FORM-2

THE PATENTS ACT 1970

(39 of 1970)

COMPLETE SPECIFICATION

SECTION 10

A METHOD TO TRANSFORM METALLIC SINGLE WALLED CARBON NANOTUBES INTO SEMICONDUCTING NANOTUBES

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THE FOLLOWING SPECIFICATIONS PARTICULARLY DESCRIBES THE NATURE OF THIS INVENTION AND THE MANNER IN WHICH IT IS TO BE PERFORMED

FIELD OF INVENTION :

The carbon has broadly four crystalline states which include diamond, graphite, fullerenes and carbon nanotubes. The carbon nanotubes exhibit a number of remarkable electrical and mechanical properties, which make them desirable for use in modern electronic devices. The exciting physical and chemical properties exhibited by SWNTs have generated a huge amount of research, especially in areas like nanoelectronics, nanodevices, optics, micro-electro-mechanical sensors (MEMS), field effect transistors (FET) and so on. The invention relates to a method, an arrangement and the use of an arrangement for converting metallic carbon nanotubes to semi-conducting carbon nanotubes.

This invention relates to the development of a method to modify the electrical transport properties of single-walled carbon nanotubes (SWNTs). More specifically, this can be used to convert metallic single-walled carbon nanotubes to semiconducting ones.

PRIOR ART :

A single-walled carbon nanotube (SWNT) is described with the aid of a planar ribbon of hexagonally arranged carbon atoms, which is rolled up seamlessly to form a tube. Several concentric tubes, arranged one inside the other, are referred to as multi-walled carbon nanotubes (MWNTs). The exciting physical and chemical properties exhibited by SWNTs have generated a huge amount of

research, especially in areas like nanoelectronics, nanodevices, optics, micro-electro-mechanical sensors (MEMS), field effect transistors (FET) and so on.

A single sheet of carbon atoms connected to each other as in the case of graphite is called graphene. When graphene is rolled up to make the nanotube, a special direction can be chosen, just as a sheet of paper which may be rolled in different directions. The direction changes the conductivity of the tube so formed. The direction of rolling is referred to in terms of chirality. Sometimes this is a metallic direction, and sometimes it is semiconducting. As any direction can be chosen, some nanotubes are metals, and others are semiconductors. Since both metals and semiconductors can be made from the same all-carbon system, nanotubes are ideal candidates for molecular electronics technologies. The direction and curvature of rolling of the graphene sheets determine the properties of the nanotubes. These are indicated by (n,m) indices specifying the rolling direction. Based on the (n,m) values, SWNTs can be divided into two main categories :-

1. Metallic – are SWNTs which satisfy the relation $2n + m = 3q$ (q being an integer). These have very low resistance to current flow and have the ability to withstand current densities of about 500 times that of metallic silver or gold.

2. Semiconducting – are SWNTs which satisfy the relation $2n + m \neq 3q$. These behave like normal semiconductors and the electrical transport can be tuned by varying the electric field or doping.

Typical SWNTs have a diameter of 0.5 nm to 10 nm while MWNTs have a correspondingly larger diameter. Typical carbon nanotubes ranges in length from 100 nm to a few tens of micrometers.

Metallic carbon nanotubes are suitable for use as molecular wires with extremely high current-carrying capacity. Semi-conducting carbon nanotubes are particularly suitable as molecular transistors. Both types represent essential components for nano-electronic circuits because of their nanoscale dimensions.

OBJECT OF THE INVENTION :

Starting with this premise, it is the object of the present invention to provide a method, an arrangement and the use of an arrangement for transforming metallic carbon nanotubes into semi-conducting carbon nanotubes.

DESCRIPTION OF THE INVENTION :

This invention pertains to the modification of electrical transport properties of SWNTs. Specifically, it involves the transformation of a metallic SWNT to a semiconducting SWNT.

The main stumbling block for using SWNTs in a manufactured device is the selective control of its electrical transport properties. The tubes are usually produced as a mixture of semiconducting and metallic SWNTs. Controlling the conductivity of nanotubes is a desirable characteristic.

The attempt is to change a nanotube from being a plain conductor to become a semiconductor.

The method herein proposes to fabricate a composite film of gold or silver nanoparticles and carbon nanotubes at a liquid-liquid interface and nanostructures based on this film. Such a film shows semiconducting properties throughout as all the metallic nanotubes were transformed into semiconducting ones. This technology is believed to have far-reaching applications in nanoelectronics, sensors and device-fabrication at the molecular level. It is possible to observe this transformation from single walled carbon nanotubes using a variety of other nanoparticles of gold, silver and other metals of various shapes and sizes.

