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利用課題名（日本語） :カーボンナノウォールの物性と応用
Program Title (English) :Properties and Applications of Carbon Nanowalls
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1. 概要（Summary）

Among other plasma techniques, microwave plasma enhanced chemical vapor deposition (MPECVD) is commonly used for the growth of carbon nanowalls (CNW). The deposition of CNWs, self-assembled vertically-standing few-layer graphene material, on Si and Si-based substrates, metal foils or other dielectric supports had been established as a part of our previous investigations.
Currently we continue the work based on CNWs grown at Toyota Technological Institute by MPECVD for: 1) the evaluation of CNW deposition by MPECVD on several technological surfaces and different processing conditions; and 2) applications of CNW as templates or functional surface materials. Particularly, i) Bi-based MOCVD of nanoparticles, ii) CNWs as potential high power anode for Li-ion microbatteries, iii) relative Humidity sensor system based on CNWs and iv) CNWs for supercapacitors and high frequency applications are being tested.

2. 実験（Experimental）

Please refer to previously reported publications for background of experimental materials for detailed description. Details for below presented applications are embedded with the results text.

- Structured Nanocarbon on Various Metal Foils by Microwave PE-CVD Rius,G & Yoshimura, M
J. Phys.: Conf. Ser. 417 012010 (2013).
- Synthesis Control for Carbon Nanowalls on Copper Supports pro Development of Green Energy Applications Rius, G & Yoshimura, M e-J. Surf. Sci. Nanotech., Vol. 10 pp. 305-309 (2012).

3. 結果と考察（Results and Discussion）

We specify the progress on CNWs applications as follows.

i) Bi-based MOCVD of nanoparticles,

CNWs are being tested as templates for the synthesis of Bi-based nanoparticles, such as nanospheres and nanoplates, as well as their application as porous surfaces for biosensors and batteries devices. This work is collaboration with the Politecnico Torino (Italy), Prof Alberto Tagliaferro.
The synthesis of Bi materials is performed by metal organic CVD (MOCVD), but mechanisms and conditions for the formation of Bi-based nanoparticles have not being extensively studied and comprehended. We are studying the effect of both the chemical elements (e.g. supports) present (and affecting) during growth in terms of rate and Bi shape and elemental contents, as well as the effects of using structured support as templates, for example CNWs (Figure 1). Under certain conditions bismoclite nanoplates can be obtained, which is similar to reference substrate materials such as silica (Fig. 1 left).

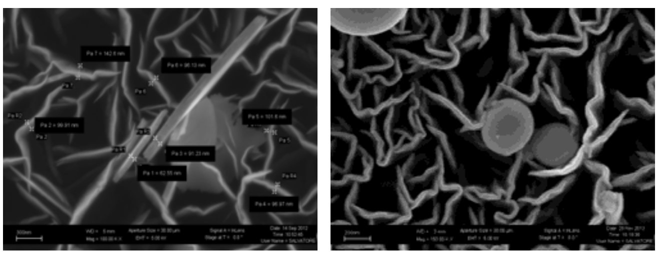

Figure 1. (Left) Top view SEM images of Bismuth nanoplates grown by MOCVD on CNWs. (Right) Examples of metallic spherical Bi nanoparticles obtained by MOCVD on CNWs.

However, using specific conditions, such as remote growth strategy often used in MOCVD, metallic Bi nanospheres can be obtained, instead of plate-shaped non-metallic bismoclite nanoparticles (Figure 1, right). We hypothesize if the presence of amorphous carbon on the CNWs surface may be the main factor to reduce bismoclite into metallic bismuth. Additionally, understanding the role of the porous microstructure of CNWs, as morphological constraint, will be considered. Among next term actions, the thermal stability of CNWs will be studied (e.g. by TGA), as well as more detailed chemo-structural analysis, combined XPS and Raman spectroscopy, will be performed on CNWs, as template materials.

ii) CNWs as potential high power anode for Li-ion microbatteries

Carbon is being used as anode in secondary lithium ion batteries (LIB) since their early commercialization. The widely used cobalt/graphite-based LIB has drawbacks; it offers relatively low charge/discharge currents. A high load would overheat the pack and its safety would be jeopardized. In the present case, we have studied the possibility of using CNWs as a potential high power anode to be used in microbatteries for power tools, medical devices and transportation systems. CNWs were deposited on Cu and carbon nanofibers (CNF) on stainless steel (SS) foils by MPECVD technique.

