Fluorescent Si nanoparticle-based electrode for sensing biomedical substances

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Abstract

We have been studying the miniaturization of silicon crystals and the transition from the solid state to the atomistic state. We demonstrated the existence of “sweet spots” in cluster size in the range 1–3 nm that have enhanced chemical, structural, and photo stability. The particles are produced by an electrochemical etching process as dispersion in liquid, and they are reconstituted in films, patterns, alloys, or spread on chips to produce super chips. Unlike bulk, these Si nanoparticle configurations have a spectacular ability to glow in distinct RGB colors. In this paper we describe an electrode sensor built by decorating metal or heavily doped silicon electrode with nanoparticles. We demonstrated amperometric response of the electrode to glucose and compared the response to that of heavily doped silicon wafer decorated with GOx. The all silicon electrode shows improved sensitivity, selectivity and stability. Light induced modulation of the response allows phase sensitive detection. The device is suitable for miniaturization, which may enable in vivo use.

Direct electrochemical detection has been explored for three decades for making stable and miniature sensors for biomedical applications. This sensing approach is adopted to replace enzyme-based sensors due to enzymes’ intrinsic instability under physiological conditions. To date, enzyme-free sensors have been made using noble metals [1,2], alloys of these metals [3], conducting polymers [4] and carbon nanotubes [5]. These sensors, while rendering device stability, still suffer from issues related to material selectivity and/or electrode poisoning due to adsorption of reaction intermediates. Presently, the enzyme, glucose oxidase (GOx), is used as the sensing element for glucose sensors. In this paper we present a high sensitivity sensor electrode using a thin film of silicon nanoparticles as the active material. Not only, nano silicon is one of the least toxic material, but due to its highly efficient luminescence properties, it will enable dual amperometric/optical sensing [6].

We prepare the silicon nanoparticles by pulverizing crystalline silicon wafers using an electrochemical treatment. The process involves gradual immersion of the wafer into a bath of HF and H2O2 while arranging for an electrical current to skim the top skin of the wafer [7–10]. H2O2 catalyzes the etching producing ultrasmall structures and cleans impurities and produces a higher electronic and chemical quality with an ideal hydrogen termination. The wafer is then immersed in an ultrasound bath, causing the fragile nanostructure network to dislodge into particles. The procedure produces a family of discrete size Si nH x particles that are 1.0 (Si29H24), 1.67 (Si123), 2.15, 2.9, and 3.7 nm in diameter which can be consequently separated [11]. This is unlike uncapped clusters Si n, whose abundance has been known to exhibit no discrete magic numbers for n > 20. The smallest four of the particles are ultrabright blue, green, yellow, and red luminescent particles respectively. A thin graphite grid is immersed in the colloid of the 1 nm particles and imaged by high-resolution TEM as shown in Fig. 1. Electron photospectroscopy shown in Fig. 2 shows that the particles are composed of silicon with less than 10% oxygen.

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Monte Carlo simulation of the particle suggests a filled fullerene structure of Si$_{29}$H$_{24}$, in which a central core silicon atom and four other silicon atoms are arranged in a tetrahedral coordination and the 24 remaining silicon atoms undergo a H-terminated bulk-like (2×1) reconstruction of dimer pairs on (001) facets (6 reconstructed surface dimers) [8]. Fig. 3a shows a schematic model of the Si$_{29}$H$_{24}$ structure.

We prepare a colloid of the 1 nm particles in benzene. We incubated particles in benzene at room temperature. After incubation in benzene, FTIR and XPS and optical spectroscopy show the formation of permanent Si–C bonds, and optical spectroscopy shows more than 30-fold enhancement in the photoluminescence. These new features are a result of the formation of a highly stressed benzene–Si$_{29}$ nanoparticle butterfly complex on Si dimers (Fig. 3b). We used GAMESS software to determine the equilibrium geometry of the Si$_{29}$H$_{24}$–benzene complex using the RHF theory with 6-311G(d,p) basis set. Fig. 3b shows the arrangement of a benzene ring when it is attached to the (100) silicon surface by anchoring via novel Si–C bonds on a reconstructed dimer site in the form of a highly strained complex. The binding to benzene tends to minimize aggregation or agglomeration of the particles on the silicon wafer.

