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(54) Title: QUANTUM TUNNELING ORGANIC COMPOSITES

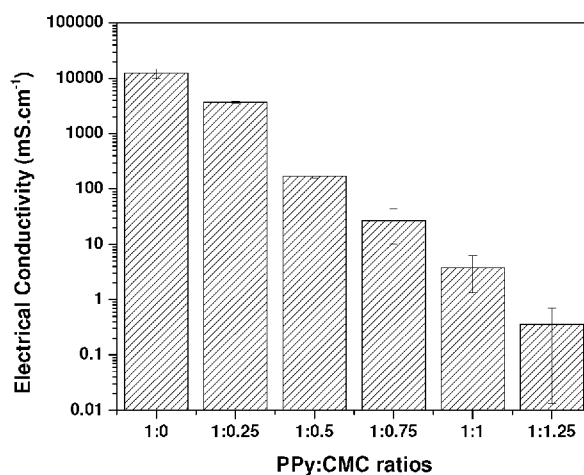


Figure 2.

(57) **Abstract:** Herein, we describe conducting polymer composites that demonstrate pressure-sensitive electrical conductivity. These composites can be fabricated by inexpensive and environmental-friendly chemical polymerization. One example thereof are polypyrrole:carboxymethyl-cellulose (PPy:CMC) composites that have a unique core-shell structure where a thin layer of non-conductive CMC matrix covers electrically conductive PPy:CMC spheres. Such a structure-assisted quantum tunneling conduction takes place whenever pressure is applied. Also described herein is the designing of pressure-sensing devices derived from conducting polymers.



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Quantum Tunneling Organic Composites

PRIOR APPLICATION INFORMATION

The instant application claims the benefit of US Provisional Patent Application serial number 63/148,805, filed February 12, 2021 and entitled “Quantum Tunneling Organic Composites”, the entire contents of which are incorporated herein by reference for all purposes.

BACKGROUND OF THE INVENTION

Quantum tunneling composites are materials based on conducting nanoparticles that are dispersed in an elastomeric matrix[1–4] . The concentration of nanoparticles is sufficiently low to remain below the percolation threshold. Consequently, conduction between particles is based on electron tunneling. Upon applying a force on the composite, the composite deforms and the average tunneling distance changes. This reduces the resistance of the composite. Conversely, when the pressure is released, the resistance recovers to its original value. This allows pressure sensing.

The first description of quantum tunneling composites (QTCs) dates back to 1997 when David Lussey observed the interesting pressure response conductivity of metallic conductive glue. Conventional QTCs are composed of spiky nickel particles placed within non-conductive elastomers[3,5]. In un-deformed condition, QTCs are electrical insulators. Upon deformation, QTCs start to conduct electricity via a quantum tunneling mechanism. Such intriguing pressure-sensing properties allow QTCs to potentially be used in wearable devices, touch screens, textile smart interfaces, and other pressure-sensing applications[2]. Despite gaining tremendous public attention, the market adoption of QTCs is limited due to their high production cost. Alternative materials that demonstrate pressure-sensing electrical conductivity behavior are being developed. For example, silicon-carbon black (Si-C) composite is considered to have quantum tunneling conduction behavior, showing a reversible 10^4 change in conductivity on repeated compression and release[6].

In order to have pressure-sensing conductivity behavior, binary composites should have a unique morphology where a non-conductive matrix sufficiently separates electrically conductive components, making the composite less conductive in its normal state.

Furthermore, the distance between adjacent conductive components should be small so as to form conduction pathways upon application of pressure. Intrinsically conducting polymers (CPs) such as polypyrrole (PPy) and polyaniline (PANI) have been used in many applications. Their limited processability is well-addressed by adding elastomers to conducting polymer
5 powders. These composites, however, do not exhibit quantum tunneling conductivity behavior because of their irregular morphology.

SUMMARY OF THE INVENTION

According to an aspect of the invention, there is provided a method for preparing a
10 quantum tunnelling composite material comprising:

mixing a quantity of an intrinsically conductive polymer with an aqueous dispersion of a non-conductive matrix material, thereby forming a composite material;

said composite material comprising a plurality of conductive components dispersed with a polymer matrix such that each respective one individual conductive component is
15 separated from at least one respective adjacent conductive component, said composite material having a first condition wherein the respective one individual conductive components are separated from the at least one respective adjacent conductive component by a first distance such that there is no contact between adjacent respective individual conductive structural elements; and a second condition on pressure being applied to said composite material wherein
20 the respective one individual conductive components are separated from the at least one respective adjacent conductive components by a second distance such that the respective individual conductive structural elements form a continuous electron conduction pathway.

