid solid (VLS) growth technique, which will be described in more detail in a later section. Since their discovery, new methods of NWs synthesis have been explored and developed. These

methods include hydrothermal method, Oxide Assisted Growth (OAG) mechanism, and VLS mechanism. Other synthesis techniques include thermal evaporation [49–51], chemical vapor deposition [46,52], laser ablation [53], sol–gel [54], Plasma-enabled growth [55], electro-deposition in AAO [56], Ion implantation [57], plasma thermal reactive ion etching [58] and from natural cellulose fibers [59]. These methods yield appreciable and dense wires with their own unique morphologies and properties. A description of most commonly used methods is presented below with examples that demonstrate the novelty and advancements each technique has contributed to the state-of-the-art.

Hydrothermal method for NWs Growth

The hydrothermal growth process is used to synthesize nanostructures such as nanorods and NWs of defined morphology and compositions. This method produces 1 D nanostructure via reduction and oxidation reactions between precursors/catalyst involved in growth process at lower temperatures. The unfilled octet of the catalytic metals makes them readily available to the reduction and oxidation events needed for NWs formation. Lin et al demonstrated the growth of silica NWs via water assisted synthesis [60]. Synthesized wires were several microns long with diameters ranging from tens to hundreds of nanometers. Grown NWs were smooth and straight with uniform diameters and length. Studies suggest that lattice vibrations were noticeable and were attributed to the Si-OH groups on the wire surface. This is also attributed to the smooth surface of the wire wherein OH⁻ and H⁺ block defects from forming on the wire surface. The authors stressed the novelty of the process by providing clear distinction between this growth method and the OAG process. The OH⁻ and H⁺ not only prevent defects on surface but are also involved in the wire formation under supercritical hydrothermal conditions during sample preparation between 400–470°C at 6–10 MPa for 20 hrs. Pei has investigated a simple hydrothermal growth using Si powder as precursor to prepare silica NWs. The result of the microscopic studies showed fabricated NWs is smooth with the average diameter of 500 nm, and length of several microns (Fig. 4) [61].

The hydrothermal method is generally effective and highly repeatable, yielding NWs of consistent length and diameter with smooth morphology. The process, as discussed is environmentally friendly due to non-use of catalyst and surfactants, the use of this method for NWs integration and growth into CMOS or pre-existing platforms would introduce difficulties that could impede device function [62,63]. For instance, the hydrothermal method by definition is water based; this would introduce moisture into a sensing device/platform. Moisture and water vapor have been observed to introduce artefacts and hamper sensor performance. For CMOS devices the water vapor/moisture could cause additional oxidation, thus augmenting device structure performances.

Oxide Assisted Growth Method for NWs Growth

Oxide assisted growth (OAG) is a mechanism of 1D nanostructure formation that occurs without metal catalyst [64]. Si wafers [65,66], silica powder [67], and a mixture of Si and silica powder [68] are used as the Si source. The oxygen come from the O₂ gas flow[66], the residue O₂ gas in the chamber [65], or even from source silica [67,68]. The silica NWs can be grown using PS wafers as the Si source due to that toxic precursor gases such as SiH₄ or SiCl₄ can be avoided [69]. For silica NWs directly grown on PS wafer; consequently there is

no need to transfer the produced nano-materials for further device manufacturing. It is a preferred method of growth because it yields dense NWs without the contamination issues that occur when metallic catalysts are used (Fig. 5). Additionally, the NWs with diameter approaching 1 nm can be synthesized with additional growth directions of $\langle 112 \rangle$ $\langle 110 \rangle$, which is in direct contrast with the $\langle 111 \rangle$ oriented growth that is dominant in VLS grown wires. Lastly, the method can also be used to synthesize wires from other group III–V materials, by using the co-existent properties of VLS and OAG.

NWs synthesized using this method is without metallic impurities. This alone makes them attractive for application where such contaminants are not preferred, however due to the high temperature environments needed to produce these structures OAG is not preferred for NWs growth method needed to accomplish the task set forth by this document.

Vapor Liquid Solid Method for NWs Growth

The Vapor Liquid Solid (VLS) growth is a bottom up approach to produce NWs via substrate vapor and metallic alloy. Silica NWs can be grown on a crystalline Si substrate by first depositing a thin metal film on its surface and then heating the system to high temperatures (1,273 K) in inert ambient (e.g., N_2 or Ar) containing trace amounts (3–5 ppm) of oxygen. During heating, the metal film breaks up into nanometer-scale islands and reacts with the Si substrate to form droplets of metal–Si eutectic composition. These droplets absorb gas-phase reactants in the form of O_2 and SiO to produce solid precipitates of secondary phases (e.g., Si or Silica). The catalysts such as Ga [46], Au [70], Ni [71], Pd [72,73], Cu [74], Zn [75], NiO [76], C [77], and SiOx [43] have been used to fabricate Silica NWs of desired properties. These precipitates then grow and extend from the droplets to form NWs. Kim et al reported the heating of Pd coated Si substrates for synthesis of Silica NWs with diameters varying from 15 to 100 nm [73]. An extended VLS mechanism is suggested as the primary contributor to the growth of these wires. Hu et al used VLS method to synthesize Silica NWs (diameter 50 nm) without metallic catalyst [65]. NWs were grown during a high temperature annealing and subsequent thermal oxidation of Si wafers, inside an alumina tube. Yang et al performed in-situ TEM studies of silica NWs grown by VLS method using Au as a catalyst [69]. This growth mechanism consists of three phases, 1) alloying process, 2) nucleation, and 3) axial growth. This work explains better understanding of growth mechanism to determine the vapor phase contribution to growth. The wires were highly crystalline and generally had a $\langle 111 \rangle$ growth direction. Huey et al produced NWs using VLS method on Si wafers using Pt catalyst. It was found that Pd silicide acts to facilitate bottom-up formation of NWs. Briefly, wafer were sputter deposited with various thickness of Pt (2, 3, 5, 10, and 100 nm), then wafers were transferred into a tube-furnace and heated to 1100°C in inert atmosphere. NWs grown with a Pd catalyst exhibited diameters varying from 60–200 nm [78]. The VLS growth mechanism can be improvised by the use of laser ablation cluster formation. Morales et al using chemical vapor deposition, was able produce this technique to grow uniform Si NWs with diameters 6–20 nm with lengths up to 30 microns [53]. Additionally, this method was used to synthesize NWs with multiple metal catalysts verifying reliability as a method of cluster formation.