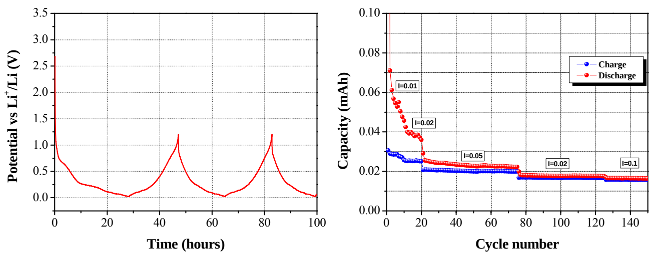

Figure 2 Ambient temperature galvanostatic cycling behavior: potential vs. time charge/discharge curves of CNW deposited on Cu (left), capacity vs. no. of cycles in a cell Li/ standard liquid electrolyte/ CNW_Cu (right).

Preliminary tests carried out on lithium cells exhibited interesting characteristics and a thorough investigation (e.g., modeling, simulation, etc.) is necessary to completely understand their electrochemical behavior. The preliminary results of galvanostatic charge-discharge cycling of CNWs deposited on Cu at different current rates are reported in figure 2. The potential vs. time current/cycle profiles are slightly different from the standard behavior of graphitic carbon, which is probably related to the presence of disordered carbon in the CNW deposits. However, one of the highlight of the material is that even if we increase the current rate to higher orders the capacity is not dropping down. So, one of the interesting investigations is to understand the role of CNW nanostructure and its disorder, and then take possible steps to control and make use of these characteristics.

Similar work was carried out on the carbon deposited on SS, which consists of CNFs. The results are encouraging as well, showing remarkable cyclability and stability thorough the cycles. A similar approach to control the disordered states in carbon must be adopted for those samples as well.

In summary, the nanostructured carbons deposited by MPECVD on various substrates are promising and worth continuing towards achieving a high power anode for lithium ion micro-batteries.

iii) Relative Humidity sensor system based on CNWs

Characterization of the electrical resistivity of the CNWs thin film of deposited on gold electrode is performed in a controlled humidity chamber, in which the relative humidity can be varied between 5% and 98%, while keeping the temperature of the measuring environment constant at 19 or 40 °C.

In this chamber, compressed air (1) is separated into two fluxes: one is dehydrated over a chromatography alumina bed (2) while the second one is directed through two water bubblers (3), generating, respectively, a dry and a humid flow. Two precision microwave (4) allows to recombine the two fluxes into one by means of a mixer (5) in order to adjust the RH content while keeping constant the testing conditions: a flow rate of 0.1 l/s at 1 m/s. Then, the relative humidity cannot be increased in a continuous mode, but as set point values. The bubblers, the coils (6) through which the two fluxes passed in, the mixer and the measurement chamber (7) were immersed in a thermostated water bath

(8), which in this case was operated at 19 or 40 °C. A commercial, humidity and temperature probe (9) was used as reference for temperature and RH values (Delta Ohm DO9406, accuracy: ±2.5% in the 5–90% RH range).

Based on the sensing mechanism, signals of CNWs film deposited on gold electrode are eliminated by an external alternating voltage of this electrical circuit (V = 3.6 V at the rate of 1 kHz). A 2000 Keithley digital multimeter is used to measure the tension VDC at the output of the circuit. The sensor resistance was determined by substituting them, in the circuit, by known resistances and then plotting a calibrating curve R=f(VDC). Two sensors of each composition were tested at a time.

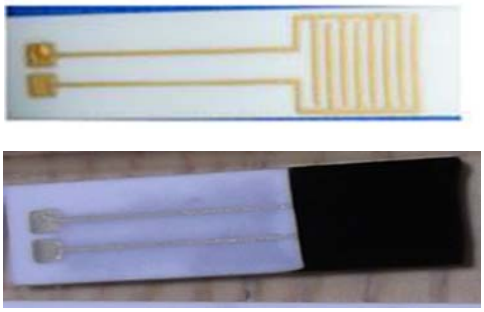

Figure 3 (Top) Interdigitated gold electrode deposited on alumina. (Bottom) CNWs thin film deposition on gold ceramic electrode.

Interdigitated gold electrodes are used for sensor assembly: starting from a commercial ink (ESL EUROPE 8835 (520C)), the gold paste is screen-printed onto a α-Al2O3, having a thickness of ~1-3 µm. CNWs were deposited non-selectively on the electrodes and ceramic support by MPECVD (Fig. 3). However, the sensor response of the deposited CNWs sample for RH% sensing was negligible or null. We are now testing the same approach on interdigitated electrodes using Pt instead of gold.

iv) CNWs for supercapacitors and high frequency applications.