The nanoparticles of gold, stabilized by citrate groups (Au@citrate) were synthesized by a procedure reported in the literature. The size of the nanoparticles can be varied from a range of 1 nm to 150 nm in diameter. However, the typical size of the particles synthesized by this method is 12-15 nm in diameter.

The method according to this invention comprises the steps of fabricating a composite film having nanoparticles and single walled carbon nanotubes as the components. This composite film was formed at the liquid-liquid interface. SWNTs, obtained from a commercial source, were purified by methods in the literature. Typically, this sample of SWNTs consists of 33% of metallic tubes and 67% semiconducting tubes. This sample was processed to extract the metallic nanotubes as per a known procedure (Maeda, Y. et al, J. Am. Chem. Soc., 2005, 127, 10287). The resulting samples are composed of metallic single walled nanotubes (mSWNTs) to the tune of 80%. The as-prepared gold and silver nanoparticles, using the citrate reduction route (Turkevich, J.; Stevenson,P.L.; Hiller, J. Discuss. Faraday Soc.1951, 11, 55), was the aqueous phase (liquid phase 1) while diethyl ether formed the organic phase (liquid phase 2). To this biphasic system, the dispersion of mSWNTs in tetrahydrofuran (THF) was added. The film formed at the liquid-liquid interface was transferred to a glass substrate and allowed to dry in ambience. The concentration of the nanoparticles or nanotubes can be varied to get a composite of desired composition.

The electrical behavior of the purified metallic nanotubes and Au-mSWNT composite was studied by point-contact current imaging atomic force microscopy (PCI-AFM) and Raman spectroscopy.

For Raman characterization, the film was irradiated with a 514.5 nm Ar ion laser, 40 mW maximum power through a 100X microscope objective and the light

obtained from the sample were collected by the same objective and sent to a spectrometer through a multimode fiber. A super-notch filter placed in the path of the signal effectively cuts off the excitation radiation. The signal was then dispersed using a 600 grooves/mm grating and the dispersed light was collected by a Peltier cooled charge coupled device (CCD). Single spectra over a smaller range were also acquired at higher resolution using the 1800 grooves/mm grating. Various other Raman spectrometers were also used.

On irradiating the sample with the excitation laser source, a red visible emission between 600 – 700 nm was obtained. Typical signatures of single walled carbon nanotubes, namely the radial breathing mode (RBM) and the D and G bands were found to be superimposed on the background of this emission, confirming that the emission was an inherent property of the carbon nanotubes. This has been documented earlier (Indian Patent No 421CHE/2006 dated 9th March 2006).

For the point-contact current – atomic force microscopy (PCI-AFM) analysis, the composite film was transferred onto a freshly cleaved mica surface and dried in vacuum. One half of the sample surface was masked using a cover glass slip and gold electrode was fabricated on the other half by thermal vacuum deposition of pure Au metal at a thickness of 30 nm. The PCI-AFM measurement was carried out on a JEOL JSPM-4210 instrument equipped with 2 function generators (WF 1946, NF Corporation). The current-voltage (I-V)

characteristics along the long axis of the nanotube composite were measured using Pt coated conductive cantilevers. From the large area topographic image, it was ensured that the tubes selected for I-V measurements were indeed in contact with the gold electrode. The bias voltage was applied on the gold electrode and the cantilever was grounded. The entire experiment was carried out in a housing purged with N_2 gas to minimize the effects of humidity. The tubes studied here exist predominantly as bundles and each tube makes multiple contacts with others in a given bundle. The I-V data correspond to the point of contact which reflects the local symmetry. The PCI-AFM image was constructed for 128 X 128 pixels with topographic and I-V characteristics acquired simultaneously.

Specific example of the working of the device

Experiment with gold nanoparticles

As-synthesized citrate reduced gold nanoparticles of 12-15 nm mean diameter in aqueous medium and diethyl ether were taken in equal volumes to form the aqueous-organic liquid-liquid interface. To this biphasic system, a dispersion of mSWNTs in THF was added. This was immediately followed by the formation of a composite film at the interface. This film was transferred onto a 0.2 mm cover-glass substrate and dried in ambience. This sample was mounted on a sample stage of a confocal Raman spectrometer, the details of the instrument being provided in the earlier section.

