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# The Use of a Multiple Roughening Scheme to Enhance Sensing Performance of pH Sensors with NiO Nanosheets/MWCNTs on KOH-etched Si Substrates

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## Abstract

**The use of KOH-etched Si (100) substrates with pyramidal cones is proposed for the spray deposition of multi-walled carbon nanotubes (MWCNTs) and hydrothermally grown (HTG) NiO nanosheets (NSs) to improve the pH sensing performance is proposed for the first time. With an optimized KOH/IPA based etching process at 90 °C for 40 min, a surface area (SA) gain of around 2.31 can be obtained from the etched Si substrate. The sensing electrode (SE) based on the as-sprayed MWCNTs sprayed on a 90 °C-KOH-etching Si substrate with 160 times exhibited a higher sensitivity of 54.95 mV/pH than that one on planar Si (52.15 mV/pH), which due to surface roughening by KOH etching increases the sensing area for ion adsorption. Moreover, we utilize HTG of NiO NSs on the sprayed MWCNT to further improve the pH sensing performance, reaching a near-Nernstian response of 57.56 mV/pH. It is attributed to the multiple surface roughening scheme (NiO NSs/ MWCNT/ Pyramid-Si) that maximizes SA and the number of ion adsorption sites.**

## 1. Introduction

Recently, the use of nanostructured materials such as zinc oxide (ZnO) based materials, titanium oxide ($TiO_2$), tin oxide ($SnO_2$), vanadium pentoxide ($V_2O_5$), tungsten oxide ($WO_3$), etc., to enhance the detection sensitivity of pH sensors were demonstrated. [1-3] It shows that the increase in the amount of ion adsorption sites through increasing the surface area (SA) of metal oxides nanostructures, in addition to material itself, is very beneficial for ion sensing. Among nanostructured materials, multi-walled carbon nanotubes (MWCNTs) and nickel oxide (NiO) nanosheets (NSs) have attracted considerable attentions for pH sensing, due to CNT its excellent electrical conductivity, high aspect ratio, strong mechanical and chemical strength, and superior tolerance to harsh conditions, and NiO NSs its excellent electro-chemical performance and thermal/chemical stability. [4-5]

In this work, Si (100) substrate with pyramidal cones prepared by a simple KOH/isopropyl alcohol (IPA) chemical etching is proposed to serve as platform for spray deposition of MWCNTs and then HTG NiO NSs on MWCNTs for pH sensing. Both SA and the amount of ion absorption sites can be maximized and improved pH sensing performance can be expected. Effects of the KOH etching conditions for Si substrate and the thickness of MWCNTs deposition layer on the pH sensitivity are investigated. Relation between the SA gains of the proposed sensing electrodes (SEs) on sensing performance is clarified. In addition, comparison of the pH performance for the SEs based on MWCNTs sprayed onto a planar Si and a KOH-etched Si substrate with different times is also made. And finally, the harvest of sensing performance from the stack of HTG NiO NSs on MWCNTs is examined and discussed.

## 2. Experimental

Fig. 1(a) depicts a schematic diagram of SEs based on MWCNTs spray-coated on a planar Si (called Type A) and a KOH-etched Si substrates (called Type B) and the stack of hydrothermally grown (HTG) NiO NSs synthesized on MWCNTs/KOH-etched Si substrates (called Type C) proposed in this work. In experiments, p-type Si (100) wafers were used. The Si substrates were subjected to a wet anisotropic chemical etching using a mixing solution of 5 wt% KOH and 7 wt% IPA at 85, 90, and 95 °C, respectively, for 40 min. Then, spray-deposition of ethanol solution based MWCNTs was made on planar Si and 90°C-KOH-etched Si substrates using a scanning ultrasonic spraying system (Fig. 1(b)) with the flow rate, the moving velocity of nozzle, and the temperature of substrate were controlled at 0.2 ml/min, 25 mm/s, and 150 °C, respectively. Effect of the thickness of MWCNTs layer modulating by the spray times (cycles) is examined. For the synthesis of NiO NSs, some type B samples were immersed in a chemical solution mixed with 70 mM $Ni(NO_3)_2 \cdot 6H_2O$ and 70 mM $C_6H_{12}N_4$ at 90 °C for different HTG times of 5, 7, 9 and 11 h, respectively, followed by a thermal annealing in air at 400 °C for 40 min to fully convert the as-grown $Ni(OH)_2$ NSs to NiO NSs.

