

DURABLE SUPER-HYDROPHOBIC NICKEL SURFACES WITH A HIGH RUBBING RESISTANCE AND THEIR APPLICATION IN TRIBOELECTRIC NANOGENERATORS

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ABSTRACT

We introduce a superhydrophobic nickel surface strong that is highly robust against repetitive rubbing. We implanted carbon nanotubes (CNTs) to protect the surfaces from contacts. We show that the CNTs implanted in nickel (hereafter, CNT+Ni) do not easily detach from the surface and maintain superhydrophobicity despite harsh rubbing (40 kPa, 600 cycles) by 800 grit sandpaper, whereas surfaces prepared by typical nanofabrication methods are visibly damaged and lose superhydrophobicity after such treatment.

In addition, CNT+Ni has been used as a rotating electrode in a triboelectric nanogenerator (TENG). The short-circuit current (I_{SC}) and the open-circuit voltage (V_{OC}) were measured 10.52 mA and 20.34 V, respectively, at 1000 rpm. The TENG demonstrated an only 2% decrease in I_{SC} and V_{OC} after working continuously for 14 days.

INTRODUCTION

Commonly, superhydrophobic surfaces have water contact angle larger than 150° and water sliding angle smaller than 10° [1]. Artificial superhydrophobic surfaces need two core technologies. Usually, nano or micro scale papillae should be formed on the substrate surface and hydrophobic thin layer should be coated on the whole area which include papillae. While bio-inspired superhydrophobic surfaces were studied over the past decades [2-5], they are being diversely commercialized as cover glass of solar cell [6, 7], glass [8] and paint [9].

By virtue of the water-repellent and self-cleaning characteristics that it can impart, surface modification for superhydrophobic surfaces is in the limelight in applying surfaces engineered to have nanostructures in scientific and engineering fields [10]. In spite of strong demand for superhydrophobic surfaces in various industrial fields, it is difficult to fabricate such surfaces if they are to be accompanied by physical contact. When nanostructures are physically damaged, the damaged area of the surface loses its high contact angle and never recovers it.

There is a new approach to create durable superhydrophobic surfaces that have self-healing ability and can repair damage caused by external touching [11-14]. Self-healing method is the way to repair the damaged superhydrophobic surfaces without adding materials. Firstly, there is an approach based on encapsulation of hydrophobic components in the pores of rough nanoporous materials. When damaged, these hydrophobic components quickly migrate to the damaged surface and recover its superhydrophobic properties. In other way, this is worked by self-organization of hydrophobic colloidal at the interface. Otherwise, repairable method uses the way of

spraying nano-material to the defects of the surfaces.

However, the aforementioned approaches for self-healing and repairable surfaces do not guarantee survival of nanopapillae and the maintenance of superhydrophobic surfaces under harsh physical contact conditions involving strong rubbing or scratching. To solve this problem, many researchers have been trying to fabricate intrinsically durable superhydrophobic surface [15, 16]. However, all of the methods were confined to the hydrophobic materials such as PDMS or plastics, which make it difficult to apply to various surfaces.

In this study, we introduce a superhydrophobic nickel surface that is highly robust against strong and repetitive rubbing. As shown in Fig. 1d, we formed CNTs to protect the surface from contact. We show that the CNT+Ni surfaces are not easily detached from the substrates and maintain superhydrophobicity despite harsh rubbing by sandpaper. In addition, CNT+Ni has been applied to a triboelectric nanogenerator (TENG), which requires direct contact of nanostructured metal surfaces and polymer surfaces.

Until now, developed TENG's surfaces were easily broken on the direct contact condition. It couldn't get higher power generation density by using nanostructure that can increase the contact area. In this study, we suggest the solution of this problem with highly durable nanostructure.

EXPERIMENT

Fig. 1 illustrates the fabrication process of a CNT (CM-250, Hanwha, Korea)-implanted nickel substrate. The fabrication of the substrate starts with the preparation of a CNT-dispersed PDMS (polydimethylsiloxane)(Sylgard 184, Dow corning, USA) mold (Fig. 1a). A copper mesh (CU-118100, Nilaco Corporation, Japan) is embedded at the bottom of the CNT-dispersed PDMS precursor and cured together. The copper mesh is utilized to enhance the conductance in the subsequent Ni electroforming process (Fig. 1c).

