High Electrical Conductivity Graphene Hybrid Composite Synthesized With Catalyst Stagger

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ABSTRACT

In the present report, the graphene hybrid composites were synthesized by the unoxidizing pyrolysis of salt-milled solid carbon precursors. The synthesis process using solid state precursor (SPNT) which had been reported [1] [2] is different from conventional process utilizing gas decomposition. In this process, the graphene hybrid composite products were synthesized using specific iron catalyst. The measurement of bulk electrical resistivity shows that at certain MS/CS ratio (MS= metal source, CS=carbon source) between 0.1 and 0.2, the hybrid composites exhibit 6.5X more conductive than pure single walled nano tube (SWNT) and 4.5X more conductive than pure graphene nano platelets (commercial products from Cheaptubes LLC).The high electrical conductivity graphene hybrid composite successfully demonstrated the improvement of electro catalyst performance in the PEMFC (Proton Exchange Membrane Fuel cell) using H_2 and air.

Keywords: catalyst stagger, graphene hybrid composite, high electrical conductivity, solid phase synthesized carbon nano tube (SPNT), SPNT process

1 INTRODUCTION

In the SPNT process, certain kinds of catalyst show different interaction with solid state carbon sources made out of natural products and significantly affect the shape of nano carbon products. Carbon nano rod, nano wire, nano tube, nano horn, amorphous etc…were observed in such kinds of process

During the catalyst doping steps, specific catalyst can form a stagger which is the accumulation of catalyst molecules at high concentration. It is assumed that at low catalyst concentration, the free radicals of C generated from the pyrolysis of solid carbon source, tend to fully surround catalyst molecules but at the high catalyst concentration, the catalyst molecules form a stagger which prevents the full adsorption and yield one-site adsorption instead. As a result, tubular shape nano carbon products are expected to form with full adsorption and sheet products (graphene like) are expected to form with partial adsorption (Fig.1). Based on this assumption, we have discovered a new way of making graphene hybrid composite with SPNT process using iron derivatives. The staging mechanism can also prevent individual sheets from sticking to each other

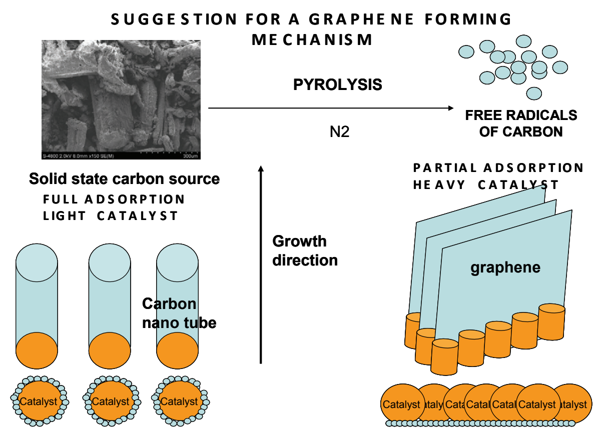

Fig.1 suggested graphene forming mechanism from SPNT process

1. EXPERIMENTS & DISCUSSION

1.1 Preparation of pyrollysis products

The solid carbon sources are selected from a wide variety of natural resources in Viet Nam including tropical plants and agricultural products such as wood, paddy husk, coffee bean, cotton etc... These products were first grounded into mm size particles then further milled with table salt (as milling media) providing sub-micron products. The sub-micron products were washed and dried yielding solid carbon source particles. These materials were doped with catalyst molecules by mixing in water and heat-stirred until the water is completely out, forming fine particle of precursor. The precursor is suddenly baked at 1200C in N2 for 1 hr. The impure products were purified with 3M HCl at room temperature to remove metal element (from catalysts). The pure products were exposed to several measurements such as electrical resistivity, FE-SEM, TEM, TGA, XRD and Raman.

2.2 Measurement of bulk resistivity

0.5 g of the pyrollysis product was strongly pressed by vacuum and piston into the micro-cylinder having diameter of 30mm, forming a tied and solid block. The electrical resistivity was calculated based on measured cylinder diameter, packing length and resistor R. For references, commercially available SWNTs, MWNTs, grapheme nano platelets from Cheaptubes LLC (USA) were used.

2.3 Effect of catalyst

Fig.1 displays the effect of MS/CS ratio on the electrical resistivity (ohm-cm) of the pyrollysis products prepared from GTM wood using two different kinds of catalyst: Ni and Fe. It is observed that both catalysts show minimal resistivity in the vicinity of MS/CS = 0.10 -0.20.

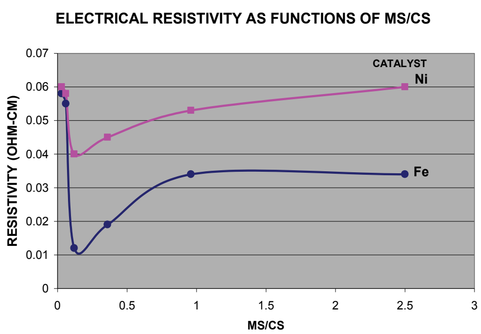

Fig1. Effect of MS/CS ratio on electrical resistivity for two different catalysts

Products from iron catalyst shows better conductivity than that of Ni .Fig, 2(a) and 2(b) shows the FE-SEM images of pyrollysis products made out of iron catalyst in a low portion (MS/CS= 0.06) and in a heavy portion (MS/CS=2.5). It is observed from these two Fig. 2(a) and 2(b) that the light portion of Fe catalyst gives rise to tubular shape product while heavily doped catalyst gives more “flake” shape or graphene look .