For pH sensing, the samples were sealed with epoxy resin expect for the defined area of sensing window with a size of 5 mm×5 mm. Finally, a metal wire was connected by silver paste on the MWCNTs sensing membrane, which was followed by a curing process at 120 °C for 30 min to remove the excess solvent in the epoxy. For pH sensitivity measurements, an EGFET configuration (Fig. 1(c)) was used and buffer solutions with pH value ranging from 2 to 12 were employed. The potential difference between the sensing electrode (SE) and the reference electrode $\Delta V$ (=$V_G$–$V_R$) at $I_D$= 0.2 mA (under $V_D$= 0.2 V) was measured, which indicates the amount of charges and the polarity adsorbed on the sensing electrode, was recorded for each buffer solution and the sensitivity and linearity of the pH sensor were evaluated from the experimental $\Delta V$–pH curve.

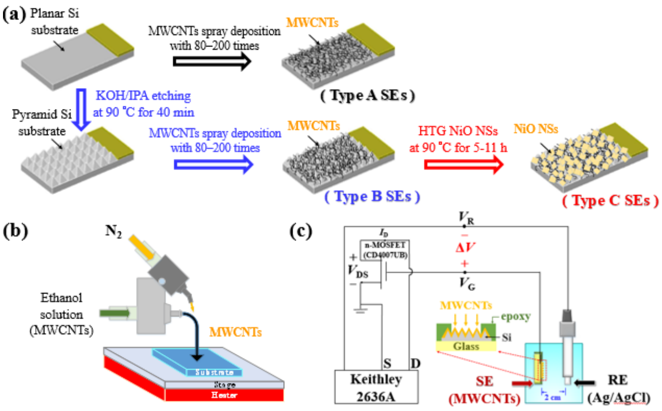


**Fig. 1** Schematic diagrams of (a) the three types of pH SEs prepared in this work, (b) the scanning ultrasonic spraying system, and (c) the EGFET configuration used for pH measurement.

## 3. Results and Discussion

Fig. 2 shows the SEM images of Si (100) substrates after KOH/IPA etching at 85, 90, and 95 °C for 40 min. The surface area gain (SAG), which is defined as the ratio of SA after and before KOH etching, of the 85, 90, and 95 °C KOH-etched Si substrates estimated from a limited area of 100 μm×100 μm are about 1.17, 2.31, and 2.08, respectively. Note that the 90 °C-etched Si substrate has the largest SAG, which might be due to both the size and density of pyramidal cones are optimized. It was then used for the preparation of type B and type C in this study.

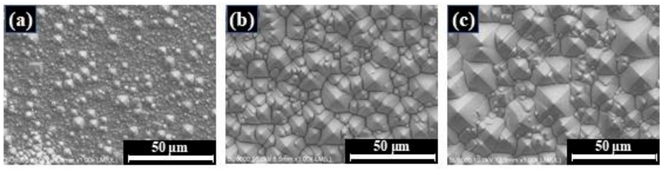


**Fig. 2** Top-view SEM images of Si (100) substrates after KOH/IPA etching at (a) 85 °C, (b) 90 °C, and (c) 95 °C for 40 min.

Fig. 3 shows the SEM images of MWCNT films sprayed on planar and 90 °C-KOH-etched Si substrates for different spraying times. It appears that the SA of MWCNT films on a planar Si substrate (Fig. 3(a)-3(d)) increases with increasing the sprayed-times, and more $H^+$ (or $OH^-$) adsorption sites for pH sensing could be expected. For the MWCNTs on the 90 ℃-KOH-etched Si substrate, one can see that MWCNT films obtained from 80, 120 and 160 sprayed-times still maintain conformity with the bottom pyramidal cones on Si substrate (Fig. 3(e)-3(g)). It found that at the MWCNT films obtained from 160 spraying times show the largest SA (SAG= 2.31). The samples obtained from 200 spraying times (Fig. 3 (h)) show a relatively poorer conformity caused by van der Waals force and a smaller SA as compared with the 160 spraying case.