The CNT-dispersed PDMS mold is fabricated by etching of the PDMS skin at its top surface (Fig. 1b). The solidified CNT-dispersed PDMS is immersed in the PDMS etching solution. Wet etching of PDMS was done at room temperature and under continuous stirring (500 rpm) in a solution of N-methyl pyrrolidinone (NMP) (Alfa Aesar, USA) and tetra-butyl ammonium fluoride (TBAF) (75 wt% in H₂O, Alfa Aesar, USA). The ration of NMP to TBAF/water was 3:1.

Then, nickel electroforming to a thickness of 100 μm is conducted by the use of a nickel electroplating solution based on sulfamic acid (Fig. 1c); the fabrication process is

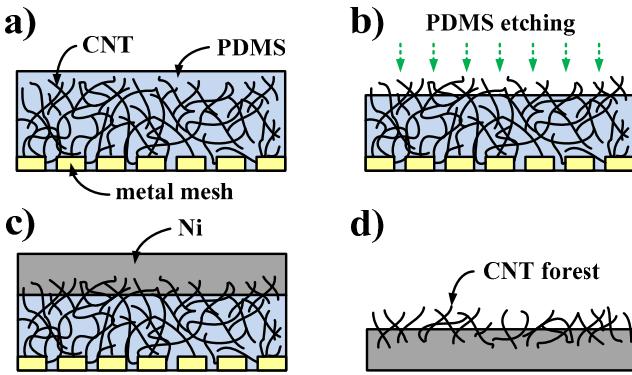


Figure 1: Fabrication process of CNT+Ni surface. (a) Fabrication of CNT-dispersed PDMS mold. (b) PDMS wet etching with NMP/TBAF solution. (c) Nickel electroplating. (d) Detachment of nickel sheet from CNT-dispersed PDMS mold.

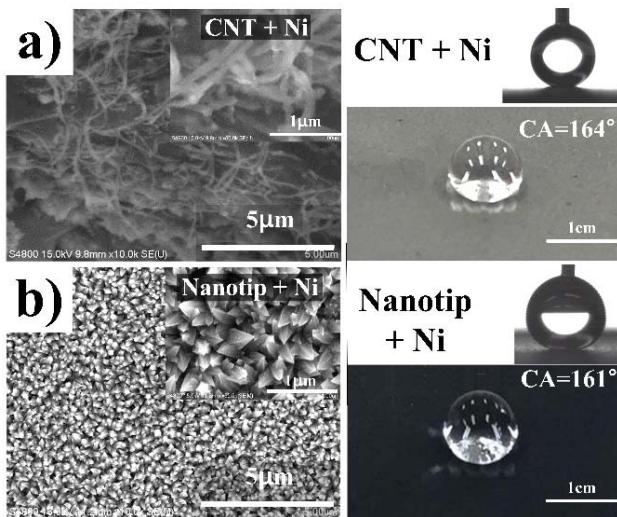


Figure 2: (a) SEM image and water contact angle of CNT+Ni surface, (b) SEM image and water contact angle of nanotip+Ni.

finished with the detachment of the electroformed nickel from the CNT-dispersed PDMS mold (Fig. 1d). In this process, CNTs are pulled out from the PDMS layer due to higher clamping force of nickel sheet.

For comparison, a nanostructured surface covered with nickel nanotips (hereafter, nanotip+Ni) has been fabricated. We obtained the nanotips using ethylenediamine dihydrochloride (EDA·2HCl, SIGMA-ALDRICH, USA) solution with a current density of 10 mA/cm² at 60 °C for 5 min on copper substrate. Finally, surface have hydrophobicity with PPFC(plasma polymerized fluorocarbon) coating method. Figs. 2a, b show scanning electron microscopy (SEM) images of the surface of the CNT+Ni substrate and the nanotip+Ni substrate, respectively.

RESULTS AND DISCUSSION

The fabricated CNT+Ni and nanotip+Ni surfaces are shown in Fig. 2a and Fig. 2b, respectively. Fig. 2a demonstrates CNTs forest on the fabricated surface. Both