According to an aspect of the invention, there is provided a method for preparing a quantum tunnelling composite material comprising:

25 mixing a quantity of an intrinsically conductive polymer with an aqueous dispersion of a non-conductive matrix material, thereby forming a composite material;

said composite material comprising a plurality of conductive components dispersed with a polymer matrix such that each respective one individual conductive component is separated from at least one respective adjacent conductive component, said
30 composite material having a first condition wherein the respective one individual conductive

components are separated from the at least one respective adjacent conductive component by a first distance such that there is no contact between adjacent respective individual conductive structural elements; and a second condition on pressure being applied to said composite material wherein the respective one individual conductive components are separated from the at least one respective adjacent conductive components by a second distance such that the respective individual conductive structural elements form a continuous electron conduction pathway,

wherein:

the intrinsically conductive polymer is selected from the group consisting of polypyrrole, polythiophene, polyaniline, polyacetylene and a derivative thereof;

the non-conductive matrix material is selected from the group consisting of: carboxymethyl cellulose; polyacrylate; and alginate; and

the non-conductive matrix material and the conductive polymer are mixed at a ratio of 1:0.1-1.25.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1. TEM image and element mapping of polypyrrole:carboxymethyl cellulose (PPy:CMC) 1:0.5 composite

Figure 2. Trend in electrical conductivity of PPy:CMC composites with different PPy:CMC ratios

Figure 3. Electrochemical Impedance Spectroscopy (EIS) of PPy:CMC 1:0.5 upon pressure release and suppression

Figure 4. High and low frequency resistance data upon pressure release and suppression of PPy:CMC 1:0.5

Figure 5. High and low frequency resistance data during pressure release of PPy:CMC 1:0.5

Figure 6. High frequency resistance data during pressure cycling of PPy:CMC 1:0.5

Figure 7. EIS (top) and high and low frequency resistance values (bottom) of Polypyrrole:polyacrylic acid PPy:PAA 1:0.5 at different pressures.

Figure 8. EIS (top) and high and low frequency resistance data (bottom) for Polypyrrole:alginate PPy:SA 1:0.5 at different pressures

Figure 9. Experimental setup for pressure-response conductivity measurement

Figure 10. EIS (a,b) and calculated resistance (c) of PPy:CMC 1:1 composite at different applied pressures.

Figure 11. EIS (a) and calculated resistance (b) of PPy:CMC 1:1 composite upon repeated pressure cycling.

Figure 12. (a) SEM and (b) TEM images of PPy:CMC 1:1 composite.

Figure 13. Characteristic FTIR-ATR spectra from CMC (bottom), PPy (middle) are identifiable as common features in the spectrum of PPy:CMC composite (top). The false colour image of the composite, top left, was created as the ratio of characteristic bands for CMC and PPy, at 1326 and 963 cm^{-1} , respectively. The colour variation within the image is principally due to variable contact with the pellets. The top edge of the image shows typical peak ratio variations when the ATR probe is lacking good contact with the sample.

Figure 13. a) Impedance spectra and fit for PPy:CMC pellets under varying pressure from 50 kPa (blue) to 400 kPa (green); b) Changes in resistance (black) and capacitance (blue) showing a strong decrease in resistance and increase of capacitance with increasing pressure; c) Pressure cycling showing that resistance values recover reversibly after application and release of pressure.

Figure 15. SIMS depth profile showing the sum of CN^- , C_3N^- fragments (red solid line) and the sum of C_2HO^- , CO_2H^- , $\text{C}_2\text{H}_2\text{O}_2^-$ fragments (blue dashed line). Additional fragments for each group were observed and behaved similarly to the presented data.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Unless defined otherwise, all technical and scientific terms used herein have the same meaning as commonly understood by one of ordinary skill in the art to which the invention belongs. Although any methods and materials similar or equivalent to those described herein can be used in the practice or testing of the present invention, the preferred methods and materials are now described. All publications mentioned hereunder are incorporated herein by reference.