An interesting aspect observed is the change in the line shape and width of the G-band of the composite when compared to the pure metallic tube. In case of metallic nanotubes, the G-band exhibits a broad, asymmetric, Breit-Wigner-Fano lineshape. This G-band, which is chirality dependent, is sharper in case of semiconducting nanotubes (Dresselhaus, M. S.; Dresselhaus, G.; Jorio, A.; Filho, A. G. S.; Saito, R. Carbon, 2002, 40, 2043). Using this difference, we studied the electrical state of the nanotubes in the composite (Figure 1). The data show that the pure mSWNTs (A) have been transformed into semiconducting SWNTs in the composite (B). Thus nanoparticles in the composite are responsible for the observed transition from metallic to semiconducting states. The nanotube structures were imaged using the Raman intensities. The Raman spectra taken from various points in the same sample and from various points in a single nanotube structure confirmed that metallic to semiconducting transformation occurs.

Figure 1. Raman spectra of (A) mSWNTs and (B) Au-mSWNTs composite. The spectra shows a stark difference in the peak shapes and linewidths (FWHM = 52 cm^{-1} in (A) and 16 cm^{-1} in (B)).

PCI-AFM analysis of pure mSWNTs and its composite with gold nanoparticle is shown in Figure 2. This is a direct measure of the electrical transport properties

at the nanoscale dimension and provides conclusive proof of the phenomenon observed.

Figure 2. AFM image of (A) Au-mSWNTs composite and (B) corresponding I-V curves measured at points specified on the image. The increase in current towards point 7 is due to the reducing distance with the contact. Similar image and I-V curves for pure mSWNTs are shown in (C) and (D), respectively. (E) Plot showing the variation of conductance versus bias voltage for pure mSWNTs (red traces) and Au-mSWNTs composite (black traces). Zero conductance at zero bias showed that the tubes in the composite are semiconducting.

On comparing the I-V traces from (B) and (D), it is evident that there is an order of difference in the current transported between pure mSWNTs and Au-mSWNTs composite. Pure mSWNTs are expected to carry more current than semiconducting tubes. Thus, the pure mSWNTs which were used for the composite preparation have been transformed into tubes with lower conductance. This confirms the transformation of metallic nanotubes to semiconducting nanotubes. The phenomenon was checked in different samples and in multiple nanotube structures seen in the same sample. At places, an order of two reduction in conductivity was obtained as a result of nanoparticle binding.

The same phenomenon was observed with silver nanoparticles of 60 - 70 nm mean diameter. Other shapes such as nanorods also show the same phenomenon when made in the form of a composite film with nanotubes.

Figure 3. A schematic of the steps used for transforming metallic single walled carbon nanotubes into semiconducting nanotubes.