Solid–liquid–solid (SLS) process can be used to grow amorphous laterally aligned amorphous silica NWs (diameter 100–350 nm and length 1–20 μm) arrays on a Si <100> substrate surface at 700–1100°C without using metal catalysis (Fig. 6). Authors explained that a carbon-assisted and lattice strain driven mechanism might be responsible for the lateral alignment of these SiO nanocrystal decorated amorphous silica NWs [77].

In addition to the technique discussed above many researchers adopted other approaches and methods to synthesize silica NWs. Bettge et al reported the spontaneous alignment of free-standing amorphous silica NWs towards and parallel to a flux of directional ion irradiation (Fig. 7). The expectations of bending and aligning finely stranded amorphous silica NWs were verified and observed that NWs are particularly susceptible to bending through ion-induced surface energy reduction. Authors also demonstrated the selective reorientation of NWs in patterned areas, as well as conformal coating of reoriented arrays with functional materials and purposed as engineered surface anisotropies in optical, fluidic and micromechanical applications [79]. However, there is a great scope to develop more novel structures which can possibly be synthesized using innovative chemistries. Park et al., synthesized silica NWs by employing inherent directionality of chemical vapor reaction between bis(ethylmethylamino)-silane ($\text{H}_2\text{Si}[\text{N}(\text{C}_2\text{H}_5)(\text{CH}_3)]_2$) precursor and water without a metal catalyst at room temperature [80]. It was observed that differences in the oxidation reactivity between Si-H and Si-N bonds with water leads to the formation of NWs (diameter, 60–80 nm and length 1.9 μm in 10 min reaction time) onto on a poly(ethylene terephthalate) film (Fig. 8).

In many cases, low conductivity limit application of silica NWs which can be overcome via preparing core-shell NWs such as Si@silica [76], Ag@silica [81,82], Au@silica [83], ZnO@silica [84], CuO@silica [85,81], TiO_2 @silica [86], SiC@Silica[48], CdTe@silica [87], CdSe@ silica [88], silica@Au [89], silica@Ag [90], silica@ Ta_2O_5 [91]. These core-shell NWs architectures improve electron transport and conductivity which led to enhanced performance.

Integration of silica NWs for applications

Many reports have explored the simple and useful techniques to integrate silica NWs into currently used microelectrode sensing devices to improve handling and performance. Oriented growth and manufacturing of silica NWs for characterization/functionalization is of great importance as NWs become more useful as sensing material in devices [92,93,78,94]. The central focus of this section is to address the challenge of mass manufacturing of NWs for integration into sensing devices using developing techniques that allow for, low cost and site-specific NWs growth on substrates.

The development of a sensor with a suitable growth substrate will offer new opportunities in research and development of NWs based sensing devices. In order to make use of NWs with retaining unique morphologies, many integration techniques have been explored. These methods seek to place NWs into patterns and positions that would make them useful in devices outside of laboratory settings. As suitable method of NWs integration into micro-scale devices would, 1) maintaining physical integrity of NWs, by preventing the physical

handling/placement of wires, 2) use materials combinations that would not compromise the thermal budgets of pre-existing device, and 3) produce NWs with size control of wires with consistent and reproducible morphology. Current technologies related to the integration and growths of silica NWs are summarized in Table 1.

Super-Lattice NWs Transfer Method for Patterning

Super-lattice NWs transfer patterning (SNTP) is capable of patterning NWs film with dimensions ranging from 7 to 9 nm [95]. The fabricated NWs exhibits electrical properties like the thin films from which they are patterned which can be improved by doping at the nanoscale (Fig. 9). Melosh et al used SNTP method (stamps or templates) to synthesize NWs on the order of 8 nm with matching boron and arsenic doping levels near 10^{18} cm^{-3} [96]. As a result, this has led to the more recent use of the SNTP technique in the development NWs based flexible sensors demonstrated by McAlpine et al [97,98]. However, this technique has a major drawback of materials loss through heating and subsequent removal, and transfer through the lab atmosphere.

Lee et al demonstrated a NWs transfer method that allows NWs patterning without the use of Si wafers [99,100]. NWs with diameters of 20–200 nm and lengths of 5 to 100 μm were fabricated as freestanding bridges using controlled micromachining processes. Back gated and top gate p-channel field effect transistors were demonstrated with varying results. As made, top gated devices work better than p-channel devices due to lack of thermal heating need to properly diffuse dopants into surface.

Di-electrophoresis Deposition of NWs

Di-electrophoresis (DEP) is a process that involves the movement of charged particles via dipole moments. The movement of particles via electrical or magnetic fields, in liquid media, is the next step from NWs pattern transfer. This movement allows for their manipulation without physical handling exposure to prolonged heat treatment. This is an advantage in the placement of cells, cellular components, and marker particles, which are affected by unnatural temperature fluxes [98,99]. Another advantage is that particles do not need to be pre-charged, since particles display electrophoretic property in the presence of the electric fields. In addition to being drifted through media randomly, particles can be arranged, separated, and concentrated (localized) by manipulation of external ac forces [101–104].