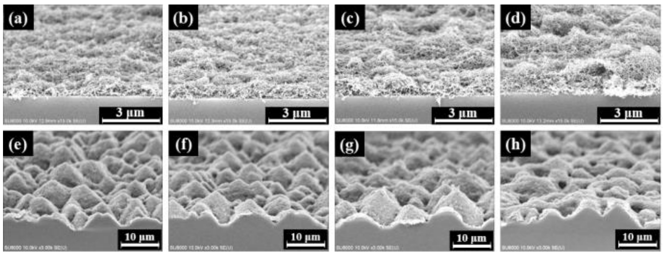


**Fig. 3** SEM images of MWCNT films sprayed on the planar Si substrate for (a) 80, (b) 120, (c) 160, and (d) 200 spraying times and on 90 ℃-KOH-etched Si substrate for (e) 80, (f) 120, (g) 160, and (h) 200 spraying times, respectively.

Fig. 4 shows the SEM images of the NiO NSs synthesized on MWCNT/pyramid Si substrate at 90 ℃ for different HTG times. The average SA and density of NiO NSs estimated within an area of 50 μm × 50 μm are summarized in Table I. The NiO NSs show a highly hierarchical upwards porous, which might be due to nuclei aggregation to a lamellar structure. [6] As shown in Fig. 4(a), the HTG-5 h sample only has a very thin NiO seed layer formed on the surface of MWCNTs. It is found that both the height and width of NiO NSs increase with increasing the HTG time in the range of 7 to 9 h (Figs. 4(b)-(c)). Nevertheless, the NiO NSs obtained from HTG-11 h shrink in size due to exhaust of reactant for a long-term reaction (Fig. 4(d)). Note that, the NiO NSs on Type C for HTG-9 h exhibited the largest SA of about 9,670 $\mu m^2$.

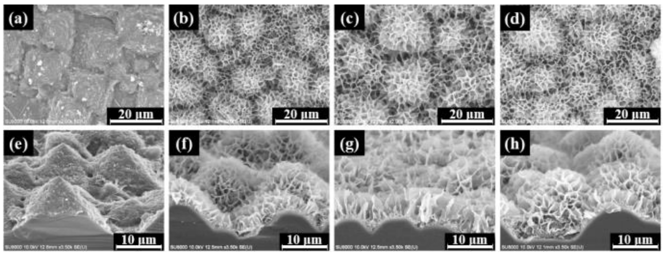


**Fig. 4** SEM images of the NiO NSs synthesized on MWCNT/pyramid Si substrate at 90 ℃ for different HTG times. (a) 5, (b) 7, (c) 9-, and (d) 11 h, respectively. (e)–(h) The cross-section SEM images corresponding to Figs. 4(a)–4(d), respectively.

**Table I** The estimated average SA and density of NiO NSs on MWCNTs

| Surface morphologies of NiO NSs | HTG time (h) 5 | 7 | 9 | 11 |
|---|---|---|---|---|
| The average height ($\mu m^2$) | - | 3.69 | 6.63 | 4.65 |
| The average length (μm) | - | 5.92 | 9.66 | 7.34 |
| Density of NiO NSs (no./ 50×50 $\mu m^2$) | - | 254 | 151 | 217 |
| Total SA ($\mu m^2$) | - | 5,548 | 9,670 | 7,406 |

Figs. 5(a) and 5(b) show the $I_D$–$V_R$ curves obtained from type A (160 times) and type B (160 times), respectively. The $I_D$–$V_R$ curves show a right shift with increasing the pH level, it is attributed to the decrease in amount of $H^+$ (or increase in $OH^-$) adsorbed on SEs lowers the electrical potential of therein. The ΔV–pH curves of type A (160 times) and B (160 times) is plotted in Fig. 5(c). It reveals that the sensitivity/linearity of type A and type B SEs are about 52.15 mV/pH/ 0.998 and 54.95 mV/pH/ 0.999, respectively. The comparison of pH sensitivity of type A and type B SEs based on MWCNT thin films with different sprayed times is illustrated in Fig. 5(d). Note that an enhancement in pH sensitivity of about 5% was obtained from type B SE as compared to that of type A SE, it thus confirms the effectiveness of the KOH-etching proposed in this study.

