Silicon Nanowires-Based Fluorescence Sensor for Cu(II)

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ABSTRACT

Si nanowires (SiNWs) were covalently modified by fluorescence ligand, *N*-(quinoline-8-yl)-2-(3-triethoxysilyl-propylamino)-acetamide (QIOEt) and finally formed an optical sensor to realize a highly sensitive and selective detection for Cu(II). The QIOEt-modified SiNWs sensor has sensitivity for Cu(II) down to 10^{-8} M, which is more sensitive than QIOEt alone. Metal ions interferences have no observable effect on the sensitivity and selectivity of QIOEt-modified SiNWs sensor. The SiNWs-based fluorescence sensor is reversible by addition of acid to replace Cu(II). The sensing mechanisms of QIOEt-modified SiNWs to Cu(II) and the rationale for the increase in sensitivity and selectivity of QIOEt-modified SiNWs over QIOEt on Cu(II) are discussed. The current sensor structure may be extendable to other chemo- and biosensors, and even to nanosensors for direct detection of specific materials in intracellular environment.

High surface-to-volume ratio, high activity, coupled with highly selectivity reagents modified one-dimensional (1D) nanomaterials can be capitalized to develop various sensors for chemical and biological detection.[1−8] Up to now, electrical or electrochemical approach has been employed in these sensors with nanostructures.[9] A sensor based on optical signal detection may have some advantages, such as immune to electromagnetic noise[10,11] and ease of data acquisition and transfer through an optical fiber. Although porous structure and 0D nanoparticles have been employed to construct optical sensors,[12−15] it is envisioned that 1D nanowire is better suited for direct sensing of specific materials in cellular environments[16] by inserting a single nanowire with chemical modification into a cell. Furthermore, multiple sensing could also be realized in a living cell with an array modified by several chemosensing agents for different analytes. The large ratio of surface to volume of 1D nanowire also makes it possible to load with more chemosensing agents in a small volume, which also improves sensitivity and selectivity of the sensors. Therefore, optical sensors based on 1D nanostructure materials are desirable to realize high-sensitivity and high-selectivity detection of chemo- and biospecies in a single cell. These nanosensors would also be a very useful and needed tool for understanding intracellular biochemical phenomena. In recent years, silicon nanowires (SiNWs), as a novel 1D nanostructure, can be prepared reliably and in large quantity.[17] This 1D nanostructure is highly stable and biocompatible, as well as potentially useful in a multiplexed environment by assembling individual nanowires in a sensor array.[18−21] These unique properties make SiNWs attractive 1D nanomaterial in conducting research for the development of chemo- and biochemical sensors. SiNWs have been employed to detect hydrogen peroxide, glucose, pH, and biological species by electrical and electrochemical methods;[22−27] however, there is no reported optical sensor based on SiNWs. To implement our optical signal detection strategy using 1D nanowire to improve the sensitivity and selectivity of chemo- and biological sensors, a fluorophore attached to SiNWs approach is used. In this paper, the surface of SiNWs is covalently modified with 8-aminoquinoline via 3-aminopropyltriethoxysilanes[28] and chloroacetyl chloride as a linker to form SiNWs-based optical sensor. Such a covalently bonded fluorophore on surface could effectively avoid leakage of free fluorophore as in some fluorescence sensors.[29] We find that this new type of sensor has high sensitivity and selectivity to sense Cu(II), which is a very important element for hemopoiesis, metabolism, growth, and immune system.[30] The sensor design and results presented here would offer a new approach to construct highly sensitive and

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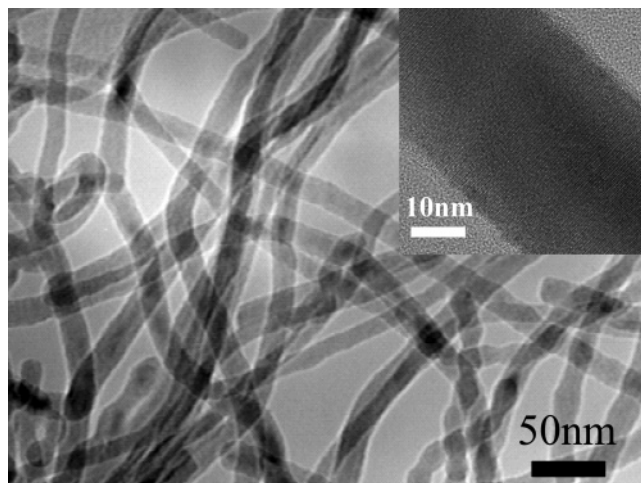
Figure 1. TEM image of SiNWs.