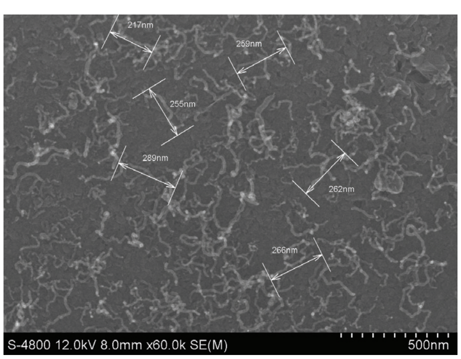

Fig.2 (a) FE-SEM of pyrollysis product made out of Fe catalyst with the MS/CS ratio=0.06 (light portion)

Fig.3 (a) shows TEM image of pyrrolysis product from heavy portion of iron derivative catalyst (MS.CS=0.48) .Fig. 3(b) shows TEM image of pyrrolysis product from light portion of iron relative catalyst (MS.CS=0.05). It is clearly in this case that the tubular shape nano carbon products were formed. In the tubular shape and one can see two distinguished tubes; the solid tube might be carbon nano rod and carbon nano wire, but the howllow tube must be carbon nano tube

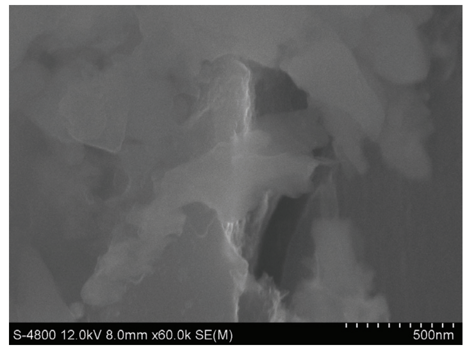

Fig.2 (b) FE-SEM of pyrollysis product made out of Fe catalyst with the MS/CS ratio=2.5 (heavy portion)

Fig.3 (a) TEM image of product from heavy doped iron catalyst

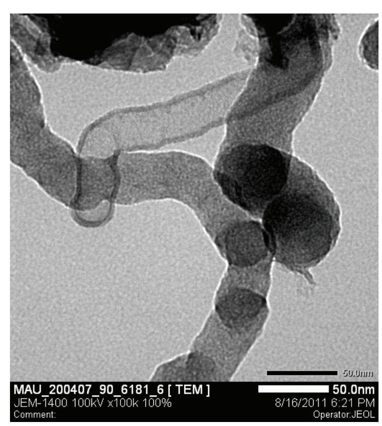

Fig 3(b) TEM image of paralysis product made out of low portion of Ni catalyst (MS/CS=0.05)

Next, Fig. 4 shows the Raman spectroscopy for SPNT products prepared at different MS/CS ratios using iron relative catalyst. It is observed that at MS/CS ratio = 0.03 , there is two peaks approximately appeared at 1580cm^{-1} indicating G band and at 1350 cm^{-1} indicating D band, revealing the structure of MWNT [3] . At MS/CS ratio =0.12 & 1.92 , a new peak approximately appeared at the vicinity of 2500-2800cm^{-1} indicating 2D band [4] in graphene and this new peak becomes more prominent for MS/CS= 1.92 product , revealing graphene related structure . So, it is clear that in the SPNT process, the tubular products are generated in the low portion of catalyst and graphene related products frequently shown in the high portion of catalyst. Thus, from the FE-SEM, TEM, Raman spectroscopy, the SPNT product exhibiting the lowest electrical resistivity should be a graphene hybrid composite.

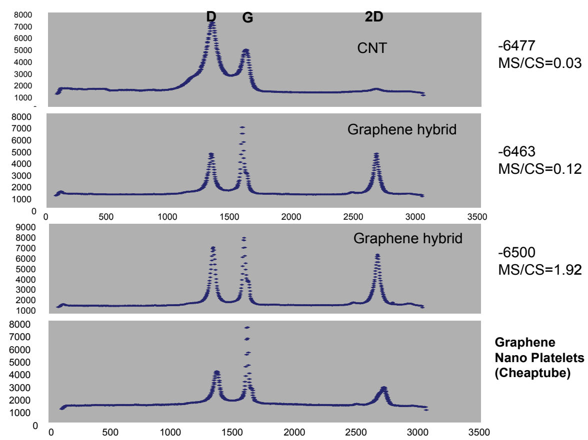

Fig.4 Raman spectroscopy of graphene hybrid composite

The measurements of bulk electrical resistivity shows that the graphene hybrid composite exhibits highest electro conductivity , approximately 6.5X higher than SWNT and 4.5 X higher than graphene nano platelet as shown in Fig.5 .