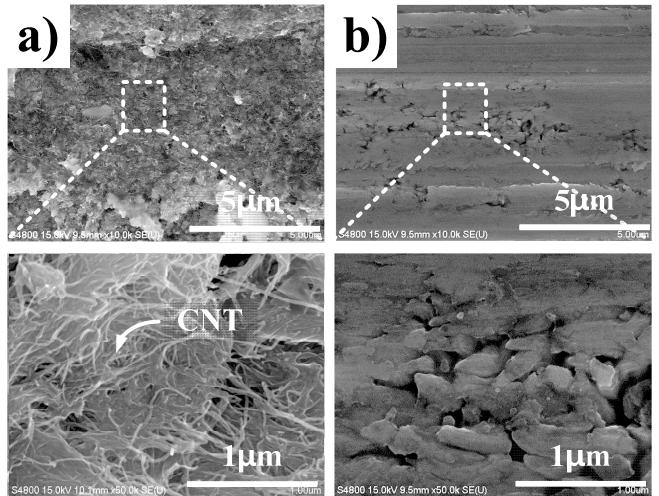


Figure 3: SEM image of substrate after friction test using sandpaper. (a) CNT+Ni surface, after 40 kPa, 600 cycles, CNTs remained on the surfaces after the wear test. (b) Nanotip+Ni surface, after 10 kPa, 100 cycles, lost their nanostructure after the wear test. Both tests used 800 grit sandpaper.

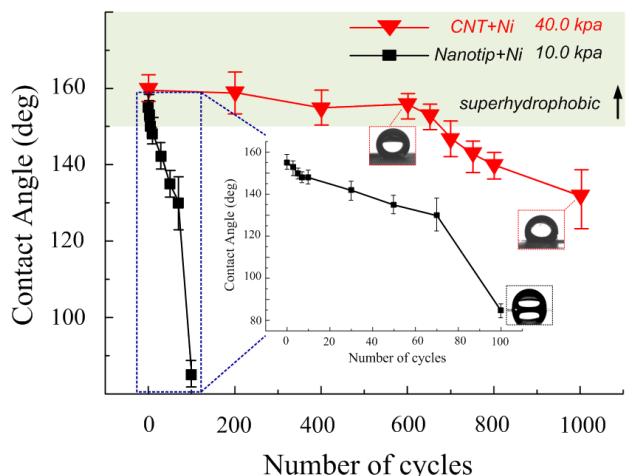


Figure 4: Comparison of durabilities between CNT+Ni and Nanotip+Ni surfaces. Inverted triangle(▼): CNT+Ni, 40 kPa applied, after 40kPa, 650 cycle, lost their superhydrophobic property. Square(■): Nanotip+Ni, 10 kPa applied, after 10kPa, 10 cycle, lost their superhydrophobic property.

surfaces exhibit superhydrophobicity, with water contact angle (CA) higher than 150°. Measured contact angle for CNT+Ni and Nanotip+Ni was 164°, 161° each.

Fabricated surfaces have superhydrophobic properties. Because CNTs basically have hydrophobic properties and whole surfaces covered with CNTs [17]. The nanotip+Ni have superhydrophobic properties with fluoro radical of PPFC coating.

These surfaces, consisting of a CNT forest and nickel nanostructure on nickel surfaces, were studied using scanning electron microscopy(S-4800, HITACHI, Japan).

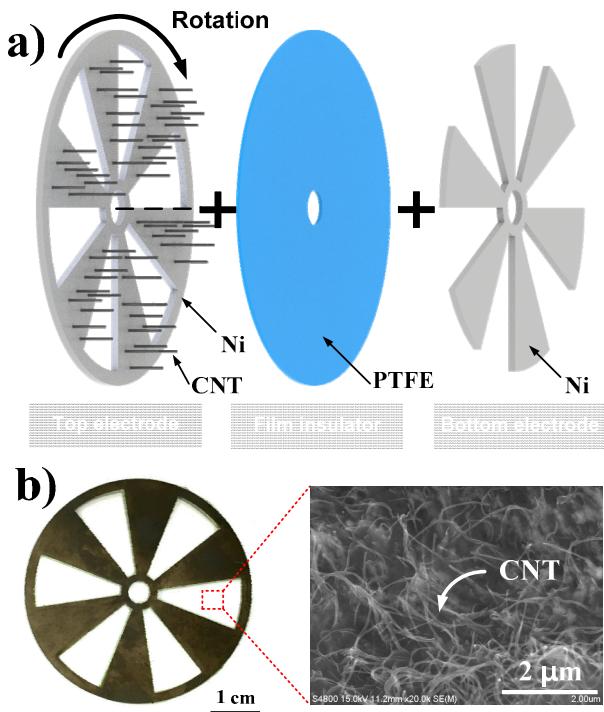


Figure 5: (a) Composition of rotation-type TENG using a CNT+Ni electrode, (b) Fabricated CNT+Ni top electrode.