Figure 2. IR spectra of SiNWs and QlOEt-modified SiNWs.

selective chemo- and biosensors. It may also be used to build a nanosensor to directly sense in intracellular environment.

SiNWs were prepared by simple thermal evaporation of silicon monoxide powder as the single source.[31] SiO powder (Aldrich, 99%) in an alumina boat was placed at the center of a horizontal alumina tube mounted inside a high-temperature tube furnace. The system was evacuated to 10^{-3} Pa. Ar (95%) and H_2 (5%) as carrier gas was introduced at the flow rate of 50 sccm, and the system pressure was maintained at 4×10^4 Pa. The furnace was heated to 1350 °C and maintained for 6 h then cooled to room temperature naturally. The slightly yellow cottonlike product was collected at airflow downstream. SiNWs were characterized using scanning electron microscopy (SEM; Hitachi S-4300FEG) and transmission electron microscopy (TEM; JEOL 2010). The as-grown SiNWs have a crystalline Si core of 15−25 nm in diameter and a silicon oxide sheath of 1−3 nm in thickness as shown in Figure 1.

As-prepared SiNWs were immersed in a $H_2O/30\% H_2O_2/NH_4OH$ 5:1:1 mixture by volume at room temperature for 3 h followed by copious rinsing with doubly distilled water and dried under vacuum before modification.

In a round bottomed flask connected to a Dean-stark apparatus under nitrogen, 20.8 mg of dried SiNWs were suspended in 40 mL of anhydrous toluene. The mixture was heated at 140 °C to remove water by azeotropic distillation. After 30 mL of toluene was evaporated, the suspension was cooled to 90 °C and 215 mg (0.53 mmol) of *N*-(quinoline-8-yl)-2-(3-triethoxysilyl-propylamino)-acetamide(QlOEt) was added. The mixture was stirred for 24 h at 90 °C. The SiNWs were collected by filtration and repeatedly washed with anhydrous toluene, dichloromethane, and then ethanol under ultrasonic condition. Unreacted organic material was removed completely by monitoring the fluorescence of the washing liquid. Modified SiNWs were dried under vacuum before IR spectra and contact angles were recorded (preparation of all organic precursors and their characterization can be found in Supporting Information). A BRUKER-ADVAN-CEII400 spectrometer was used for NMR with tetramethylsilane (TMS) as the internal standard. J-values were given in hertz. Low-resolution mass spectra (MS) were obtained
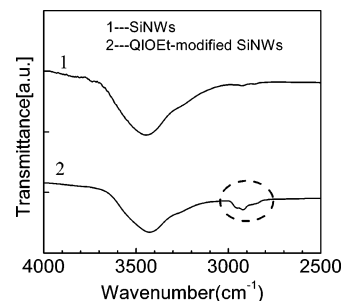
on a FINNIGAN MAT SSQ-710 mass spectrometer. Infrared (IR) spectra were recorded on a Perkin-Elmer Fourier transform infrared spectrometer as KBr pellets. Contact angles were measured with an optical contact-angle meter (OCA20, Dataphysics) at ambient temperature. Contact angle of SiNWs and QlOEt-modified SiNWs were measured by covering 700−800 μm thickness of SiNWs or QlOEt-modified SiNWs on a silicon wafer. Water droplets (1 mm in diameter) were dropped carefully onto silicon wafers covered by SiNWs or QlOEt-modified SiNWs, and four measurements were made at different positions of the same sample. The average value of four measurements was used as the contact angle.