DEP deposition involves the application of non-uniform electric fields with mild voltages, thus making it useful in wide range of applications that involve the micro assembly of 1D structure (Fig. 10) [101]. When a particle is placed in an electric field, its experiences forces applied by that non-uniform field, depending on the material whichever pole is experiencing the strongest force will dominate and the particle will move in that direction. This process works using both AC and DC field. This is due to the field gradient effects on the particles and is governed by the averaged DEP and the Classius-Mossotti function for homogenous sphere surrounded by a conducting liquid medium. CNTs have been the target of selective DEP for integration into CMOS technology as thermal sensors. Agarwal et al integrated CNT's onto a CMOS-based device using a low temperature DEP process and zincation pre-

treatment. Parylene-C was used for improving CNT contact [62]. Similarly, Chen et al assembled single wall nanotubes on CMOS for thermal sensing and observed identical thermal readings and amplifier gain measurements [92]. Recently, Murphey-Perez et al di-electrophoretically deposited VLS grown silica NWs biosensor fabrication [105]

Direct Growth Integration of NWs

The direct growth technique integrates nanostructures directly into testing devices, usually without physical handling of substrates or material pre NWs synthesis. This integration is usually accomplished by the placement of NWs catalyst or growth material directly on substrate [92,106,93,78,107,94]. This technique had yielded aligned NWs in combination with the VLS method. The direct growth integration has been used to integrate NWs in lateral growth structures for sensing applications using a device structure [78]. This technique is based on both top down and bottom up approach. For example, using a top-down approach, Conley et al. have directly assembled ZnO NWs into a working device fabricated on Si-on-insulator substrates [106]. In contrast, a bridging technique (bottom-up approach) to connect metal catalysed NWs between etch oxide grooves in Si has been developed. Islam et al. laterally grown Si NWs using connectors to bridged etch $\langle 111 \rangle$ planes that had been previously formed by anisotropically etching $\langle 110 \rangle$ oriented silicon wafers (Fig. 11) [108]. These NWs were made electrically conducting by p-type doping during growth, which was added during the CVD process used to synthesize the NWs. Also, when NWs terminate upon the opposite trench wall it was observed that the catalyst was present and the attachment is Si-Si bonding.

Hochbaum et al have integrated well-aligned and single crystalline Si based NWs into predefined structures using Au colloids as a seeding layer [93,109]. Traditionally, wire grown via VLS have diameters relating closely to their seed diameters, however NWs diameters were slightly larger than seed colloids. It was suggested that this was due to an influx of Si into the colloids and alloy causing the seed droplets to swell in size until the super-saturation needed for wire growth occurred. Using a variation of the SNTP process the Au colloids were transferred into patterned trenches (micro channels), vertical growth was observed with the above characteristics of growth still valid. Direct growth integration is effective due to the removal of physical handling of the NWs and preferential placement of NWs into preformed structures. However, the use of SiCl_4 precursor poses a risk. It is hazardous and safety protocols have to be put in place before its use. This process could be optimized if a non-volatile source or precursor could be found, that would eliminate the use of hazardous materials for NWs integration.

Huey et al reported that an ideal structure would be intact both with pre-existing and integrated structures properly formed and integrated (Fig. 12) [78]. For demonstration of this integration technique, an interdigitated microelectrode (IDE) sensing structure has been chosen due to their demonstrated use as sensors in surface acoustic wave, biological and redox applications with potassium ferro/ferrihexacyanid [110,111]. The integration of these nanostructures into this pre-existing and demonstrated device could yield promising result in terms of increased sensing area, from utilization of NWs stems and IDE planar surface. During VLS, silica use to separate the electrodes from substrate surface needed to be

removed and Au would need to be deposited in these areas. The deposited Au would serve as a catalyst for NWs growth, but only on those regions that where Au and silica were in contact with each other. The thin metallic layer between the electrode fingers will serve as the seed layer (catalyst) for NWs growth. This technique also serves as a NWs growth deterrent on the electrode, thus controlling the growth location. Silica NWs were produced by high temperature annealing using the VLS mechanism. Silica NWs integration optimization was performed to determine the optimal conditions (annealing temperature and time) that would yield the densest amount of NWs without damaging microelectrode structure. However, such integration has presented challenges that involve metallurgy (IDE composition), fabrication (barrier layer placement/removal), NWs integration (annealing temperature/time) and analytic toxicity due to NWs incompatibility.

Li et al. presented a novel technique of integrating silica NWs to carbon microelectrode arrays on Si substrates [94]. Silica NWs were grown on photoresist-derived 3D carbon microelectrode arrays during carbonization of patterned photoresist at high temperature. Carbonization-assisted nucleation and growth found to extend the metal-catalyzed VLS mechanism for the nanowire integration behavior. They also observed significant enhancement in the electrochemical performance for the nanowire-integrated microelectrodes compared to blank ones. These platforms can be used to develop large-scale miniaturized devices and systems for applications in electrochemical, biological fields.

In summary, efforts are being made for the manufacturing and integration of silica NWs with emphasis on low temperature orientation with improved properties for applications. Bottom up technique of NWs integration will remove the need for post growth processing by, a) minimizing structural damage from physical handling of the NWs, and b) growing them in place on a target (final location) substrate. Additionally, this will protect the integrity of the sensing material (NWs) and allow for more accurate testing and characterization. However, beside this in-site integration technique, ex-situ integration of NWs is in demand for device platform. For example, Wu et al suggested a simple approach to align NWs between different electrodes onto the PDMS flexible substrate using shear stress (Fig. 13). This method can be used to produce functional devices for applications [112].

Sensing application of silica NWs

Silica NWs has been synthesized, and integrated on desired substrate or pattern using above mentioned techniques for device applications. Related theoretical modeling and optimization of growth factors which affect the orientation and properties of NWs has been explored. For example, Tong et al (Fig. 14) reported the assembly of low-loss silica NWs functional micro-photonics devices on a low-index nondissipative Si aerogel substrate [113]. Linear waveguides, waveguide bends, and branch couplers were fabricated using this NWs platform. These small devices exhibited low optical loss indicating great potential in optical communication, optical sensing, and high-density optical integration.

Mohebbi numerically investigated a Mach-Zehnder optical sensor using two single modes silica NWs (12 nm diameter) [114]. The author calculated the propagation constant

differences between the NWs sensing element and references. This sensor operated at a wavelength of 325 nm, leaving related sensing parameters for further investigation. Silica NWs based micro/nano systems are considered a smart advanced platform for technological applications. Among them gas and bio sensing application of these NWs are an emergent area of research, and described in next section.

