pH-sensing characteristics of multi-walled carbon nanotube sheet

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A hybrid nanostructure multi-walled carbon nanotube (MWCNT) sheet decorated with a nickel (MWCNT/Ni) was synthesized for utilization as a pH sensor. Different sizes of Ni particles were coated onto MWCNT sheets by electrodeposition, which is a simple fabrication technique for binary composites. Electrical resistance of the pH sensor increased linearly with an increase in pH value. The performance of the pH sensor was significantly influenced by Ni particle size, which was easily regulated by controlling the electrodeposition time. The measured output characteristics were stable, reliable, and reproducible.

1. Introduction

Measurement and control of pH is essential to observing many important biological and environmental signals, as pH values have remarkable effects in chemistry, biology, environmental monitoring and medicine. Recently, nanostructure carbon materials, including zero-dimensional fullerenes, one-dimensional carbon nanotubes (CNT), and two-dimensional graphene, have shown potential in pH sensor applications [1–3]. These materials have many advantages, including higher mechanical and chemical stability, a larger surface to volume ratio, and improved conductivity [4,5]. Especially, CNTs are well suited to sensor applications due to their graphite structure including higher mechanical and chemical stability, a larger surface area, well aligned distribution, and good adhesion to substrates. We fabricated the pH sensor using multisheets by overlaying multiple individual sheets (10 times). The electrodeposition method was employed to fabricate the nanocomposite sensor (MWCNT/Ni). As seen Fig. 2, this produced 10 ± 10, 70 ± 10, 100 ± 30, and 200 ± 20 nm thick composites.

2. Experimental details

Detail process of CNT growth is described in Ref. [11]. As shown in Fig. 1(a), the MWCNT sheets were produced by means of continuous pulling from the super-aligned MWCNTs onto the substrate. We fabricated the pH sensor using multisheets by overlaying multiple individual sheets (10 times). The electrodeposition method was employed to fabricate the nanocomposite sensor (MWCNT/Ni). As seen Fig. 2, this produced 10 ± 10, 70 ± 10, 100 ± 30, and 200 ± 20 nm thick composites.

3. Results and discussion

It is well known that sensor performance is highly dependent on the surface area of the sensing material. To determine the size of particles that confers the highest sensitivity, the size of Ni particles was controlled based on electrodeposition time. As shown in Fig. 2, the morphology and size of Ni particles on MWCNT sheets changed dramatically according to electrodeposition time. After 5 s, circle-shaped Ni particles with a 10-nm thickness were sparsely deposited onto the MWCNT sheet. After 15 s, the density and size of Ni particles increased to a thickness of 70 nm. When the time was increased to 30 s, the size of the Ni particles increased to 100 nm, and the particles formed connections with each other. At the longest time of 60 s, flower-shaped Ni particles formed while the CNT sheet was completely covered by Ni particles.
The XRD patterns of the sensor are shown in Fig. 3. Four characteristic peaks at 26°, 43.29°, 51.86°, and 76.39° were observed in the XRD patterns after electrodeposition. The characteristic graphitic peak of CNTs at 26° (002) was clearly observed. The second peak at 43.29° corresponds to planar NiO (200). The other two peaks located at 51.86° and 76.39° represent planar Ni (200) and Ni (220), respectively.

To evaluate pH-sensing characteristics, the sensor was immersed into buffer solutions with different pH values at room temperature. The sensitivity of the MWCNT sheet-sensor was determined using the following equation:

\[
\text{Sensitivity} (\%) = \left( \frac{R - R_0}{R_0} \right) \times 100
\]