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Heavily doped ($\rho < 0.005 \, \Omega \, \text{cm}$) n-type silicon wafers is used to support Si$_{29}$ particles as sensing elements for electrochemical detection. The wafer with its surface containing the native oxide is cleaned with ethanol, isopropanol and de-ionized water. The wafer surface is then covered with a mask to achieve a working area of 1 mm × 1 mm. A drop of 0.1 ml of the Si$_{29}$ colloid is spread on the wafer surface, and the sample is incubated for 10 h and then rinsed with de-ionized water. The particle-covered wafer is used as the working electrode in a typical three-electrode electrochemical cell for cyclic voltammetry measurements. An Ag/AgCl electrode is used as the reference electrode. The electrochemical cell will be controlled by a high-sensitivity potentiostat with current sensitivity on the femtoampere level. The lowest current scale of this potentiostat is 10 pA full scale with a resolution of 20 fA. The potentiostat can be used to perform both cyclic voltammetry and pulse voltammetry. The cell is put inside a Faraday cage, which provides shielding for low-current measurements. Voltammograms is generated at different scan rate of the potential. Substances to be detected using the Si$_{29}$–Si electrode will be dissolved in a phosphate buffer solution (PBS) and introduced into the cell for measurements. Note that
the bare silicon wafer showed no electrochemical response to the substances used in this work up to a potential as high as 1.6 V.

Fig. 4a is an atomic force microscopy (AFM) image of a typical Si$_{29}$–Si electrode in which silicon nanoparticles are deposited on a silicon wafer. This is an all silicon electrode, consisting of a silicon substrate and a silicon nanoparticle surface film deposited on it. The image shows that the silicon surface is only partly covered with particles. The image also shows minimal agglomeration due to binding to benzene rings. It shows isolated spots. The size of each spot is nearly 9 nm. In the lateral direction, resolution of AFM in the sub 10 nm regime is dominated by the tip effect. It is known that AFM is only accurate in the vertical direction in the sub 10 nm regime. Performing line profiles through the particles, however, gives a height difference between the maximum and the background edge of 1 nm. This is in agreement with previous TEM imaging of the nanoparticle. Estimation based on Fig. 4a shows that typically there are only 1000 Si$_{29}$ particles within this area. When this electrode is exposed to UV light, blue luminescence is emitted. Also when it is exposed to femto or pico second infrared radiation, the blue luminescence is observed due to a two photon absorption process in the range 680–800 nm as shown in Fig. 4c.

Fig. 5 shows the Si$_{29}$–Si electrode’s response to glucose at pH 7. The curves are the cyclic voltammograms (CVs) of the electrode. The increase of the anodic current due to the presence of glucose (curve b) above the background (curve a) is clearly shown. The calibration curve of the electrode at pH 7 as shown in the inset is linear over a range of 0–50 mM of glucose, which covers the physiological level of 3–8 mM [12]. The absence of electrode poisoning is reflected in the electrode’s reversible response to varying the glucose concentration as indicated by the arrows. Curve b in Fig. 5 indicates that glucose is oxidized at the electrode. As mentioned above, the bare silicon wafer shows no response to glucose. Thus, the Si$_{29}$ particle shows a catalytic character in the detection of glucose. A study on the effect of sweeping speed of the potential indicates that the current of curve b in excess of curve a is mainly due to glucose and charging current is negligible.
The time domain response of this all silicon electrode glucose is shown in Fig. 6. It also shows that the presence of three interference agents, ascorbic acid (AA), uric acid (UA) and 4-acetamidophenol (AP), at the physiological levels does not leave any measurable trace on the electrode’s response. The electrode’s response to glucose under identical conditions over a period of 14 weeks was examined. During this period the electrode was repeatedly used every other day and 10 times per day on the average and was stored under ambient conditions. The measurements showed that the electrode’s response has reduced by only 10% of its initial value on the average.

We prepared another electrode by immobilizing GOx as the active films on the same kind of silicon wafer we used above [13]. This provides us with an enzyme-based electrode (GOx–Si). We now compare the glucose response of the all silicon Si29–Si electrode to that of the GOx–Si electrode. Fig. 4a was an atomic force microscopy (AFM) image of the Si29–Si electrode, showing a typical particle distribution on the silicon surface, which is only partly covered with the particles. Fig. 4b is an AFM image showing the GOx–Si electrode, where the entire electrode surface is covered with a monolayer of the enzyme. Estimation based on Fig. 4a and b shows that typically there are 4000 GOx molecules or 8000 FAD centers within an electrode surface area of 1 μm × 1μm, while there are only 1000 Si29 particles within the same area. Fig. 7 shows the amperometric responses of both kinds of electrode having the same size as the glucose concentration is varied. The response of the Si29–Si electrode is at least 4-fold larger than that of the GOx–Si electrode.