Gas Sensing application of silica NWs

Properties such as electro-active surface charge, easy surface modification, tunable properties and porous morphology of silica NWs are advantageous for adsorption/desorption of gases molecules which is crucial for gas sensor development. An interesting system of a wide band gap SiO_x NWs that absorbs visible light (532 nm) via the surface plasmons (SP) of embedded AuNPs is reported to detect gas. SP resonance enhanced selective molecular oxygen sensing was performed using single AuNPs@SiO_x NWs under room temperature luminescent at 532 nm. AuNPs@SiO_x NWs were reported to be non-stoichiometric with Si/O atomic ratio of 1:0.6, which implies affinity for oxygen molecules. The presence of Au nanoparticles helps the electron hopping and enhancement of sensing. When illuminated with 532 nm light, Au nanoparticle surface electrons get excited by SP resonance absorption and improve the sensing further by contributing charge carriers (Fig. 15). The sensing parameters such as response and recovery time improved by illumination due to the photo-generated hole-mediated oxygen desorption [115].

An optical fiber methane gas sensing [low concentration below 3.5% (v/v)] device was fabricated which operates at room temperature on the basis of luminescence quenching of cryptophane-A/silica NWs [116]. On exposure to UV light, the sensing element showed an intensive and stable blue luminescence, which quenches by molecular methane. The progressive quenching of light by increasing quantity of methane has been reported (Fig. 16). At 339 nm, methane gas sensing device exhibited a linear range from 0.1% to 3.5% (v/v) and detection limit of below 0.1% (v/v). This luminescent methane sensing element exhibited fast response and recovery, good repeatability. The sensor was exposed to O₂, N₂, CO₂, SO₂ and H₂S for 600 s, but no quenching has been observed, which shows the selectivity of sensor for methane sensing.

Paska et al fabricated gated FET gas sensors using native SiO₂ coated Si NWs to detect octane, decane, ethanol, butanol and humidity[117]. Authors used systematically changed trichlorosilane (TS)-based organic monolayers to study the interactive effect of hysteresis and surface chemistry during sensing. The evaluation of sensing performances of NWs correlated to the concentration of the un-passivated hydroxyl (Si–OH) groups within the adsorbed TS monolayer. The elimination of these Si–OH by analyte adsorption improves the electrical properties of FET. The improvement has been expressed in the terms of decrease in hysteresis magnitude and hysteresis drift of the Si NW FET on exposure to analytes. Based on findings, a model is proposed that provides the correlation between the adsorbed organic molecules, the hysteresis, and the related fundamental parameters of gated nanowire FET characteristics. The lowest detected limits as 22 ppm, 17 ppm, 88 ppm and 15 ppm for octane, decane, ethanol and butanol, respectively were estimated. The minimum and saturation humidity sensing values of 15 % and 80 % have been reported.

Bio-sensing Application of silica NWs

Silica NWs due to functionalized surface and bio-compatibility has pronounced potentials for usage in the development of highly sensitive biosensors for biomarker detection and biomedical applications such as cell-selective drug delivery and bio-imaging [105,118–120]. Easy functionalization allows them for the conjugation or encapsulation of important biomolecules. Thus careful analysis of NWs toxicity is required prior to placing these sensors within the human body. Although recent *in-vitro* studies suggested that silica NWs are nontoxic [78,121,105,122], another study using embryonic zebrafish as a model system, claimed that silica NWs with aspect ratios greater than 1 are highly toxic ($LD_{50} = 110 \text{ pg g}^{-1}$ embryo) and cause embryo deformities, whereas an aspect ratio of 1 may neither be toxic nor teratogenic at the same concentrations. Silica NWs also interferes with neurulation and disrupts expression of sonic hedgehog, which encodes a key midline signaling factor [38]. Author suggested the need of nano-toxicity demonstration for further use of silica NWs before their use as platforms for drug delivery. This finding suggests that materials with large surface areas and elongated shapes may generate mechanical disturbances in animal tissues that spherical materials do not.

Recently, single step methodology was used for integrating silica NWs into the $5\mu\text{m}$ spacing on the IDE structures VLS growth process (Fig. 17) [111]. The analysis of breast cancers cells in NWs containing media explored to verify the biocompatibility of a silica NWs. Micro-scale device containing integrated nanostructures could be of use for diagnostics. A new multi-spatial electrode design and real-time impedance monitoring system were used to demonstrate a potential application of monitoring the bio impedance of biological systems.

A real-time and quantitative analysis of silica NWs cytotoxicity using electrochemical impedance spectroscopy (EIS) may utilize over traditional assays. Silica NWs mixed with Dulbecco's Modified Eagle Medium (DMEM) and exposed to Hs578T epithelial breast cancer cells at concentrations of 0 mg mL^{-1} , 1 mg mL^{-1} , 50 mg mL^{-1} and 100 mg mL^{-1} . Impedimetric response studies confirm that while not cytotoxic, silica NWs at high concentrations (50 and 100 mg mL^{-1}) are toxic to cells, and also suggest that cell death is due to mechanical disturbances of high numbers of NWs. This developed platform offers quantitative, real-time, and nondestructive measurements of NWs-cell interactions which can be used as a viable complement to standard endpoint assays [111].

Ramgir et al suggested that the high surface to volume ratio and high aspect ratio of silica NWs enhances the loading of a specific capture antibody toward a particular cancer antigen and amplified signal generation [123]. A voltammetric immunosensing protocol has been used to detect cancer marker via immobilizing alkaline phosphate (AP) enzyme attached to the cancer antigens (IL-10 and OPN) with silica NWs (Fig. 18). The electron produced via an enzymatic reaction of AP enzyme changes the color of dye used to detect cancer antigen optically and electrically [70]. The developed immunosensor showed a detected limit of $3 \mu\text{L}$ and linear range of detection found to be dependence of captured antibody onto silica NWs and antigen concentrations. Authors found that the density of silica NWs exhibits a significant impact on the response which improves sensitivity and selectivity upon using silica NWs with controlled aspect ratio and density. The utilization of aligned silica NWs

can be extended to develop system-on-chip leveraging the electro-active nature of silica NWs as multimodal sensing platform for diagnostics [123].

