Fabrication and Design of Carbon Nanomaterials Based Scale Monitoring Smart Sensor Systems

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ABSTRACT

The deposition of scale in oil pipelines leads to unavoidable damage of the equipment parts. Therefore, suspension of oil operations becomes essential to replace the damaged parts. Such interruptions are escorted by extremely high costs. In this paper, we report the fabrication of a new type of sensor and system for complete online monitoring of scale deposition with great accuracy and reliability. The fabricated sensors are based on CNTs and graphene. The sensors are fixable that can cover large area of the pipelines. Two different methods are used to prepare the CNMs sensor; smear casting and the inkjet printing technique, in addition, the sensor is integrated into membrane structure and fabricated in cleanroom.

Keywords: scale, sensors, carbon nanotubes, graphene, inkjet printing.

1 INTRODUCTION

Carbon nanomaterials (Carbon nanotubes (CNTs), graphene etc….) have received considerable attention as a new class of nanomaterials since their discovery in by Lijima 1991[1]. The sp^2 carbon–carbon bond in the plane of the graphene lattice is among the strongest of all chemical bonds. CNTs show unique mechanical, chemical and physical properties [2, 3 4] which led to a variety of applications, i.e. nanofluids[5-8], scanning probes[9], sensors[10 11, 12], grease [13, 14], nanocomposites[15 16] and electron magnetic shielding interface [17-19]. Scale is the creation of inorganic soluble salts from aqueous brines during the oil and gas production, which deposits at the internal surface of the pipelines under the supersaturation conditions. It is often managed or mitigated by the use of scale inhibitors. The current industry practice for managing scale programs relies on the determination of scale inhibitor concentration in the scaling brine and then relates this concentration to program performance. In most cases, scale inhibitors tailored to the specific oil well are used. Often, monitoring and testing for scales requires offline sample testing which impacts safety and productivity. The deposition of the scale leads to unavoidable damage of the equipment parts. Therefore, suspension of oil operations becomes essential in order to replace the damaged parts. In petroleum industry, such interruptions are escorted by extremely high costs. There has been multiple studies and research conducted on scale monitoring, testing and optimization of inhibitors [20 21 22]. In general, these studies focused on the development of using new sensor materials that enabled monitoring and offline testing. In this paper, the sensitivity and selectivity of CNTs and graphene to detect scale in oil and gas pipelines for online monitoring is dicussed.

2 EXPIREMENTAL PART

Single wall carbon nanotubes (SWNT) were purchased from sigma Aldrich USA Inc. in. The CNTs inkjet “CNTRENE® 3015 A3-R” used for this printing was purchased from Brewer Science, Inc USA. DMP2831 Inkjet Printer was used to print the CNT inkjet and the recipe was optimized. The chemical surfactant sodium dodecyl benzene sulfonate (NaDDBS) were purchased from Sigma–Aldrich. Epoxy resins and hardener were purchased from west system Inc, Zayed port Abu Dhabi. Releasing agents, Frekote, were purchased from Logistics Company Limited, in Dubai, UAE. Sonication was performed using a Branson Digital Sonifier, model 450. Scanning electron microscopy (SEM) images were acquired using the backscattered electron detector on a Zeiss Supra40VP variable pressure system. The electrical conductivity was obtained by Elite 300 Semi-automatic Probe Station & Keithley 4200-SCS Parameter Analyzer.

Casted technique: NaDDBS surfactant was added to epoxy with a weight ratio of 4 times carbon nanotubes and mixed manually for five minutes. The mixture was then sonicated until the surfactant was dissolved completely and clear solution was obtained. 0.5 weight percentage of carbon nanotubes were added to the mixture and sonicated again. The mixture was then mixed manually for 5 min with hardener by weight ratio of 10:2.63. Glass plate was coated with a layer of releasing agent (freekote) and the mixture was casted on the glass plate by smear casting technique. The sample was cured at room temperature for 24 hours. The CNTRENE® 3015 A3-R ‘the CNT ink used for this printing’ was purchased from Brewer Science, Inc USA. DMP2831 Inkjet Printer was used to print the CNT inkjet and the recipe was optimized in order to have a very uniform continuous printing.

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3 RESULT AND DISCUSSION

As it was stated early two different techniques were used to prepare the carbon nanomaterials used to fabricate the sensors; smear casted technique and the inkjet printing technique.