Herein, we describe conducting polymer composites that demonstrate pressure-sensitive electrical conductivity. These composites can be fabricated by inexpensive and environmental-friendly chemical polymerization. Specifically, polypyrrole:carboxymethyl-cellulose (PPy:CMC) composites have a unique core-shell structure where a thin layer of non-conductive CMC matrix covers electrically conductive PPy:CMC spheres. Such a structure-assisted quantum tunneling conduction takes place whenever pressure is applied. Also described herein is the designing of pressure-sensing devices derived from conducting polymers.

Specifically, the method described below allows synthesis of a purely organic quantum tunneling composite. A conjugated polymer is synthesized in the presence of an aqueous polymer dispersion. The conjugated polymer forms nanospheres within the polymer matrix and serves as the conductive component. The composite micro-structure is analogous to a traditional quantum tunneling composite, but based on conjugated polymer nanospheres as conducting component, rather than inorganic nanoparticles.

According to an aspect of the invention, there is provided a method for preparing a quantum tunnelling composite material comprising:

mixing a quantity of an intrinsically conductive polymer with an aqueous dispersion of a non-conductive matrix material, thereby forming a composite material;

said composite material comprising a plurality of conductive components dispersed with a polymer matrix such that each respective one individual conductive component is separated from at least one respective adjacent conductive component, said composite material having a first condition wherein the respective one individual conductive components are separated from the at least one respective adjacent conductive component by a first distance such that there is no contact between adjacent respective individual conductive structural elements; and a second condition on pressure being applied to said composite material wherein the respective one individual conductive components are separated from the at least one respective adjacent conductive components by a second distance such that the respective individual conductive structural elements form a continuous electron conduction pathway.

As will be appreciated by one of skill in the art, the respective individual conductive structural elements may be of any suitable geometry for use within the invention. While in the

examples provided herein, the conductive structural elements are in the shape of pellets and for convenience may be referred to as pellets herein, the pressure sensing behavior of the composite material will of course be independent of the geometry of the respective conductive structural elements. For example, depending on desired applications, different geometries can be obtained by using special die sets. Alternatively, an aqueous dispersion of the composite material can be casted and/or dried directly, for example, for direct application to a surface.

As will be appreciated by one of skill in the art, the intrinsically conductive polymer may be any suitable intrinsically conductive polymer known in the art, for example, any polymer having conjugated bonding along their backbone, thereby allowing for electron delocalization over the length of the polymer.

In some embodiments, the intrinsically conductive polymer is polypyrrole, polythiophene, polyaniline, polyacetylene or a derivative of any one of these.

The non-conductive matrix material may be selected from any suitable polymer that contains negatively charged functional groups. As will be apparent to those of skill in the art, negatively charged functional groups allow for strong coulombic interactions with positive charges in the intrinsically conductive polymer, as discussed herein.

In some embodiments, the non-conductive matrix material is selected independently from the group consisting of: carboxymethyl cellulose; polyacrylate; and alginate.

In some embodiments, the non-conductive matrix material and the conductive polymer are mixed at a suitable ratio that is optimized for mechanical stability, as well as overall conductivity and pressure sensitivity. For example, the mass ratio may be 1 part non-conductive matrix material to 0.1:1.25 parts conductive polymer, for example, at approximately 1:0.5 and 1.0 mass ratio. As will be appreciated by one of skill in the art, within this mass ratio range, the composite composition can be changed to obtain desired sensitivity for different applications.

In some embodiments, the non-conductive matrix material and the conductive polymer are mixed at approximately a 1:1 ratio.

In some embodiments, the non-conductive matrix material is carboxymethyl cellulose and the conductive polymer is polypyrrole.

In some embodiments of the invention, the quantum tunneling composite material is an organic quantum tunneling composite material, for example, a purely organic quantum tunneling composite material or a substantially organic quantum tunneling composite material or an essentially quantum tunneling composite material in that the material comprises
5 conjugated polymer nanospheres as conducting component, rather than inorganic nanoparticles. That is, the quantum tunneling composite material is an organic quantum tunneling composite material with the proviso that the organic quantum tunneling composite material comprises essentially no inorganic nanoparticles, that is, with the proviso that no inorganic nanoparticles comprise or are an essential part or are required for functioning of the
10 material.