Characteristic rate constants for the conversion of glucose to glucose-lactone have been calculated using the above results [6,14–18]. The results suggest that the Si29particle film is more efficient than GOx active film in performing the oxidation of glucose and in transducing the detected electrical signal to the silicon electrode. This enhanced detection is likely to be the result of two effects. First, the particle is accessible to glucose, allowing oxidation to take place. In the case of GOx, glucose needs to enter a small opening on the enzyme in order to reach the FAD center. Moreover, when GOx is immobilized on an electrode, random molecular orientation may reduce the possibility for glucose to reach the FAD centers. Second, if the signal transduction process involves electron tunneling across the particle to the silicon electrode, the 1 nm tunnel distance is less than that for GOx, whose shortest tunnel distance is about 2 nm [13]. The schematic depicted in Fig. 8 suggests an additional advantage of using the Si29particle in making miniature devices. The size of the
particle is 1 nm³, while the size of GOx is 6 nm × 5.2 nm × 7.7 nm. Thus, assuming each material forms a monolayer, the surface density of active sites is higher for the particle electrode than that for the GOx electrode. Within the two-dimensional extent of a GOx molecule, about 30 Si₂₉ particles can be accommodated.

We also studied the response while the sensor is exposed to external radiation. First we recorded the optical activity of the 1 nm colloid. When the colloid is excited by 355 nm pulsed radiation, blue luminescence can be observed with the naked eye, in room light, as shown in Fig. 9. The excitation, i.e., the absorption monitored at a specific emission wavelength (product of absorption and emission) was recorded on a photon counting spectro-fluorometer with a Xe arc lamp light source and 4 nm bandpass excitation and emission monochrometers. Fig. 10 gives the spectrum for excitation wavelength at 330, 350, 365, and 400 nm, showing a strong blue band that maximizes for 350 nm. Fig. 11 proves some optical properties of the other sizes of particles available to us under illumination by light from a mercury lamp at 365 nm [11]. The bottom image in Fig. 11 (right to left) gives the emission of colloids of four members of the magic family 1.0, 1.67, 2.15 and 2.9 nm in diameter, after they have been separated, under excitation using a commercial low intensity UV source with an average wavelength of 365 nm. The top view of the figure shows luminescence from blue, green and red colloidal crystals segregated according to magic sizes 1.0, 1.67 and 2.9 nm diameters. Fig. 12 gives the excitation spectra of the 1.0, 1.67, 2.15 and 2.9 nm diam particle monitored at emission wavelengths of 400, 540, 570 and 600 nm, respectively. They show local resonance structures at 3.44, 2.64, 2.39 and 2.11 eV respectively. In addition to these properties, the particle exhibits interesting nonlinear optical properties such as laser oscillation [9] and second harmonic generation [10] in the visible part of the spectrum.

Since the constituent nanomaterial in our sensor are highly luminescent particles then the effect of light irradiation on the amperometric sensing of substance adds another dimension and functionality to our sensor that allows cross checking and extend its utility to more substances and possibly add to its selectivity and discrimination. Preliminary results show that the oxidation current depends on the intensity of the impringing light. UV light results in the creation of excitonic charge that may radiatively recombine to produce visible photoluminescence.
cence, while white light produces excitonic charge that do not efficiently produce luminescence. We used light irradiation to modulate the charge in the sensor and hence modulate the amperometric response. Plans are underway to use this light effect in phase sensitive detection configuration to enhance the sensitivity. In fact, other nanoparticle configurations have shown to efficiently convert UV light into an electric signal, which enabled sensitive UV photoconductor devices [19,20]. Sensitive ultraviolet light detection may find applications as diverse as military and consumer and biological applications. Detection in the UV portion of the spectrum has applications in detection of biological agents in air. The photodetector configuration may be useful as a UV filter for monitoring enzyme reactions for example. High efficiency allows the study of extremely small samples, assays in small volumes, and sensor array for high-speed screening. Moreover, a thin film of particles coating the active region of a solar cell down converts UV to visible radiation, hence shifting and perhaps increasing the efficiency.

In conclusion, we demonstrated that highly doped silicon substrate or conducting substrates that are decorated with fluorescent silicon nanoparticles can be used as amperometric sensors for glucose. We showed that the device is more sensitive than GOx electrode with improved selectivity, stability, and amenability to miniaturization and implantation for in vivo use. External light may be used to modulate the response, enabling phase sensitive detection.

References


Fig. 12. Excitation spectra of the 1.0, 1.67, 2.15 and 2.9 nm diam particle monitored at emission wavelengths of 400, 540, 570 and 600 nm, respectively. They show local resonance structures at 3.44, 2.64, 2.39 and 2.11 eV respectively.