The Pd nanocluster-dielectric silica NWs composite of an excellent Surface Enhanced Raman substrate (SERS) exhibited a sensitivity of 1×10^7 toward micro-molar detection ($100 \mu\text{g mL}^{-1}$ to 0.1 ng mL^{-1}) of cancer biomarker (Interleukin-10) with high spatial resolution [124]. The new SER configuration also separates the plasmon phenomenon of the adsorbate molecules from the electronic resonances of the substrate. In this report, a standard sandwich assay protocol was used for the modification of the amine group functionalized silica NWs with IL-10. A specific capture antibody (Ab) for IL-10 antigens was immobilized over night at 4°C followed by blocking of the nonspecific binding and incubation for 2 h in blocking solution. The effect of the addition of IL-10 concentration onto silica NWs based immunosensor was studied using SERS. Implementation of such a generic configuration on Si would facilitate a wide variety of applications, which include integrated micro-Raman on chip, a multimodal sensing platform for bio-diagnostics, and a sensitizing medium for enriching the optical activity of erbium. This metal-decorated silica NWs architecture holds a great potential for a lab-on-a-chip development for diagnostic applications [124].

The VLS grown silica NWs based electrochemical immunosensor was developed on an IDE structure to detect prostate-specific antigen (PSA) using EIS [78]. Silica NWs-IDE is a preferred structure for electrochemical biosensors, due to the ability to amplify electrochemical signal and a low detection limit, which is strongly dependent on the inter-electrode separation. Although, IDE with an electrode separation of less than one micrometer are desired for maximum signal amplification, due to lithographic limitations, the microelectrodes have been designed to have a $5 \mu\text{m}$ separation [125]. This distance will facilitate the interaction of NWs with the biomolecules and result in a fast detection of PSA at ppm level (Fig. 19). In this report, Anti-PSA antibodies immobilized on to silica NWs-IDE via electrostatic interaction. The binding of antibodies and sensor fabrication were studied using EIS via understanding observed changes in charge transfer constant. Authors claimed that high surface charge and better electron transport helps in high loading of biomolecules and signal amplification [78].

Phyto-fabricated silica NWs prepared on different surfaces using pomegranate leaf extracts used for sensing application [126]. The NWs developed on Zn surfaces were functionalized with amine groups and used for the covalent immobilization of *Candida rugosa* lipase. The immobilized enzyme displayed better pH and temperature stability and retained 80 % activity after 20 cycles. This paper highlights a novel route for the phyto-mediated growth of NWs on Zn surfaces, their characterization and effective use as a matrix for enzyme immobilization. Silica NWs integrated onto IDE by di-electrophoresis method were used for the covalent immobilization of glucose oxidase (GOx) to detect glucose. 3-aminopropyltriethoxysilane (APTES) modification and N-ethyl-N-(3-dimethylaminopropyl) carbodiimide and N-hydroxysuccinimide chemistry was used for the covalent immobilization of enzyme [105]. The electrochemical response current of the GOx/Silica NWs/Au sensor increases as a function of glucose concentration ($25\text{--}300 \text{ mg dL}^{-1}$). The observed increase in response is attributed to enzymatic catalytic action of GOx bound on

the silica NWs surface that acts as a high surface area matrix and facilitates higher electron transfer rate (Fig. 20). This sensor exhibited a detection limit of 11 mg dL^{-1} , sensitivity: $0.463 \text{ mA (mg dL}^{-1})$.

Zhang et al reported the synthesis of CNT@silica NWs (Fig. 21) with uniform meso-porous silica shell, perpendicularly aligned/orientated and accessible mesopores via the interfacial surfactant (octadecyltrimethylammonium bromide, ODTMA) template approach [127]. CNT@silica NWs shows including good dispersibility in aqueous solution, high adsorption capacity, biocompatibility, and facile functionalization without the disruption of the CNTs structure. These NWs were utilized to electrochemical biosensing of dimethyl sulfoxide (DMSO) via immobilizing sulfoxide reductase (DMSOR) as enzyme in $[\text{Co}(\text{transdiammac})]^{3+}$ mediator which facilitate the electron transport. Absorption occurred on the external surface of the CNT@silica NWs reacts with both DMSO (substrate, the electron acceptor) and the Co^{II} of the mediator ($[\text{Co}(\text{trans-diammac})]^{2+}$, the electron donor), which also undergoes diffusional heterogeneous electron transfer at the electrode. The CNT@silica NWs based electrode produces extremely higher catalytic current as comparison to CNT based electrodes, and electrodes without NWs (Fig. 22E–F). The CNT@silica NWs and the mediator enhance the electron transfer between DMSOR and electrode. Hence these hybrid NWs with unique properties arising from conductivity of CNTs and meso-porosity of silica made this material promising in the applications of electrochemical detection and biosensors.

Dean et al reported an effective way to prepare silica NWs to fabricate DNA biosensor. This group organically modified coatings on metal cylindrical NWs using a variety of Si alkoxides with different functional groups in suspension by the hydrolysis and polycondensation of Si alkoxides [128]. These modified NWs were used to attach desired biomolecules such ssDNA oligonucleotides and protein. Author verified bio-recognition via hybridization of 50-thiolated DNA oligonucleotides with fluorescent complementary or non-complementary DNA oligonucleotides.

Metal/silica hybrid core-shell NWs have been prepared by coating bar-coded metallic NWs with a silica shell of controllable thickness (6–150 nm), and the assay performance of coated versus uncoated NWs has been compared [83]. The coating provided protection against chemical etching of metal by nitric acid, and did not interfere with Au/Ag stripping pattern identification. For the detection of target sequences, the attachment of probe DNA oligonucleotides to surface the siloxane-based modification chemistries were used. The attachment was found to be stable at the high temperatures required for thermo-cycling reactions. In comparison to metallic, the hybrids NWs show higher and more uniform fluorescence intensities for dye-labeled ssDNA. It was observed that 3 pathogen-specific target sequences immobilized onto Silica-coated NWs exhibited discrimination with respect to complementary from non-complementary targets using multiplex DNA hybridization assays developed for (Fig. 22). It was observed that thiolated probe DNA fabricated via siloxane chemistry to Silica-coated NWs repels de-sorption under thermo-cycling conditions than other utilized chemistry. The application of Silica-coated NWs in discrimination of single base mismatches corresponding to a mutation of the p53 gene was also demonstrated.