Fluorescence spectra were recorded on a Hitachi F-4500 spectrofluorimeter. Perchloric acid salts of various metals used were purchased from Aldrich Chemicals. QlOEt-modified SiNWs were dispersed 30% EtOH−water solution of 0.05 M HEPES buffer (pH 7.0) to form 68μg/mL suspension. Assuming Zn(II) complexes of QlOEt and QlOEt-modified SiNWs have equal quantum efficiency, the following formula was used to compute the average coverage of QlOEt on SiNWs:
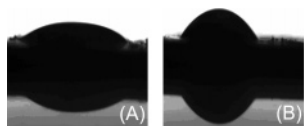
$$\eta_S = \eta_R \frac{I_S A_R}{I_R A_S} \qquad (1)$$

Here η is quantum efficiency, S, R represents sample and standard substances, respectively, I is integral intensity of fluorescence, and A is absorbance at excited wavelength
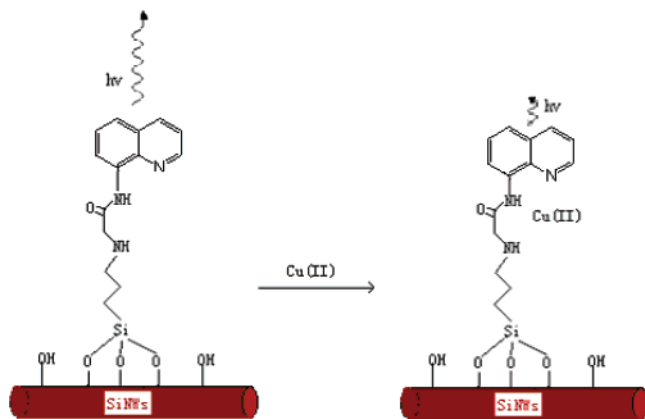
$$A = \epsilon b c \qquad (2)$$

Therefore, the number of molecules of QlOEt on a microgram of SiNWs could be calculated to be 8.3×10^{13}. That is to say, 68 μg/mL QlOEt-modified SiNWs used in our experiments correspond to 9×10^{-6} M QlOEt.

To characterize QlOEt-modified SiNWs, IR spectra and contact angles of the modified and as-prepared SiNWs were carried out at ambient temperature, and the results are shown in Figures 2 and 3, respectively. The band at 3400−3500 cm^{-1} is due to −OH stretching on silanol. It is obvious that not all the silanol on SiNWs have been covalently modified. Compared with SiNWs, QlOEt-modified SiNWs (see Scheme 1) had additional peaks at 2921 cm^{-1} and 2952 cm^{-1} that correspond to the -CH vibration of QlOEt. The contact angles

**Figure 3.** Contact angles of SiNWs (A) and QlOEt-modified SiNWs (B).

Scheme 1

Figure 4. Absorption (A) and fluorescence spectrum (B) of QlOEt-modified SiNWs (68 μg/mL: 9×10^{-6} M QlOEt) and QlOEt (1.0 $\times 10^{-5}$ M). EtOH−water (30%) solution of 0.05 M HEPES buffer (pH 7.0). $\lambda_{ex} = 324$ nm.

of as-prepared SiNWs and QlOEt-modified SiNWs measured from Figure 3A,B were 17.8° and 41.9°, respectively. These results indicate that QlOEt was covalently bonded on the surface of SiNWs.

The fluorescence properties of 8-aminoquinoline derivatives have been extensively reported in literatures.[29,32] Within the 8-aminoquinoline framework, the intramolecular H-binding led to proton transfer from the amine to the heterocyclic nitrogen atom in the excited-state. This excited-state proton-transfer coupled with a photoinduced electron transfer from the 8-amino residue to the quinoline nitrogen atom would strongly suppress the fluorescence of 8-amino-quinoline derivatives. This same phenomenon is also present in QlOEt. Figure 4 shows the fluorescence and absorption spectra of QlOEt and QlOEt-modified SiNWs. Both the absorption and fluorescence peaks are red-shifted. The intensity of fluorescence is further increased after attachment to SiNWs. Nevertheless, for QlOEt-modified SiNWs, there are unreacted silanol groups ($pK_a = 6.8$)[33] present at the surface of SiNWs as shown in the IR spectrum (Figure 2). These silanol groups might form hydrogen bonding with the NH group[34] of QlOEt, which could partly suppressed the proton transfer from the NH group to the heterocyclic nitrogen atom within 8-acylamidoquinoline framework. As a result, the QlOEt-modified SiNWs had higher fluorescence quantum yield than QlOEt. This phenomenon is similar to coordination of Zn(II) complex with the carboxylic acid in β-cyclodextrin that emitted blue-green fluorescence at 490 nm.[35]