While reference is made to “said composite material comprising a plurality of conductive components”, it is to be understood that in some embodiments each of the plurality of conductive components is a conjugated polymer nanosphere, that is, an organic conjugated polymer nanosphere. Furthermore, each or all of the conductive components, for example,
15 each or all of the organic conjugated polymer nanospheres are composed of or derived from or formed from or formed of the same intrinsically conductive polymer or one intrinsically conductive polymer.

According to another embodiment of the invention, there is provided a method for preparing a quantum tunnelling composite material comprising:

20 mixing a quantity of an intrinsically conductive polymer with an aqueous dispersion of a non-conductive matrix material, thereby forming a composite material;

said composite material comprising a plurality of conductive components dispersed with a polymer matrix such that each respective one individual conductive component is separated from at least one respective adjacent conductive component, said composite material
25 having a first condition wherein the respective one individual conductive components are separated from the at least one respective adjacent conductive component by a first distance such that there is no contact between adjacent respective individual conductive structural elements; and a second condition on pressure being applied to said composite material wherein the respective one individual conductive components are separated from the at least one

respective adjacent conductive components by a second distance such that the respective individual conductive structural elements form a continuous electron conduction pathway,

wherein or characterized in that:

the intrinsically conductive polymer is selected from the group consisting of

5 polypyrrole, polythiophene, polyaniline, polyacetylene and a derivative thereof;

the non-conductive matrix material is selected from the group consisting of:
carboxymethyl cellulose; polyacrylate; and alginate; and

the non-conductive matrix material and the conductive polymer are mixed at a ratio of 1:0.1-1.25.

10 In some embodiments, the non-conductive matrix material is carboxymethyl cellulose and the conductive polymer is polypyrrole. The invention will now be further explained and/or elucidated by way of examples; however, the invention is not necessarily limited to or by the examples.

15 Example 1 - Synthesis procedure

Conducting polymers were polymerized in the presence of polyanions. The chosen conducting polymer is polypyrrole.

Polyanions are Carboxymethyl Cellulose, Polyacrylate and Alginate.

Weight ratio of 1:0.5 and 1:1 = conducting polymer:polyanion were chosen.

20 Pyrrole was dissolved in an aqueous dispersion of the polyanion. Polymerization of pyrrole was induced by slowly adding 2.5 equivalents of ferric chloride.

The product was mixed with ethanol to induce precipitation, filtered and washed with ethanol. The conducting polymer composites were dried in the vacuum oven at 80 °C for 24 hours before testing.

25 The conducting polymer composites were dispersed in isopropanol and sonicated for 10 mins before dropping onto TEM grids. The TEM measurements were performed on FEI Talos F200X at the accelerating voltages of 80 keV. The elemental mapping was captured with EDX detector attached to the TEM machine.

30 Electrical conductivity and pressure-sensing testing procedure

Conducting polymer composite powders were ground and compressed into a 13 mm diameter pellet by using a hydraulic press. To minimize contact resistance, pellets were sputter-coated with Au//Pd. The pellet is placed between two 13 mm diameter stainless steel rods covered by insulating sample holder (Figure 9).

5 Pellet diameter $d = 13$ mm

Pellet surface area $S = \pi(d)^2/4 = 1.33 \text{ cm}^2$

Pressure (kPa)	Weight (kg)
100	1.35
200	2.7
300	4.05
400	5.4

Example 2 - Results

10 Electron microscopy of a synthesized composite of polypyrrole and carboxymethyl cellulose shows the formation of nanospheres of approximately 50 nm diameter (Figure 1).

Elemental mapping of this structures exhibits a homogenous distribution of oxygen, which can be used as indicator for CMC presence, and nitrogen, as indicator of Polypyrrole. Both elements are well distributed over the whole composite.

15 The conductivity of the composite declines exponentially with addition of CMC (Figure 2).

This confirms that percolation of conducting polymer particles is not achieved and rather conduction by quantum tunneling is observed. As the non-conductive layer of CMC increases in thickness, tunneling efficiency decreases exponentially, leading to a corresponding decrease in conductivity.