3.1 Smear Casting Technique

Figure 1 shows the dispersion of the CNTs in the epoxy matrix. As it can be seen in the figure the CNTs are dispersed very will among the matrix and form a network structure.

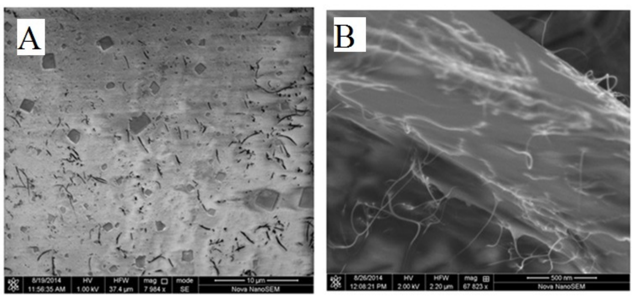


Figure 1 SEM images for A: surface, B: cross section of the 1.0 wt % of CNTs in epoxy.

Electrical characterization was conducted on the CNT-epoxy to determine the conductive path within the sample Fig. 2 shows the IV curve for a voltage sweep of 0-1 V. The resistance was found to be about 40.00 kΩ. This is because of a good dispersion of the CNTs into the epoxy resin and the network structure that the CNTs has formed as it can be seen in the SEM images figure 1. One drop of brine solution was added to the same film and the resistance was measured again and was found to be about around 90.00 kΩ. As it noticed that adding one drop of brine changed the electrical rsistance of the CNTs casted film. The film was washed with water and the electrical resistance measured again and found close to electrical resistance of the virgin sample.

After adding a drop of brine solution to the surface of the CNTs casted film, EDAS was conducted in order to detect the brine on the film. figure 3 shows SEM images for the surface of the casted CNTs. As it can be seen on the figure there are some white sopts, which was anticipated to be sodium chloride, therefore EDAS was performed. Figure 4 shows the EDAS spectrum for the white sopte marked with red cross as it can be seen in figure 3. As it can be seen in the spectrum, the sample has sodium and chlorine which confirms the presence of the brine solution.

Conductive atomic force microscopy C-AFM was carried out for virgin and with brine sample. The C-AFM of casted CNTs shows that virgin sample is more conductive than the with brine sample which matches the resistance curve for virgin sample that has less resistance. For with brine sample the CAFM shows less conductivity with higher resistance than virgin sample as it is shown in figure 5.

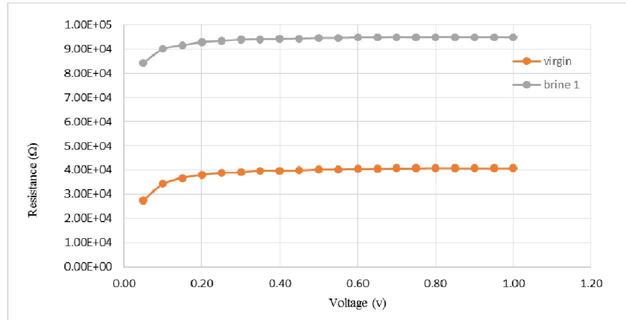


Figure 2 Four-probe voltage-resistance curve of nano-composite showing modulating resistance of the virgin sample in response to brine and DI water

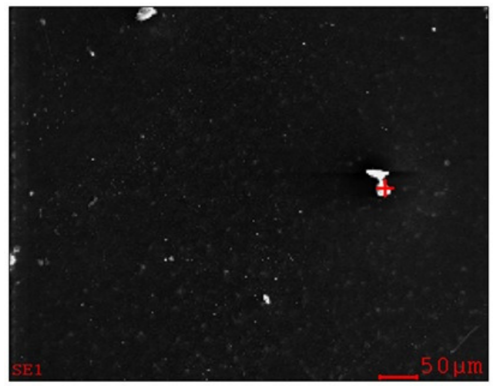


Figure 3 SEM image for the surface of smear casted CNTs shows a spot of NaCl.