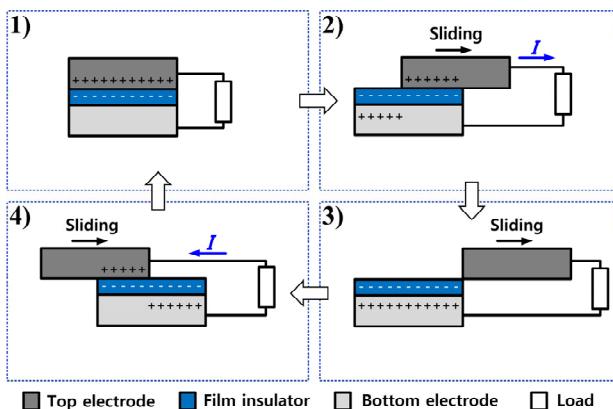


Figure 6: Working principle of the rotating TENG.

While the nanostructures on the nanotip+Ni surface were found to entirely disappear after the wear test (condition: 10 kPa, 100 cycles) using 800 grit sandpaper (Fig. 3b), nanostructures on the CNT+Ni surfaces still survived after the harsh test conditions (40 kPa, 600 cycles) (Fig. 3a). As long as the nickel region where CNTs are implanted is not removed perfectly by friction of sandpaper, remained CNTs on the surfaces can keep hydrophobic properties. But in the case of nanotip+Ni surface, it is difficult to maintain its superhydrophobic properties because nanostructures are destroyed instantly by rubbing.

The nanotip+Ni surfaces lost their superhydrophobicity after the wear test (inverted triangle(\blacktriangledown) in Fig. 4) after 10cycle. However, the CNT+Ni surfaces retained their superhydrophobicity ($CA > 150^\circ$) even in much harder test conditions (square(\blacksquare) in Fig. 4). And CNT+Ni surfaces lost superhydrophobic properties at least 650 cycles. We also investigated the potential of this

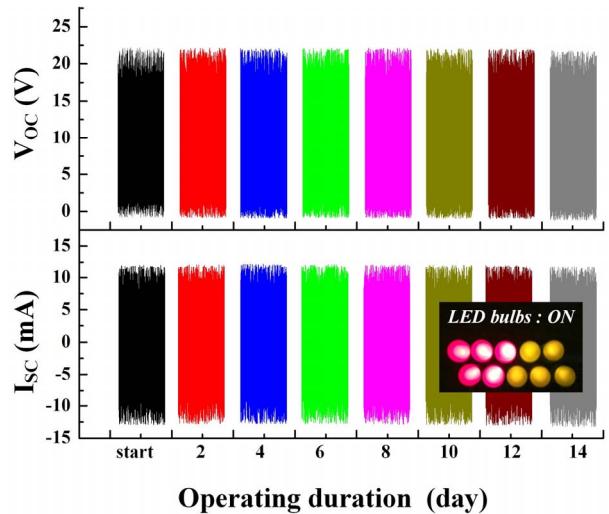


Figure 7: Mechanical robustness test results of the TENG. The LED bulbs were “ON” after 14-day running test.

surface for use in the development of a triboelectric nanogenerator (TENG).

The TENG consists of three layers (Fig. 5a), which were sequentially stacked from the top as top electrode (CNT+Ni), film insulator (PTFE), and bottom electrode (Ni). The fabricated CNT+Ni top electrode is shown in Fig. 5b. Fabricated top electrodes have dark color different with pure nickel due to CNTs.

Fig.6 shows power generating principle of TENG(Lateral sliding mode). In the fully contact state, surface is charged with triboelectrification(1). Charge symmetry breaking occurs when rotating makes the contact area smaller so that current circulates through outer electrode until charge symmetry is restored(2). If not contacted, bottom electrode becomes charged (3) and current circulates as the contact area is increased(4). By repeating this process, Alternating current circulates continuously between two electrodes.

Embedded CNTs on the surface improved the performance of the TENG. The instantaneous short-circuit current I_{SC} and the open-circuit voltage V_{OC} were 10.52 mA and 20.34 V, respectively, at 1000 rpm. The TENG demonstrated an only 2% decrease in I_{SC} and V_{OC} after working continuously for 14 days (Fig. 7).

CONSLUSION

A nanostructured surface that is highly robust against strong and repetitive rubbing has been developed. CNTs were implanted into nickel so that they could not be easily detached from the surface; these CNTs were able to maintain their superhydrophobicity despite harsh rubbing condition using sandpaper.

In addition, a TENG was developed using a CNT+Ni plate as its rotating electrode and showed excellent durability in a sustainability test.

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