20 The figures below show impedance spectra and resistance values in dependence of the applied pressure. Figures 3 and 4 show that increasing pressure reduces the resistance within the composite. This resistance recovers to the most part upon releasing the pressure (Figure 4).

Over multiple samples, it was found that the initial pressure application typically serves to improve contact between the electrode and the metallized pellet surface. Hence, we are only

plotting the pressure release curve from here on (Figure 5) that shows an increasing resistance as the pressure is released.

The resistance change with applied pressure is reversible over multiple cycles. By applying alternately 400 kPa and 100 kPa pressure, the recovery of the low resistance at high pressure over many cycles can be observed (Figure 6).

Similar results are obtained for composites of polypyrrole:polyacrylate (Figure 7) and polypyrrole:alginate (Figure 8).

Composite material usually demonstrates a sharp increase in their electrical conductivity whenever the conductive filler concentration goes beyond their electrical percolation threshold. However, as shown in Figure 2, the electrical conductivity of PPy:CMC composites seems to not follow the typical trend across many mass ratios of PPy and CMC, assuming that PPy:CMC composites composed of spherical PPy particles were embedded in the non-conductive CMC matrix. According to the effective medium approximation (EMA) theory, the electrical conductivity of PPy:CMC composites should follow the Bruggeman relationship[7–9]. However, their electrical conductivity failed to follow the Bruggeman relationship with a large Bruggeman coefficient discrepancy as described previously[10].

This indicates that PPy:CMC composites can demonstrate a quantum tunneling conductivity mechanism, where their unique morphology plays a vital role. Specifically, PPy:CMC 1:1 composite is CMC-rich on the surface, rather than a homogenous component distribution within the single-particle scale. These conclusions on composite morphology are supported by XPS and STXM results reported previously[10]. Specifically, the thin layer of CMC on the surface of PPy particles prevents the formation of continuous electron conduction pathway, but it is sufficiently small to induce quantum tunneling conduction after deformation.

To verify the quantum tunneling conductivity behavior of PPy:CMC composites, a custom-cell was designed and used as shown in Figure 9. PPy:CMC 1:1 composite was selected to investigate pressure-responsive conductivity due to their low electrical conductivity compared to other composites. The impedance spectra of Au/Pd-coated PPy:CMC pellets were recorded and analyzed to get resistance value upon the changes of applied pressure. As shown in Figure 10 (a,b), the EIS spectra of PPy:CMC 1:1 composite at different applied pressures shared a similar shape, which represented the equivalent circuit of a resistor connected in

series with a capacitor. The calculated resistance of PPy:CMC 1:1 composite is shown in Figure 10 (c). The resistance reduces gradually when the applied pressure increases. In other words, the electrical conductivity increases upon compression.

As can be seen in Figure 11, the resistance reversibly changes 10 times when pressure varies between 100 kPa and 400 kPa. Compared to traditional QTCs, the extent of resistance changes of PPy:CMC composite is much lower. There are several underlying reasons for this difference. First of all, PPy:CMC 1:1 composite was compressed at 25 MPa and coated with Au/Pd film before testing. Even though this treatment prevents misinterpreting contact resistance of sample under pressure, only minimal change in the distance between adjacent particles is allowed, leading to smaller changes in resistance than that of QTCs.

Unlike traditional QTCs, which form high electric field at tips of spiky nickel particles that support field-assisted quantum tunneling conduction, spherical PPy particles are not sufficient to create a strong electric field. Moreover, the complete absence of conducting pathways within PPy:CMC composite has not been achieved as a result of the agglomeration of adjacent PPy particles. These effects reduce the sensitivity of PPy:CMC composite to compression. Yet, modification of the conducting polymer synthesis conditions can affect particle shape and agglomeration to improve sensitivity.

The study demonstrates the proof of concept of using conducting polymer composites as pressure sensors. The surface of PPy was covered by CMC non-conductive matrix, preventing them from forming sufficient conducting pathways. After applying stress, the distance between adjacent particles is reduced, forming a new tunneling conduction pathway. The quantum tunneling conductivity of PPy:CMC was observed but at a lower sensitivity than conventional QTCs.