Figs. 6(a) and 6(b) illustrate the typical $I_D$–$V_R$ curves obtained from type C (9 h) SE and comparison of ΔV–pH curves of type B (160 times) and type C (5, 7, 9 and 11 h) SEs. The corresponding pH sensitivity and linearity are listed in Table II. According to Fig. 5(c) and Fig. 6(b), it is noted that the average isoelectric point (or point of zero charge) of MWCNT and NiO NSs/MWCNT are estimated to be about 10.05 and 10.15, respectively, indicating that both MWCNT and NiO NSs have negatively charged surface. Experimental results indicate that type C (9 h) SE exhibits a sensitivity and linearity as high as 57.56 mV/pH and 0.999, respectively. It suggests that proposed pH SEs with multiple roughening structure (NiO NSs/MWCNT/Pyramid-Si) could maximize SA and the number of ion adsorption sites for pH sensing.

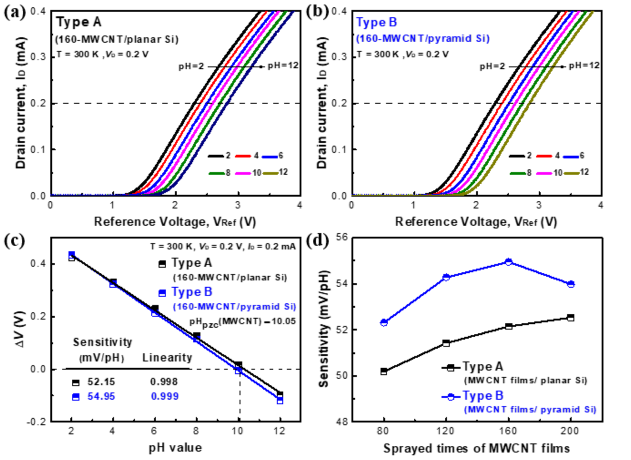


**Fig. 5** Measured $I_D$−$V_R$ transfer characteristics of the prepared pH sensor with SEs based on (a) type A and (b) type B. (c) Comparison of the ΔV–pH characteristics. (d) Sensitivity as a function of sprayed times.

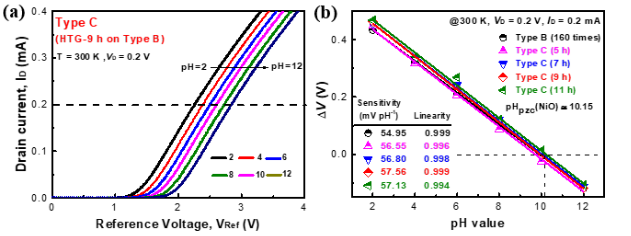


**Fig. 6** (a) Measured $I_D$−$V_R$ transfer characteristics of the prepared pH sensor with SE based on type C for HTG-9 h. (b) Comparison of the ΔV–pH characteristics of pH SEs prepared in this work.

**Table II** Sensing performance of pH sensors with Type C SEs

| Sensing performance | HTG time (h) 5 | 7 | 9 | 11 |
|---|---|---|---|---|
| Sensitivity (mV/ pH) | 56.55 | 56.80 | 57.56 | 57.13 |
| Linearity | 0.996 | 0.998 | 0.999 | 0.994 |

## 4. Conclusions

A multiple surface roughening scheme using MWCNTs, NiO NSs and KOH-etched Si substrates have been demonstrated to promote pH sensing performance. According to the pH measurement based on EGFET configuration, it has been clarified that SEs based on NiO NSs synthesized on MWCNTs/90℃-KOH-etched Si substrates could exhibit excellent pH sensing performance with a near-Nernstian response of 57.56 mV/pH and superior linearity of 0.999. Our experimental studies confirms that the use of a variety of different materials together with surface area enlargement through the proposed multiple surface roughening scheme could be very potential in improving the sensing performance of pH sensors.

## Acknowledgements

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