It is well known that the 8-aminoquinoline derivatives could effectively coordinate with specific metal ions. Q1OEt is expected to be a stronger coordinating agent because it is a tridentate ligand. When Q1OEt is selectively coordinated with metal ions, the fluorescence from Q1OEt is modified appropriately by the metal ions. This phenomenon can be utilized to construct a metal ion sensor based on SiNWs.
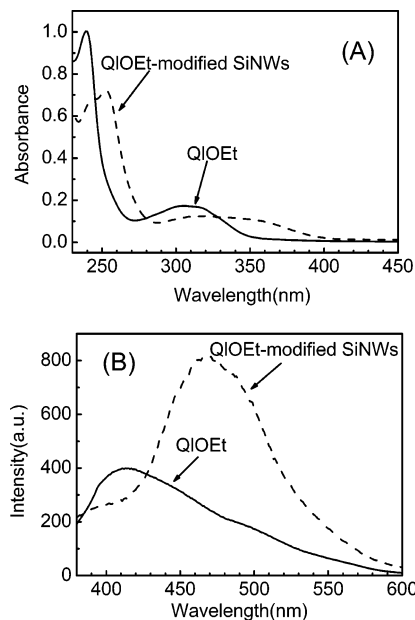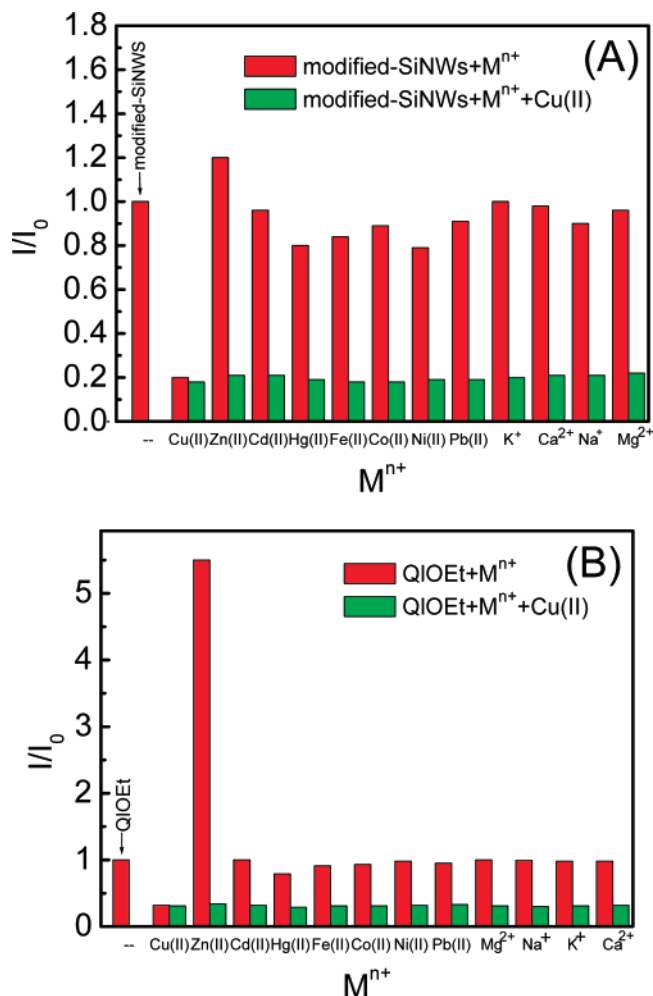
Accordingly, titration of various metal ions in the presence of QlOEt-modified SiNWs in 30% EtOH-water solution at pH = 7.0 (HEPES buffer) was performed, and the results are summarized in Figure 5A. After titration of various metal ions, it was observed that the change in intensity of fluorescence from QlOEt-modified SiNWs can be divided into four groups. For Cu(II), fluorescence was suppressed by about 80%. For an equal amount of Zn(II), the fluorescence of QlOEt-modified SiNWs increased by 15%. On the other hand, Hg(II), Ni(II), Co(II), and Fe(II) led to fluorescence quenching of around 20%. Other metal ions, such as Mg^{2+}, Na^+, Ca^{2+}, K^+, Pb(II), and Cd(II), at the same concentration had an insignificant influence on the intensity of fluorescence of QlOEt-modified SiNWs. From these results, it is evident that QlOEt-modified SiNWs have a high selectivity for Cu(II).
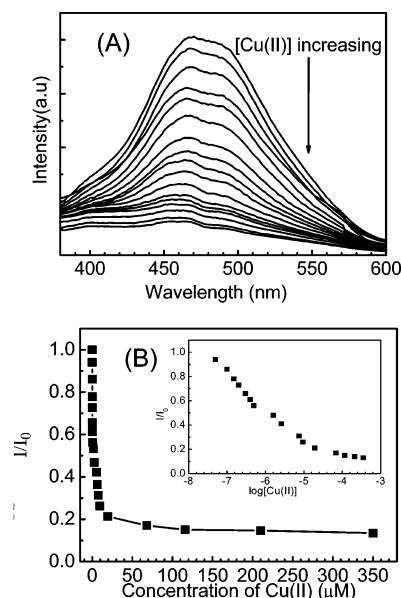
To further characterize the performance of the sensor for Cu(II), a comparison experiment was carried out with Q1OEt-modified SiNWs. As shown in Figure 5A, addition of 20 μM Cu(II) to QlOEt-modified SiNWs solution containing any one of the above-mentioned metal ions resulted in similar amount of quenching of 80% on fluorescence intensity. We thus conclude that the presence of these metal ions with Cu(II) does not affect the sensitivity of QlOEt-modified SiNWs for Cu(II) detection. The strong formation constant of Cu(II) determines the selectivity, and thus the strong coordination of Cu(II) in the square planar environment with Q1OEt-modiefied SiNWs is not perturbed by the presence of the interfering metal ions.