Table 2 summarizes the sensing performance of silica NWs based biosensor reported in literature.

The outcomes of various sensor reports conclude that silica NWs of various functionalities (COOH, NH₂, OH, etc), surface charged, integration with other electro-active nanomaterials to fabricate nanocomposite/hybrids/core-shell structure in combination with micro/nano scaled sensing surface can potentially be used for the development of gas/biosensor with improved performance. These devices are of use for environmental and personalized health monitoring. Efforts can be made to promote these sensing strategies for point-of-care applications.

The silica is most studied biocompatible material with established functionalities and chemistry which give the silica nanostructures advantage over the other oxide materials. The silica NWs grown under normal conditions are amorphous, containing various defects within the NW, such as nonbridging oxygen atoms, dangling bonds, strain bonds and oxygen vacancies, and the silica matrix is nonstoichiometric (SiO_x instead of SiO₂ with Si/O atomic ratio of ~1:0.6), which implies affinity for oxygen and O-H molecules [129]. This kind of surface results in enhancement of the bio-molecules immobilization on silica NWs. Therefore, the silica NWs have advantages over the other oxide NWs like ZnO, SnO₂ etc in the field of bio-sensing. The insulating nature of these NWs is a limitation for the transportation of charge from analyte to electrode or contact. To overcome this shortcoming, these NWs need functionalization to achieve good conductivity required for charge transportation.

Future Prospects and Conclusion

Potential methods have been investigated to grow silica NWs and integration into micro/nano scale device without damaging the pre-existing structure, by tailoring NWs catalyst placement and synthesis atmosphere. These techniques overcome the issue of physical transfer thus silica NWs retain structure and performance integrity, which could lead to reductions in fabrication cost. Efforts are continuously towards the growth of silica NWs onto flexible substrates that provides access to properties such as shock resistance, biocompatibility, softness and material transparency which can be taken advantage for further experimentation and device development. The potentials of silica NWs based sensing structures for environmental monitoring and detection of clinically relevant biomarkers such as gases, metabolic, cancer markers etc. has been explored.

We conclude that among 1D nanostructures, silica NWs can be chosen a material of choice in sensor development due to easy/well-established surface modification, integration with IDEs and enhancement in properties via doping and composite fabrication. A variety of concerns remain when considering integrating systems and materials, such as process parameters, system functionality, and limitations of integrated structures. The issues related to silica NWs integration with micro systems, the experimentation of pertaining synthesis, biocompatibility, and integration are under consideration to improve device performance. The future prospects of the presented review is focused towards the use of nanostructures in unison with pre-existing micro-scale platforms as a gateway to improving drug delivery,

environmental monitoring, point of care testing, and personalized diagnostics for health monitoring. The experiments discussed here serve as a guideline to addressing the challenges in NWs integration for devices and to understand the effects of silica NWs on biological structures when in contact with human body and exposure of gases.

Acknowledgments

This work was supported by the National Science Foundation (NSF) ASSIST Nanosystems ERC (EEC-1160483) and National Institute of Health (NIH) 1RO1-DA027049. The author Rajesh Kumar acknowledges the University Grant Commission (UGC), India for the award of Raman Fellowship (ID 1001, 2013-14).

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Fig. 1.

a) SEM image of oriented Ni NWs, which alter with the direction of an applied magnetic field and utilized in nano-scale electronic, magnetic, optical, and mechanical devices especially in increasing the memory capacity of computer hard disc drives, b) NWs farm, planted on the windows which allowed growing and collecting solar radiation that will be used to power the buildings larger utilities[18], c) SEM images of mouse embryonic stem cells growing on SiNWs, d) confocal microscope image of Si NWs as black dots inside the cells, which are glowing with green fluorescent protein [19], e) 1-D Arrays of metal oxide nanostructures (60–260 nm) of ZnO NWs, CuO NWs, and α -Fe₂O₃ nanotubes synthesized via a low cost, generalizable, and simplistic template method grown on geometrically significant substrates such as curved plastic and glass rod motifs. The morphology dependent optical, magnetic, and catalytic properties of these 1-D nano-arrays investigated to be better than their bulk oxides,[20] f) Nano-furnace, an array of NWs [green] convert heat from the temperature difference between two Ag of a microchip. Current in flowing through a heater [red] causes the temperature difference. NWs Thermoelectric converter, the difference in temperature between two sides of a chip [red is hot, blue is cold] cause electrons to flow in a roughened Si NWs [21].

Fig. 2.

A) sponges use silica to make array of nanostructure [42]. B) Sunflower-like silica prepared using chemical vapor deposition method. Sunflower-like SiO_x nanostructures provide a chance to probe the growth process. A typical Ga-assisted vapor–liquid–solid (VLS) model is responsible for the incipient SiO_x nanostructures, while the growth of their branches is governed by a SiO_x self-catalysis mechanism. Elemental analysis unveils the initial stage and evolution of SiO_x nanostructure formation. The optical properties of SiO_x nanostructures are also investigated [43].

Fig. 3.

a) SEM of a NWs wrapped around a human hair [45]. They have been produced in lengths of up to 2 cm and were fabricated by wrapping thicker silica NWs around a sapphire taper that was held over a flame. b) Cherry or Jellyfish like structure composed of NWs, c) Carrot-shaped structures were produced from bundles of aligned NWs grown on a silicon substrate. Each carrot contains hundreds of thousands of NWs[46]. d) SEM image shows a group of silica NWs bundles grown from Ge droplets, which are the dark spots atop each bundle.[47] e) Helical nanosprings, have accidentally discovered a way of making helical nanosprings. The springs could have applications in composites, and nanomechanical and nanoelectromagnetic devices, inset is a bright-field TEM image of an individual nanospring, which shows that it is formed from multiple, intertwined, NWs.[48]

Fig. 4. SEM (left) and TEM (right) image of silica NWs grown using hydrothermal method [61].

Fig. 5.
SEM image of silica NWs grown using oxide assisted [65].

Fig. 6. Optical studies of silica NWs grown without using metal catalysts. Laterally aligned amorphous NWs arrays have been successfully synthesized on a Si (100) substrate surface at 700–1100°C, with dispersive silica nano-crystal decorated on the NWs surface [77]

Fig. 7.