where \(R\) and \(R_0\) are the resistances at any given pH value and pH 1, respectively. We experimentally found that the resistance of the MWCNTs was dependent on the pH range. Fig. 4 shows changes in the resistance of the MWCNTs in pH buffer solution within a pH range of 2–10. It demonstrated that resistance of the sensor increased with a higher pH value. It has been reported that changes in the electronic properties of MWCNTs are due to interactions...
between hydroxide ions (OH⁻) in the pH buffer solution and the surface of the MWCNTs [14]. Since hydroxide (OH⁻) groups are attached to the surface of the MWCNTs, the pH solutions will increase or decrease the resistance of the MWCNTs depending on whether the solution is acidic or basic. Previous study has shown that MWCNTs have a p-type property [12] which means that the majority of charge carriers are holes. When MWCNTs are immersed into pH solutions, hydrogen (H⁺) or hydroxide (OH⁻) ions interact with the carboxyl groups covalently attached to the MWCNTs. Hydrogen (H⁺) plays role as an acceptor in which one electron is transferred from the p-orbital of a nanotube to hydrogen (H⁺) ions bound to the surface of MWCNTs. This produces a positive hole in the MWCNTs and reduces their resistance [15]. On the other hand, hydroxide (OH⁻) ions cause the opposite effect, wherein transfer of electrons from hydroxide (OH⁻) ions to CNTs increases the resistance of the MWCNTs. Consequently, the production of holes or electrons in the MWCNTs is affected by the concentrations of hydrogen (H⁺) and hydroxide (OH⁻) ions in the pH solutions. The resistance of the MWCNTs is therefore altered by this charge transfer process.

On the other hand, the sensitivity of the pH sensor increased linearly with increasing electrodeposition time up to 30 s while decreased rapidly when the time was further increased to 60 s. The sensitivity of the pH sensor was dependent on the electrodeposition time and the optimum time for that size of Ni particles was approximately 30 s. It is well known that the surface area of a sensor has a dramatic effect on its sensing characteristics [13] Based on the Raman results (not shown here), longer electrodeposition processes were able to generate more oxidation and/or defects on the surface of the MWCNT/Ni composite, offering larger sites for attachment of H⁺ and OH⁻ ions [16]. Therefore, the sensitivity of the sensor was dependent on the concentrations of H⁺ and OH⁻ ions as well as the density of these defect sites. On the other hand, Ni articles mostly covered the CNT sheet after 60 s, which resulted in complete coverage of the MWCNT surface. This causes a hard reaction between the MWCNTs and H⁺/OH⁻ ions. The size of Ni particles played an important role in the pH response, as sensitivity can be related to the Ni particle surface area, which can be easily regulated by controlling the electrodeposition time. Meanwhile, the metal-oxide (NiO) mainly adsorbed H⁺ ions, and therefore the CNT/Ni could not readily adsorb OH⁻ ions. As a result, the sensitivity of the sensor increased less at high pH than at low pH when the size of Ni particles increased.

The sensing repeatability of a CNT-based sensor is an important parameter for evaluating performance, especially for pH sensors since they are usually used in liquid solutions that can modify the distribution and alignment of CNTs [17]. In addition, CNT-based sensors often exhibit resistance hysteresis when undergoing multiple tests, which suggests irreversible deterioration of MWCNT/Ni interfaces. Moreover, imperfect recovery of original resistance values after removal from pH solutions is a serious problem in regards to practical applications. This resistance drift is thought to be caused by damage and breakdown of the CNT shell structure as well as by the re-distribution of CNTs due to their low density in the sensor. In order to investigate the repeatability of the sensor, multiple tests were conducted within a pH range from 2–10. Fig. 5(a) shows that cyclic behavior was almost identical, with only minor hysteresis. This repeatability of the sensor can be attributed to robust firmness of the CNT/Ni interaction, providing excellent electrical contact between the Ni and CNT sheets. Furthermore, the resistance of the sensor showed good stability over 1 day of measurement. The stability of the sensor was the result of a steady as well as large contact area among the MWCNT/Ni through strong van der Waals forces.

One major strength of using a MWCNT sheet for sensor fabrication is that high flexibility can be achieved, which is obviously not the case with a metal or glass electrode-based sensor. During the bending test, bending was performed several times to confirm the flexibility of the pH sensor. After the bending test, no obvious visible modification in morphology was observed, and identical sheet resistance was observed regardless of the bending tests applied to...
the sheet. Similar sensitivities were confirmed before and after bending deformation (Fig. 5(b)). This performance might be due to the stability and flexibility of the CNT/Ni with the substrate.

4. Conclusion

We reported the fabrication and characterization of pH sensors using MWCNT sheets decorated with Ni particles. The pH-sensing properties of the composites were found to be highly dependent on the size of the Ni particles. The simple fabrication process along with stable response and high flexibility of the sensors will facilitate their applications in a wide range of areas.

References