Example 3 - Experimental

PPy:CMC composites were synthesized via chemically *in-situ* polymerization as described previously study[10]. Briefly, aqueous mixtures of pyrrole and Na-CMC were polymerized by FeCl₃ for 4 hours in an ice bath. After immersing in ethanol solution overnight, PPy:CMC suspensions were filtered with ethanol and then dried at 80° C in a vacuum oven.

Morphologies of PPy:CMC composites were investigated by TEM (FEI Talos F200X microscope) and SEM (FEI Nova NanoSEM 450 microscope). The electrical conductivity of PPy:CMC composites with different PPy:CMC mass ratios was measured by four-point probe method (Miller Design FPP-5000 instrument) on 0.6 mm-thick PPy:CMC pellets compressed at 200 MPa.

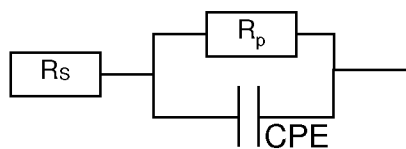
The pressure-response electrical conductivity measurement was performed on Au/Pd-coated PPy:CMC pellets by potentiostatic electrochemical impedance spectroscopy (EIS). Briefly, ~50 mg PPy:CMC composites were grounded and compressed at 25 MPa to form 0.3 mm-thick, 13 mm-round PPy:CMC pellets. Compressing pellets to 25 MPa instead of 200 MPa conserve plasticity of pellet for pressure sensing testing due to their stable conductivity[11]. These pellets were then coated with 15-20 nm-thick Au/Pd on both sides to eliminate contact resistance during measurement. The experimental setup was shown in Figure 8, where Au/Pd-coated PPy:CMC pellets were placed between two 13 mm in diameter, T-shaped stainless-steel rods covered by a insulating sample holder. The EIS measurement was performed by Gamry Interface1000 running from 1 MHz to 0.1 kHz at different pressures. The pressure was varied from 0 kPa to 400 kPa by placing a weight on top of the sample holder.

Example 4 – Analysis of composite structure and composition.

Electron microscopy was performed on the composite, revealing a homogenous composite with a spherical nanostructure (Figure 12). The observed nano-spheres exhibit a diameter of 50 nm.

Chemical composition and micro-scale homogeneity was confirmed by FTIR-ATR microscopy. Figure 13 shows spectra of PPy and CMC separately as well as a spectrum of the composite (created by Kathleen Gough and Gorkem Bakir, 2021). Chemical uniformity was assessed by processing the PPy:CMC images for the ratio of the CMC signature band at 1326 cm^{-1} to that of PPy at 963 cm^{-1} . The ATR-FTIR surface scan, rendered as a false-colour image, confirms that both polymers are homogeneously distributed at the microscale. Further chemical characterization by X-ray Photoelectron Spectroscopy has been reported previously, confirming the presence of polypyrrole and CMC, as well as traces of iron and chloride in the composite [10].

Pressure-sensing materials, named quantum tunneling composites (QTCs), have been built based on similar structures [2]. These materials consist of metallic micro-particles in an elastomeric matrix. Conduction occurs upon tunnelling and is minimal in the unstrained material. Under compressive strain, the elastomeric matrix is compressed, distances between particles are reduced and quantum tunnelling conduction is drastically increased. The prepared material exhibits similar behavior. We measured the impedance of PPy:CMC composite pellets between two stainless steel electrodes. The pressure between the two electrodes was controlled. Stassi *et al.* studied the impedance response of QTCs to changing pressure [12]. Their work proposed an equivalent circuit of a series resistor (R_s), representing contact resistance, and charge transfer resistance (R_p) and Constant Phase Element (CPE) in parallel, representing resistance to electron transfer between conducting particles within the non-conductive matrix, and the particles' capacitive behavior respectively:



A constant phase element is used in place of a capacitor to account for a slight dispersion in particles sizes and non-conductive film thickness. However, in all cases, the constant phase element's exponent β is above 0.8, approaching ideal capacitor behavior. Figure 14 shows that the application of pressure to PPy:CMC significantly increases its conductivity, similar to the behavior of typical QTCs. At the same time, increased pressure increases the determined capacitance, as the distance between conductive particles is reduced. This behavior is reversible, showing that high resistance is recoverable upon release of pressure over multiple cycles. While conductivity changes are less pronounced than in typical QTCs, which apply spiky metal particles with large localized electric fields, the conductivity behavior is clearly similar to typical QTCs, suggesting electron tunneling may be responsible for conduction in the produced PPy:CMC composite.