A) Silica NWs grown by plasma-enhanced VLS mechanism, without additional bombardment to improve alignment. The image on the right depicts a section of an array of vertically aligned NWs. The inset section on the left depicts a close-up view of one of the NWs found on the right. The substrate is tilted by 30°. The bundles of individual strands forming each NW are clearly visible beneath the indium droplets. Up to a few tens of strands can form from a single NWs. Individual strands have diameters of less than 10 nm immediately beneath the droplet. The scale bar is 100 nm for the inset. Ion-induced surface relaxation: controlled bending and alignment of NWs arrays. Demonstration of bending and alignment of NWs using FIB instrument. B) SEM cross section along the edge of a silicon wafer, showing arrays of unexposed and irradiated oxide NWs. The large depth of field of the SEM makes some nearby untreated NWs visible in the background of each image [79].

Fig. 8.

Reported growth mechanisms of silica NWs: (a) vertical growth by hydrolysis and condensation; (b) Nucleation on hydroxylated surfaces by chemisorption reaction; (c) cross-linking of adsorbed intermediates for lateral growth by hydrolysis and dehydrogenation; (d) brief growth schematics of the cone-shaped (at low pressure) and cylinder-shape NWs (at high pressure) [80].

Fig. 9.

Top-down-based fabrication of silicon NWs. a) SEM image of silicon anisotropic etching using DRIE and wet etching in KOH solutions sequentially. The scale bar corresponds to 1 μm . b) and c) Si NWs obtained by thermal oxidation thinning. The scale bars correspond to 1 μm and 200 nm in b) and c), respectively. (d) Si NWs bridge obtained by removing surrounding Silica. The NWs in d) is 10 μm long and 50 nm in diameter. The scale bar corresponds to 2 μm . e) Si NWs bridge with different diameter and dopant concentrations. The NWs in e) is 10 μm long and has 15 and 120 nm top-width in the thin and thick sections, respectively. The inset shows a partially boron doped NWs using high angle annular dark field (HAADF) scanning transmission electron microscopy (STEM). The bright area in the HAADF image corresponds to implanted boron impurities. f) Si NWs bridge with constant diameter and different doping concentrations [100].

Fig. 10.

Process to create micro-assembly sensors Au electrodes patterned on Si are submerged in a dispersion of either 1D NSs. An AC voltage is applied, and the NWs is blown off to produce micro-assemblies [62,103].

Fig. 11.

A) Cross-section SEMs of (a) a 4 μm-wide, anisotropically etched trench in a Si(110) wafer; (b) Au-catalyzed, lateral epitaxial NWs growth from a (111) sidewall surface into a 15 μm-wide trench; (c) Au-catalyzed, lateral epitaxial NWs growth across an 8 μm-wide trench, connecting to opposing sidewall. (d) Ti-catalyzed lateral growth of a Si NWs to form a bridge across a 2.5 μm-wide trench. The direction of NWs growth is from the right to the left in (b)–(d). [108]

B) Schematic of PDMS patterning of Au colloids. Briefly, a PDMS stamp is molded to the relief pattern of a photoresist master. After curing the polymer, the stamp is removed from the master and “inked” with a solution of poly-L-lysine. The stamp pattern is transferred to the Si (111) substrate, which is then immersed in the Au colloid solution. The colloid-patterned substrate is grown using the conventional VLS-CVD synthesis, resulting in a corresponding pattern of Si NWs arrays. [93]

Fig. 12.

a–b) Angled SEM view of IDE microelectrode with dense silica NWs grown between the working electrodes using VLS, c–e) TEM of silica NWs [78]

Fig. 13.

By stretching the substrate, complex NWs patterns can be generated upon the same rhombus-patterned pillar-structured PDMS surface. Microscopic optical observation of (a) original, (b) vertically stretched, (d) diagonally stretched, (f) asymmetrically stretched, and (h) one side stretched rhombus-patterned micropillar arrangements. The white arrows show the stretching directions. After placing a calcein/PVF hybrid droplet (1:10, w/w) onto these surfaces, diverse NWs patterns can be formed accordingly. (c, e, g, i). Corresponding NW patterns on (b), (d), (f), and (h) surfaces, respectively. Owing to tension-induced K value changes, the dominating structural cohesive force (F_s) will be different under different stretching models. Thus, (c) one NWs bridging the horizontal micropillar pair, (e) parallel NWs between the two pairs of diagonal micropillars, (g) herringbone-shaped NWs, and (i) only one NWs grown on the top left of the micropillar pattern can be generated on the same pillar-structured PDMS surface [112].

Fig. 14.

Guiding of light by straight and curved wires mounted on aerogel. a) SEM image of a 450-nm wide silica wire supported by silica aerogel. b) Optical microscopy image of a 380-nm diameter silica wire guiding 633-nm wavelength light on the surface of aerogel. The green arrow indicates the direction of light propagation; at the right end of the wire, the light spreads out and scatters on the aerogel surface. c) SEM image of an aerogel-supported 530-nm wide wire with a bending radius of 8 μm . d) Optical microscopy image of an aerogel-supported 530-nm wide wire guiding light around a bend with a radius of 8 μm . e) Optical microscope image of a micrometer-scale X-coupler assembled from two 420-nm wide wires. The two wires overlap less than 5 μm at the center (see SEM image in inset). The assembly acts as a 3-dB splitter for light launched into the bottom left branch. f) Two 390 nm wide wires intersect perpendicularly on the surface of an aerogel substrate. There is virtually no crosstalk between the two wires. Inset: SEM close-up of intersection [113].

Figure 15.

Electron transport mechanisms for the (a) plain SiO_2 NWs and (b) Au-NPs@ SiO_2 NWs under dark and illuminating conditions, respectively. Surface defects control the conductivity of the plain SiO_2 NWs with no photoresponse due to the wide band gap. The conductivity of the Au-NP@ SiO_2 NWs is controlled by both the surface states and carriers contributed by the Au NPs. Under 532-nm excitation, SP absorption creates excess carriers that contribute to the higher conductivity [115].