The corresponding experiment using QlOEt was also carried out (shown in Figure 5B). Compared to SiNWs-modified QlOEt, all metal ions have little or no impact on the fluorescence properties of Q1OEt, except for Zn(II) and Cu(II). Thus, QlOEt by itself is a sensitive and selective

Figure 6. Fluorescence spectra (A) and titration curve (B) of QlOEt-modified SiNWs (68 μg/mL: 9×10^{-6} M QlOEt) with Cu(II). EtOH−water solution (30%) of 0.05 M HEPES buffer (pH 7.0). λ_{ex} = 324 nm, λ_{em} = 490 nm.

Figure 5. Relative fluorescence intensity of (A) the QlOEt-modified SiNWs (68 μg/mL: 9×10^{-6} M) and (B) the QlOEt (1.0 $\times 10^{-5}$ M) in the presence of various metal ions alone (20 μM, red) and interfering ions with Cu(II) (20 μM, green), respectively. EtOH−water solution (30%) of 0.05 M HEPES buffer (pH 7.0). λ_{ex} = 324 nm, λ_{em} = 490 nm.

sensor for Zn(II) and Cu(II). The fluorescence of Zn(II) complexes with QlOEt is increased by a factor of 6, while Cu(II) complexes quenched 70% of the original Q1OEt fluorescence. As for selectivity of QlOEt to metal ions, Zn(II) and Cu(II) both form a complex with QlOEt with their suitable radius and electronic structure. A complex with Zn(II) inhibits the excited-state proton transfer and photo-induced electron-transfer that strongly suppress the fluorescence of QlOEt, thus Zn(II) considerably enhanced the fluorescence of QlOEt. The same effect existed in the Cu(II) complex. However, redox or energy transfer in the Cu(II) complex with QlOEt easily occurred due to Cu(II) $3d^94s^0$ structure, which led to fluorescence quenching of QlOEt.[29,32,35] When the SiNWs are covalently modified by QlOEt, the quantum efficiency of QlOEt-modified SiNWs is increased due to the presence of silanol groups on the surface of SiNWs, which partly inhibits the proton transfer. Consequently, the Zn(II) complex with QlOEt-modified SiNWs gives rise to less fluorescence enhancement than the Zn(II) complex with QlOEt. As a result, the QlOEt-modified SiNWs show a selectivity to Cu(II).