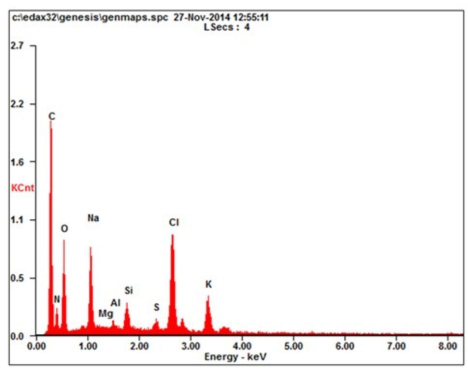
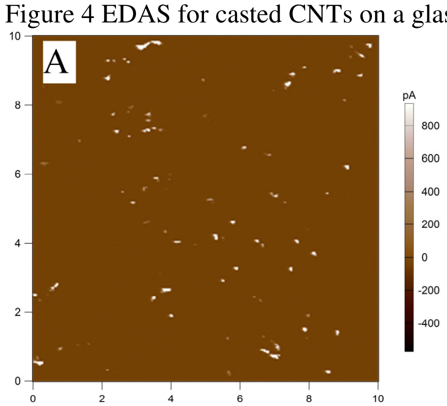


Figure 4 EDAS for casted CNTs on a glass substrate



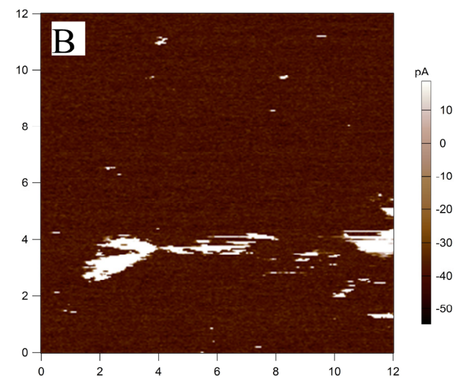


Figure 5 CAFM for current mapping of rough casted CNTs, A: Virgin sample B: with brine sample

3.2 Inkjet Printing Technique

3.2.1. Carbon nanotubes inkjet printing

The CNTs inkjet was printed on a silicon oxide substrate using DMP2831 Inkjet Printer. Fig 6 is an SEM image taken by Helios SEM shows that CNTs are bundles of CNTs that form network structure.

In general, the electrical conduction in such nanocomposites occurs either (1) tube−tube within the same bundle, (2) between neighbor bundles through their contacts. Therefore, the electrical conductivity (σ) depends on the conductivity of the nanotubes themselves and the ability of the electric carriers to tunnel between adjacent nanotubes or adjacent bundles.

The electrical resistance of the virgin CNTs inkjet printed was measured and found to be 1.00E+03 ohm. Figure **7** shows the ability of resetting film that made of CNTs inkjet printing. It was found that washing the film with DI water for one hour is essential to obtain a consistent electrical resistance. The electrical resistance for the virgin film made of CNTs inkjet printing is 1.0E+03 ohm by dipping the film for one hour in DI water the electrical resistance decreased to 5.0E+02 ohm. Adding one drop of brine increases the electrical resistance up to 4.2E+03 ohm and decreases with sweeping voltage to 3.6E+03 ohm. By immersing the film for one hour in DI water we were able to obtain an electrical resistance very close to the electrical resistance that was obtained after the DI water treatment.

3.2.1. Graphene inkjet printing

The graphene inkjet was printed on a silicon oxide substrate using DMP2831 Inkjet Printer.

The graphene inkjet printed film was subjected to two resetting cycles. As it is seen in fig 7 the virgin's electrical resistance is almost found to be 4.00E+03 ohm. Adding one drop of brine increases the electrical resistance to 9.00 E+03 ohm. The first resetting decreases the electrical resistance. The electrical resistance was found to be close to the electrical resistance of the virgin sample when the measurement was done after two days from the first reset. Adding a drop of brine for the second tine obtained the