Fig. 16. Variation of luminescence intensity of the sensing element at emission wavelength of 439 nm versus time for various methane concentrations. FE-SEM image of NWs modified with cryptophane-A and chemical structure of cryptophane-A [116].

Figure 17.

a) SEM image of silica NWs grown using VLS method, b) photolithography-Pattern of interdigitated electrodes, c) SEM image of NWs on interaction with cells, outcomes revealing high density of NWs causing cell death, d) Average $|Z|$ at a frequency of 96.49 kHz recorded from each electrode on a single device with the standard deviation for a minimum of 24 hrs. Lower concentrations (0 and 1 mg mL⁻¹) of silica NWs maintain stable impedance while those with higher concentrations (50 and 100 mg mL⁻¹) undergo decreased impedances [111]. Figure 17 a) SEM image of silica NWs grown using VLS method, b) photolithography-Pattern of interdigitated electrodes, c) SEM image of NWs on interaction with cells, outcomes revealing high density of NWs causing cell death, d) Average $|Z|$ at a frequency of 96.49 kHz recorded from each electrode on a single device with the standard deviation for a minimum of 24 hrs. Lower concentrations (0 and 1 mg mL⁻¹) of silica NWs maintain stable impedance while those with higher concentrations (50 and 100 mg mL⁻¹) undergo decreased impedances [111].

Fig. 18.

An immunosensing protocol to detect cancer marker via immobilizing AP enzyme attached to the cancer antigens (IL-10 and OPN) with silica NWs using voltammetric technique [123,70].

Fig. 19.

Electrochemical Impedance spectroscopy studies of a) IDE (curve i), Anti-PSA immobilized (curve ii), and PSA/Anti-PSA/IDE electrode. B) silica NWs (curve i), Anti-PSA immobilized silica NWs (curve ii), and PSA bonded Anti-PSA immobilized silica NWs electrode (curve iii). The remarkable changes in charge transfer resistance confirm the formation of immunosensor and detection of PSA [78].

Fig. 20.

a) SEM image of GOx modified NWs electrode, inset: TEM image of VLS grown Silica NWs. b) CV characterization of GOx/APTES/Silica NWs/Au bio-electrode fabrication in phosphate buffer saline (PBS) 10 mM, pH 7.5 containing 0.1 mM $\text{Fe}(\text{CN})_6^{3-/4-}$ at 50 mV s^{-1} . c) CV studies of GOx/APTES/Silica NWs/Au for 25–300 mg dL^{-1} of glucose concentration in phosphate buffer saline (PBS) 10 mM, pH 7.5 containing 0.1 mM $\text{Fe}(\text{CN})_6^{3-/4-}$ at 50 mV s^{-1} . Inset c: linearity curve for various glucose concentrations. Results of triplicate sets are indicated by error bar [105].

Fig. 21.

(a–d) TEM and HRTEM images of water-soluble CNTs and CNT@silica NWs. e) Cyclic voltammograms of the DMSOR-CNTs/pyrolytic graphite electrode and (f) DMSOR-NWs/pyrolytic graphite electrode in 50 mM purged tris-buffe solution (pH 8.0) with 30 μM [Co(transdiammac)]³⁺ mediator in the (curve a) absence and (curve b) presence of 115 μM DMSO. Scan rate at 20 $\text{mV} \cdot \text{s}^{-1}$ [127].

Fig. 22.

Mean fluorescence intensities for triplex assay. Silica NWs have attached probe DNA for HBV (gray), HCV (black), and HIV (open). Fluorescence intensities are significantly brighter for silica coated as compared to bare NWs, with good specificity. (Inset) Mean fluorescence intensities for same experiment conducted on bare wires. Error bars shown are the 95 % confidence intervals [83].

Table 1

State-of-the-art of the growth and silica NWs growth and integration

Integration Technique	Mechanism	Integration Process	Application
Superlattice NWs Pattern Transfer	VLS	Polymer Coated Transfer (Pick & Place)	Memory Circuits, Thermo electronics
Di-electrophoresis	As- prepared	Electric Field	Interconnects, Gas Sensing
Direct Integration	VLS		Gas Sensing (FET)
Top-Down	Wet etching	Photolithography	Photo-conductivity

Table 2

Summary of the performance of silica NWs based biosensors.

Sensing platform	Sensing performance	Ref
[SM] = silica NWs [T] = voltammetric [IM] = alkaline phosphatase enzyme [TA] = cancer antigen i.e., interleukin-10 and osteopontin	[DR] = 1 pg mL ⁻¹ to 1 µg mL ⁻¹ [DL] = 1 fg mL ⁻¹	[123]
[SM] = Pd nanocluster- silica NWs [T] = surface enhances Raman [IM] = alkaline phosphatase enzyme [TA] = interleukin-10 and osteopontin	[DR] = 100 µg mL ⁻¹ to 0.1 ng mL ⁻¹ [S] = 10 ⁷ towards molecular detection of Antigen [DL] = 1 ng mL ⁻¹	[124]
[SM] = silica NWs decorated IDEs [T] = electrochemical impedance spectroscopy [IM] = anti- prostate-specific antigen antibody [TA] = prostate-specific antigen	[DR] = 100 µg mL ⁻¹ to 0.1 ng mL ⁻¹ [DL] = 1 ng mL ⁻¹	[78]
[SM] = DEP silica NWs-IDEs [T] = voltammetry [IM] = glucose oxidase [TA] = glucose	[DR] = 25 to 30 mg dL ⁻¹ [S] = 0.463 µA mg dL ⁻¹ [DL] = 11 µg mL ⁻¹	[105]
[SM] = CNT@silica NWs [T] = voltammetry [IM] = sulfoxide reductase [TA] = DMSO	[DR] 115 µM	[127]
[SM] = metal@silica NWs [T] = florescent [IM] = DNA [TA] = complimentary and non- complimentary DNA, p53 gene	3 pathogen-specific target sequence have been identified using complimentary and non- complimentary DNA	[83]

[SM]= sensing materials, [T] = technique, [IM] = immobilizing molecules, [TA] = target analyte [DR] = detection range, [S] = Sensitivity, [DL] = detection limit,