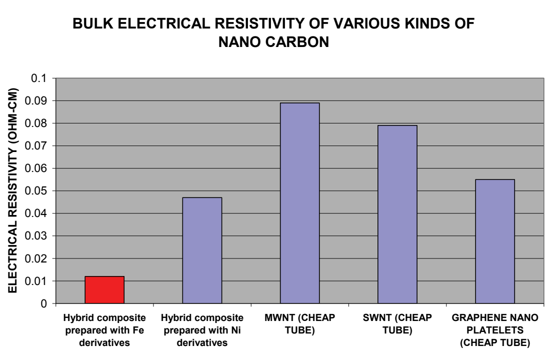

Fig.5 Bulk electrical resistivity of graphene hybrid composite (red) as compared with other well known nano carbon

It should be concluded right here that the catalyst plays a key role in the physical structure and electrical properties of the nano carbon products coming out from the SPNT process. Especially, for specific catalyst such as iron derivatives, the graphene related products are more easily formed with large concentration of catalyst. Such kind of specific catalyst somehow creates a physical divider to separate out the layer of nano carbon to form graphene products.

Next, generally speaking, PEMFC (Proton Exchange Membrane Fuel cell) using the Pt catalyst to ionize H2 gas into proton H+ and electron which contributes to the electricity source. For practical application purpose, the Pt powder has to be formed into nano scale and adsorbed onto a surface of a conductive support, usually, carbon black Vulcan XR72 or XR72C (Cabot) in order to successfully deliver electrochemically generated electron to the outside circuit system. In the present study, we are trying to replace the Vulcan XR72 or Vulcan XR72C with the graphene hybrid composite made out of Fe catalyst in a heavy dose, for example MS/CS>0.12 as above described, to see if this new nano carbon material can affect the efficiency of the H_2 PEMFC . In order to test out the electro catalytic performance of this graphene hybrid composite, the proton transporter Nafion film211 was sandwiched between two different kinds of catalyst which is over brushed onto gas diffusion materials (TCP, Toray Carbon Paper) following USP publication US2007/0077478 A1. In this case , the cathode catalyst is composed of Pt nano powder adsorbed on the surface of the graphene hybrid composite in a ratio of graphene/Pt =40/60 by weight and the anodic catalyst is composed of Pt/Ru (60/20 by weight)co- adsorbed on the surface of the same graphene hybrid composite above described .The system was incorporated into a PEMFC using in-house copper bipolar plates having active area of 59.85cm2 and was exposed to the H_2 source (100ml/min) on anode site and oxygen source(O2 flow rate 50ml/min) in cathode site using Fuel cell Test Station made by Electrochem. Fig 6(a) exhibits V-I characteristics curves of the system and Fig.6 (b) exhibits power efficiency curves

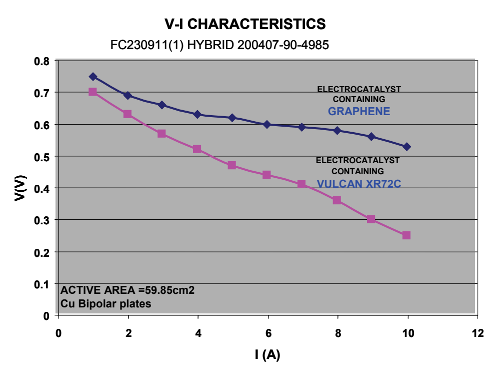

Fig.6 (a) V-I characteristic curves of PEM FC utilizing graphene hybrid composite

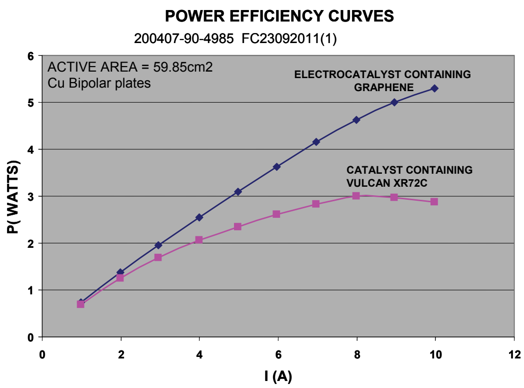

Fig. 6(b) Power Efficiency curves of PEMFC utilizing graphene hybrid composite in the catalyst

These Fig, 6(a) and 6(b) clearly show the improvement of power efficiency of the PEMFC in the order of 66% with a current of 10A and output power of 5W

CONCLUSION

It is concluded that certain catalyst such as iron derivatives can convert the solid state carbon source into a new type of nano carbon during pyrollysis under unoxidizing environment. These nano carbon materials are graphene hybrid composite which shows very high electro conductivity, and improved compatibility to form certain kind of nano composite which is successfully used as electro catalyst for PEM FC. The layer structure of these graphene related materials need further investigation, however the graphene like structure might be formed due to the excess amount of catalyst which could act as dividers to separate the carbon sheet into more single layer that graphite oxide researchers targeted .

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