The same MPECVD materials, in particular the CNWs deposited on conductive supports, are also considered for supercapacitor devices, in collaboration with Cambridge University (UK), Professor Amaratunga's lab. As mentioned, the advanced version of the project includes applying additional patterning and diversification of substrates, which is a challenging work in terms of growth engineering and synthesis knowledge, as well as, dedicated electrochemical characterization. Results for CNW supercapacitor devices obtained to date are presented next.

Recently, in 2010, Miller et al. demonstrated that CNWs structured nanomaterials were ideal for high frequency operation. The high porosity and conductivity of these electrodes was shown to perform at ac frequencies, something not yet achievable by electrochemical capacitors, which opens up a variety of applications previously reserved for bulkier electrolytic capacitors.

Some of our own results fabricating high frequency capacitors based on CNWs have shown promising performance (Figure 4). In this case, the CNWs are prepared by MPECVD directly on Cu foils. Full capacitors are fabricated from cellulose based separator soaked in 1M propylene carbonate sandwiched between two CNW electrodes and packaged in a coin cell configuration. The fabricated devices were characterized using an Autolab potentiostat system.

The cyclic voltagrams resulting from these CNW devices are shown in Figure 4 (left), and compared to that of an activated carbon device (right). Although the capacitance is higher for the activated carbon, as expected from higher mass content and film thickness, it should be noted that the CNWs maintain their "near-ideal" shape even at 5 V/s, whereas the internal resistance quickly distorts the activated carbon voltagrams beyond 0.1 V/s.

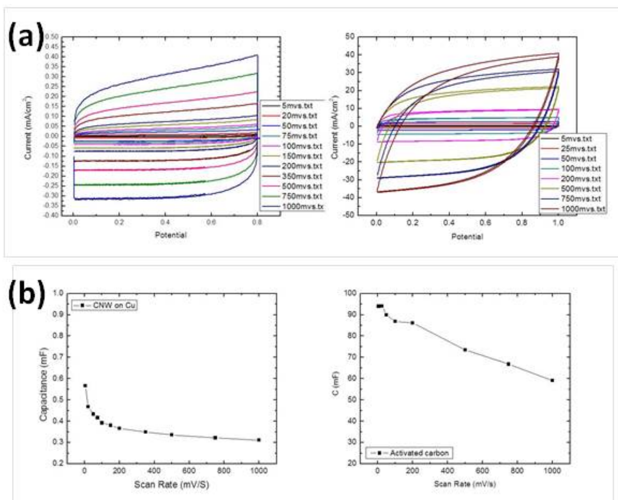

Figure 4. (a) Cyclic voltagrams at varying scan rates for CNW devices (left) and activated carbon devices (right) (b) the effect of cycling rate on the capacitance of the device.

As expected, AC impedance characterization also revealed significantly lower ESR than that of activated carbon device. The faster ion and electron transport through the device results in an overall lower ESR, which in turn translates into a better response at higher frequencies. The CNW capacitor is observed to maintain its capacitive behavior over 100 Hz, whilst the activated carbon device degrades at much lower frequencies.

In conclusion, EC electrodes fabricated from CNWs on metal may open up a new array of applications such as ac line filtering, currently limited to electrolytic capacitors due to their frequency response. This is an excellent example of how device functionality and features may be tailored by controlling the nanoscale morphology of a particular material.

5. 論文･学会発表（Publication/Presentation）

Publications

(1) P. Hiralal, G. Rius, P. Andrew, M. Yoshimura and G. A. J. Amaratunga Tailoring Carbon Nanostructure for High Frequency Supercapacitor Operation. Accepted J Nanomaterials

(2) P. Hiralal, G. Rius, M. Yoshimura, G. Amaratunga. Graphene based Electrochemical Capacitors. Chapter for the Handbook of Graphene Science, Taylor and Francis Ed. (Under revision)

(3) Miniaturization of Bi nanoparticles deposition on CNW templates. (In prep.)

(4) Characterization of Li-ion batteries based on CNWs. (In prep.)

Conference presentations

(1) G. Rius, P. Hiralal, M. Yoshimura and G. Amaratunga. Physical Vapor Deposition of Carbon Nanowalls for Charge Storage and Field Emission Applications. Recent Progress on Graphene Research (Tokyo September 2013) (Poster)

(2) G. Rius Role of graphene as a modifier of metal surfaces for electrochemical cell charge storage. EMN Spring (Las Vegas, USA 2014) (Invited talk)