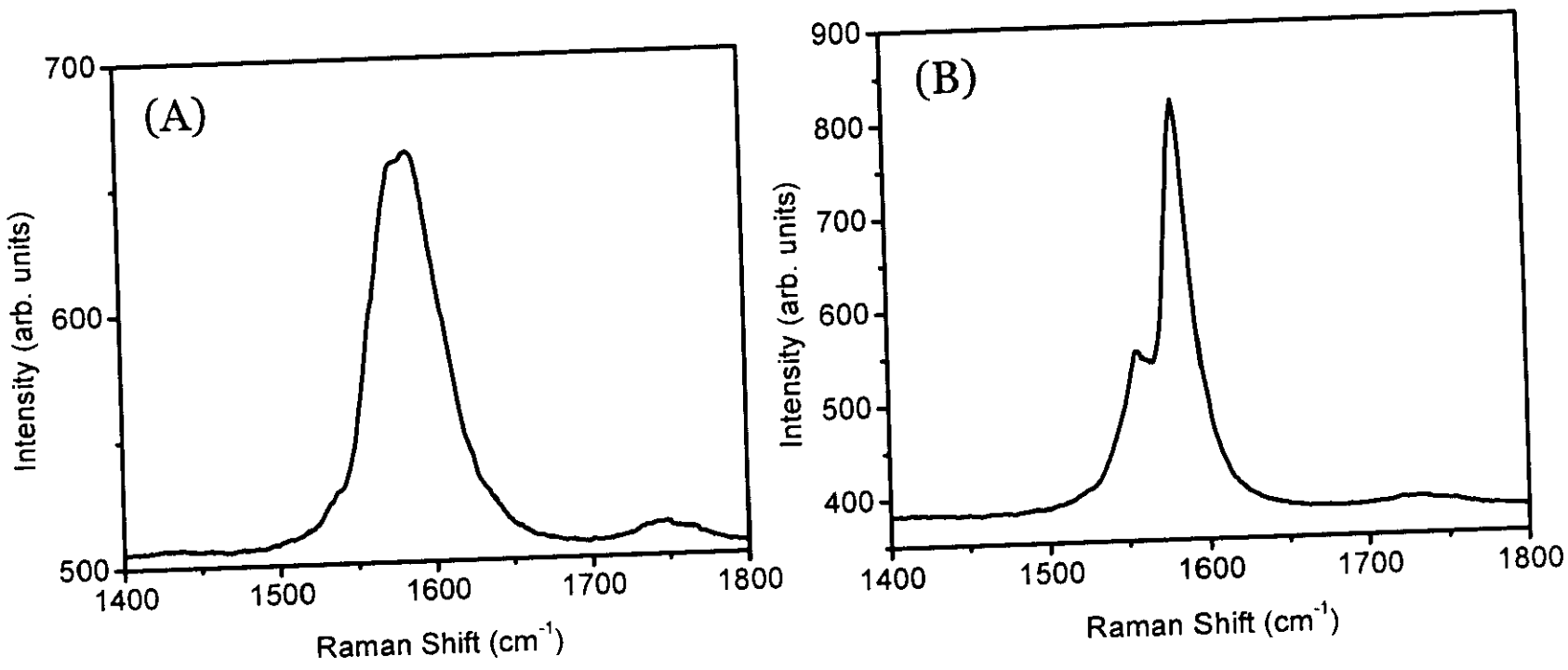

Figure 1.

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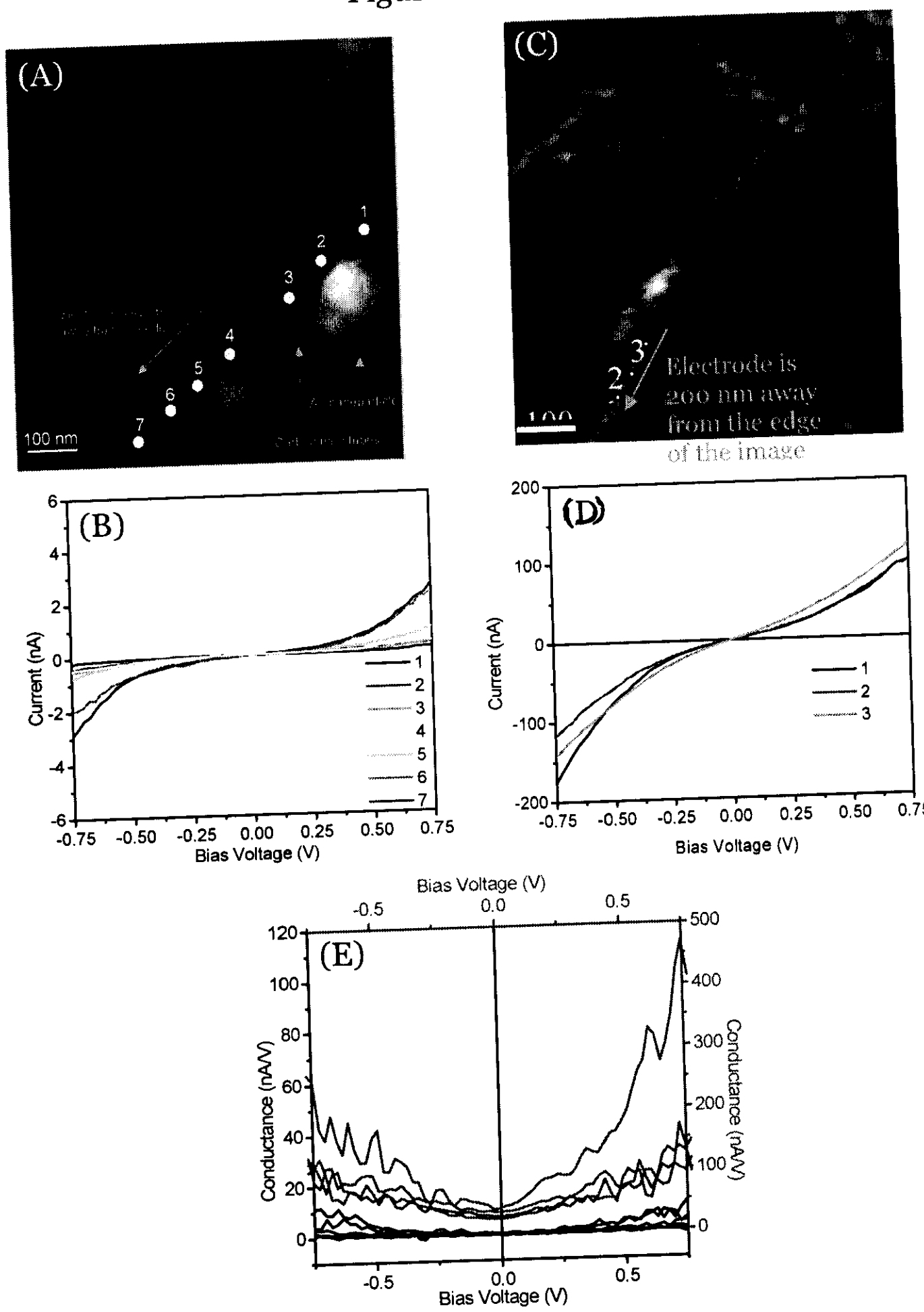
Figure. 2