The sensitivity of fluorescence quenching from QlOEt-modified SiNWs by Cu(II) was further investigated, and the results are showed in Figure 6. The fluorescence intensity of QlOEt−modified SiNWs gradually decreased with increasing Cu(II) concentration and finally reached at a plateau at about 20 μM. The detection limit for Cu(II) is established at 10^{-8} M under current experimental conditions. If the same criterion (10% fluorescence quenching) was employed to define the sensitivity of the optimized QlOEt, a value of only 10^{-6} M was achieved.

To thoroughly evaluate the sensing properties of QlOEt-modified SiNWs toward metal ions, it is important to compare the fluorescence properties between QlOEt and QlOEt-modified SiNWs. The response of QlOEt with different concentrations of Cu(II) was investigated. Figure 7 shows the titration curve of Cu(II) in the presence of Q1OEt with optimized concentration. The inflection point corresponds to a 1:1 complex between Cu(II) and the ligand. Because Cu(II) desires a square planar geometry when coordinated, while the three nitrogen on Q1OEt can only provide a tridentate ligand, the fourth coordination can come from either the solvent or the silanol oxygen on SiNWs. Fluorescence quenching via complex formation has also been observed for other ligands, such as DANQUIN.[29,32]

On the basis of the formation of 1:1 complexes between QlOEt and Cu(II) or Zn(II) (Figure 7), log K = 4.47 and 3.61 were obtained for the QlOEt−Cu(II) and QlOEt−Zn(II), respectively. The interaction between Cu(II) and QlOEt is stronger than that of Zn(II) and QlOEt, which is consistent with the observation that addition of Cu(II) quenches the fluorescence of Zn(II)−QlOEt complex. On the other hand, the binding affinity of QlOEt-modified SiNWs and Cu(II) is log K = 5.73 based on Langmuir-type analysis.[33] This value is larger than that of QlOEt and
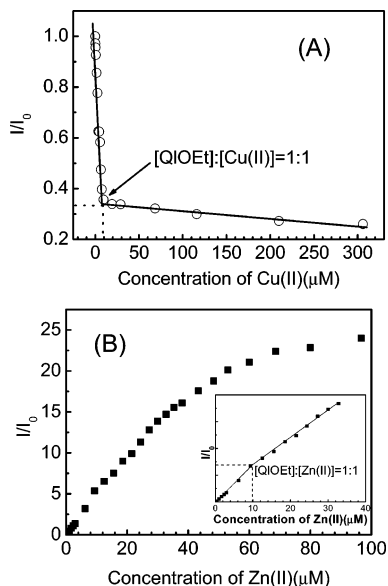
Figure 7. Relative fluorescence intensity of QlOEt at different concentration of Cu(II) (A) and Zn(II) (B). [QlOEt] = 1.0×10^{-5} M. EtOH−water solution (30%) of 0.05 M HEPES buffer (pH 7.0). $\lambda_{ex} = 324$ nm, $\lambda_{em} = 490$ nm.
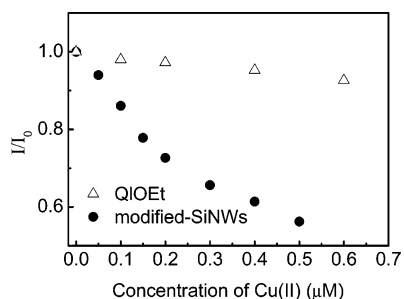
Figure 8. Comparison of sensitivity of QlOEt (1.0×10^{-5} M optimized) and QlOEt-modified SiNWs (68 μg/mL: 9×10^{-6} M QlOEt) to Cu(II). EtOH−water solution (30%) of 0.05 M HEPES buffer (pH 7.0). $\lambda_{ex} = 324$ nm, $\lambda_{em} = 490$ nm.

Cu(II), indicating that interaction of Cu(II) with QlOEt-modified SiNWs is stronger than with QlOEt.