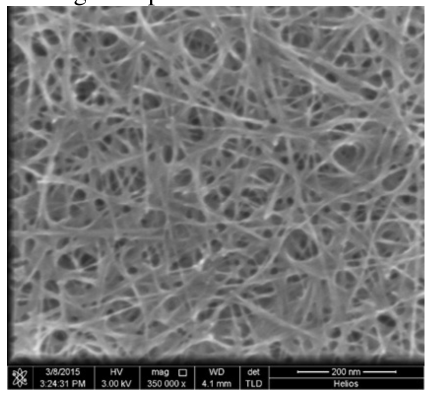


Figure 6 SEM image for CNTs inkjet printing

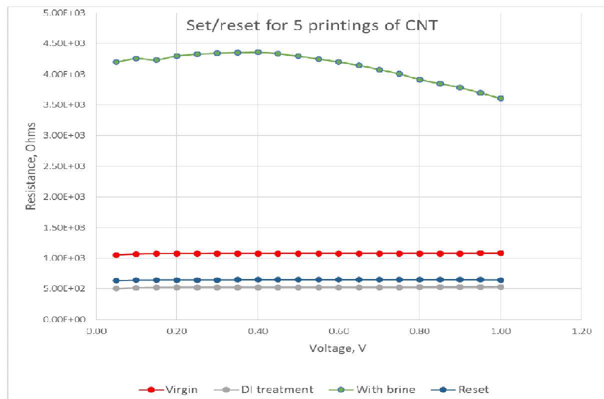


Figure 7 ability to reset the resistance values for 5 layers of CNTs printed on silicon oxide substrate.

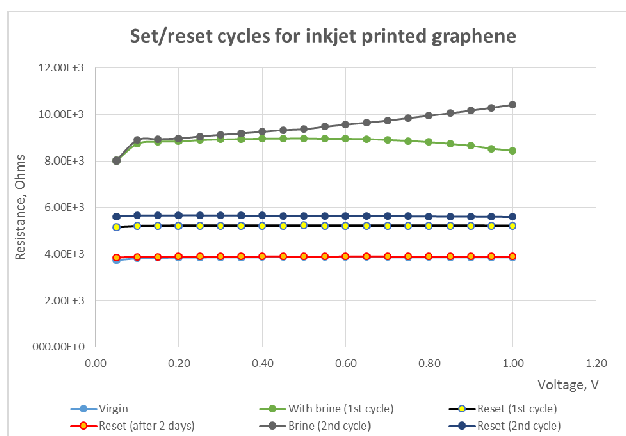


Figure 8 ability to reset the resistance values for 5 layers of graphene printed on silicon oxide substrate

same electrical resistance that was obtained for the first time that brine was added; in addition, the second resetting was close to the same values for the first resetting value.

3.3 Sensor Fabrication

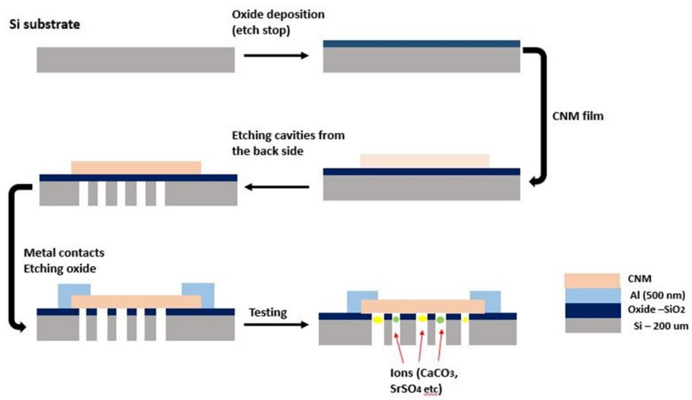


Figure 9 process flow of the membrane structure

Figure 16 shows the process flow for membrane structure. Sensor design and operation principle is based on a piezoresistive effect observed in carbon nanotubes, which undergo changes in their band structures when subjected to mechanical deformations. This phenomenon makes carbon nanotubes applicable for strain sensing applications. Fabrication steps are described in figure 16. The sensor design requires through silicon vias of different aspect ratio (with diameter in a range 20-50 µm) which can be formed using DRIE technique. In this case a layer of SiO2 is deposited on the front size to have an etch stop layer. On top of oxide layer, we apply a carbon nanomaterial film; inkjet printing technique is used for this purpose. Formation of cavities on the backside is implemented with dry etch method followed by wet etch in hydro fluoride solution to remove the oxide. Metal contacts are deposited on top of the films using thermal evaporator for further electrical testing.

4 CONCLUSION

Two methods were used to prepare the carbon nanomaterials for the sensors fabrication; casting technique and inkjet printing technique. In addition the sensors were integrated into membrane structure. The electrical resistance of both CNTs smear casted and CNTs& graphene inkjet printed were measure with and without using brine. Adding one drop of brine solution on the top of the sensor surface changed the electrical resistance by 50% 60% and 75% for the smear casted CNTs, inkjet printed CNTs and inkjet printed graphene respectively. The re-setting process was done successfully by soaking the sensors in DI-water for some time. SEM and AFM images show that the CNTs are dispersed in bundles and form network structures.

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