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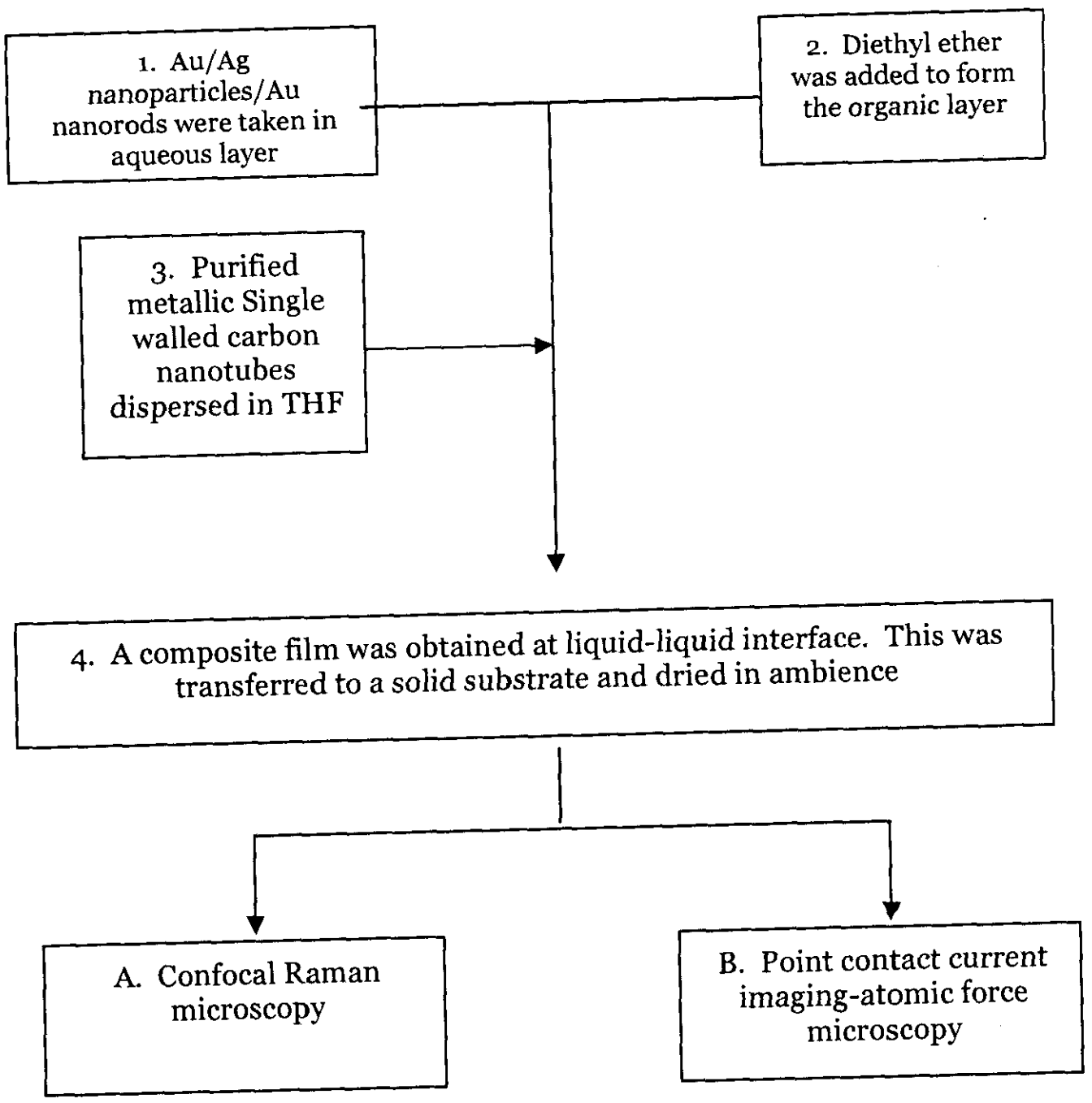

Figure. 3

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