Figure 8 shows the titration curves of QlOEt and QlOEt-modified SiNWs to Cu(II) in the lower concentration range. Although variation of both fluorescence intensities had a similar shape, the titration curve is more abrupt for QlOEt-modified SiNWs than for QlOEt. These results confirmed that QlOEt-modified SiNWs are superior to QlOEt as a sensor for Cu(II). It is worthwhile to note that the sensitivity of QlOEt-modified SiNWs to Cu(II) has not been optimized by the amount of QlOEt covalently bonded to Si nanowires. It is believed that the sensitivity and selectivity of QlOEt-modified SiNWs to Cu(II) could be further improved through optimization. These results also indicate that QlOEt-modified SiNWs are a more sensitive detector for low concentration of Cu(II). To utilize the high sensitivity feature, one can either dilute the solution or use a larger amount of Q1OEt-modified SiNWs or with higher loading of QlOEt on SiNWs.

Current results might be attributed to the special electronic structure of Cu(II)−Q1OEt complex, which might arise from electron or energy transfer in the complex between Cu(II)
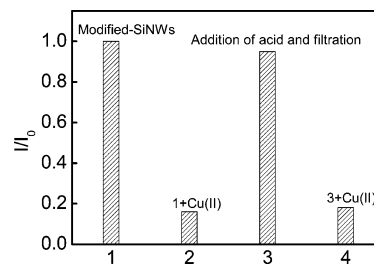
Figure 9. Reversibility of QlOEt-modified SiNWs Cu(II) fluorescence sensor.

and QlOEt.[32] Usually, the efficiency of energy transfer causing fluorescence quenching is strongly dependent on the distance between the fluorophore and metal ions.[36] As for QlOEt-modified SiNWs, there were many QlOEt units on the surface of an individual SiNW. When one QlOEt unit is coordinated with Cu(II), several other QlOEt units located in the proximity could also interact with the coordinating Cu(II) when the system was excited. The synergistic effect between the QlOEt units covalently immobilized on SiNWs enabled a small amount of Cu(II) to quench more fluorophores, and thus a signal amplification effect was realized.[37] From Figure 8, 0.04 equiv of Cu(II) led to 40% fluorescence quenching of QlOEt-modified SiNWs, which indicated that one Cu(II) ion can quench 10 QlOEt units on the surface of SiNWs. Consequently, QlOEt-modified SiNWs were more sensitive than QlOEt alone to Cu(II) especially at low concentration. At high concentration of Cu(II), the signal amplification effect would become insignificant due to the formation of 1:1 Cu(II) Q1OEt complex. As a result, the response of QlOEt-modified SiNWs to Cu(II) became similar to Q1OEt. This phenomenon has also been reported for polymers, dendrimers, and particles.[38−40]

In addition, the present sensor is also reversible by the addition of acid and filtration. As shown in Figure 9, after addition of acid, filtration, and repeated washing with double-distilled water, fluorescence of QlOEt-modified SiNWs could be recovered as high as 95% under the same experimental conditions. It indicates that the present SiNWs-based fluorescence sensor could be repeatedly used. Thus, once the Q1OEt-modified SiNW is properly calibrated, it could be used to quantitatively determine Cu(II) in other samples. Meanwhile, considering its stability and ease to use as solid, such SiNWs-based sensors may be used for many applications.

In conclusion, surface modification of SiNWs via reaction of outer hydroxyl groups with the silanol of QlOEt produced a highly sensitive and selective sensor for Cu(II). The QlOEt-modified SiNWs exhibited responses to Cu(II) down to 10^{-8} M. The presence of metal ions such as Hg(II), Zn(II), Cd(II), Fe(II), Co(II), Ni(II), and Pb(II) had little influence on the selectivity and sensitivity of Cu(II). The sensitivity and selectivity of QlOEt-modified SiNWs to Cu(II) could be further improved by optimization of loading of Q1OEt on SiNWs. This type of optical sensor design is promising for potential application to multiplex sensing of different analytes through distinct surface functionalization

of individual nanowires assembled in an arrays, as well as intracellular biochemical detection by a single nanowire sensor.

Supporting Information Available: Preparation of all organic precursors and their characterization. This material is available free of charge via the Internet at http://pubs.acs.org.

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NL072164K