To test this hypothesis, depth profiling by Secondary Ion Mass Spectrometry (SIMS) was applied to the composite material. SIMS spectra show fragments of polypyrrole, containing C, H and N (dominantly CN^- , C_3N^-) as well as fragments of CMC, containing C, H, and O (C_2HO^- , CO_2H^- , $C_2H_3O_2^-$, and others). Moreover, consistent with previous XPS

measurements on similar samples, iron and chloride containing fragments were observed, originating from the pyrrole polymerization. Depth profiling shows a CMC rich surface (Figure 15). Polypyrrole concentration increases from the material surface to a constant value as the signal is averaged over multiple particles at different depths of ion milling. Iron and
5 chlorine signals change similarly to that of polypyrrole, suggesting co-location of iron and chloride with polypyrrole.

While the preferred embodiments of the invention have been described above, it will be recognized and understood that various modifications may be made therein, and the appended claims are intended to cover all such modifications which may fall within the spirit and scope
10 of the invention.

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CLAIMS

1. A method for preparing a quantum tunnelling composite material comprising:

mixing a quantity of an intrinsically conductive polymer with an aqueous dispersion of a non-conductive matrix material, thereby forming a composite material;

said composite material comprising a plurality of conductive components dispersed with a polymer matrix such that each respective one individual conductive component is separated from at least one respective adjacent conductive component, said composite material having a first condition wherein the respective one individual conductive components are separated from the at least one respective adjacent conductive component by a first distance such that there is no contact between adjacent respective individual conductive structural elements; and a second condition on pressure being applied to said composite material wherein the respective one individual conductive components are separated from the at least one respective adjacent conductive components by a second distance such that the respective individual conductive structural elements form a continuous electron conduction pathway.

2. The method according to claim 1 wherein the intrinsically conductive polymer is polypyrrole polythiophene, polyaniline, polyacetylene or a derivative thereof.

3. The method according to claim 1 wherein the non-conductive matrix material is selected from the group consisting of: carboxymethyl cellulose; polyacrylate; and alginate.

4. The method according to claim 1 wherein the non-conductive matrix material and the conductive polymer are mixed at a ratio of 1:0.1-1.25.

5. The method according to claim 1 wherein the non-conductive matrix material is carboxymethyl cellulose and the conductive polymer is polypyrrole.

6. The method according to claim 5 wherein the non-conductive matrix material and the conductive polymer are mixed at a mass ratio range of 1:0.1-1.25.

7. The method according to claim 1 wherein the quantum tunneling composite material is an organic quantum tunneling composite material.

8. The method according to claim 1 wherein each or all of the conductive

components are formed of the same intrinsically conductive polymer.

8. The method according to claim 1 wherein each or all of the conductive components are formed of one intrinsically conductive polymer.

9. A method for preparing a quantum tunnelling composite material
5 comprising:

mixing a quantity of an intrinsically conductive polymer with an aqueous dispersion of a non-conductive matrix material, thereby forming a composite material;

said composite material comprising a plurality of conductive components dispersed with a polymer matrix such that each respective one individual conductive
10 component is separated from at least one respective adjacent conductive component, said composite material having a first condition wherein the respective one individual conductive components are separated from the at least one respective adjacent conductive component by a first distance such that there is no contact between adjacent respective individual conductive structural elements; and a second condition on pressure being applied to said composite
15 material wherein the respective one individual conductive components are separated from the at least one respective adjacent conductive components by a second distance such that the respective individual conductive structural elements form a continuous electron conduction pathway,

wherein:

20 the intrinsically conductive polymer is selected from the group consisting of polypyrrole, polythiophene, polyaniline, polyacetylene and a derivative thereof;

the non-conductive matrix material is selected from the group consisting of: carboxymethyl cellulose; polyacrylate; and alginate; and

the non-conductive matrix material and the conductive polymer are mixed at a
25 ratio of 1:0.1-1.25.

10. The method according to claim 9 wherein the non-conductive matrix material is carboxymethyl cellulose and the conductive polymer is polypyrrole.

11. The method according to claim 9 wherein the quantum tunneling composite material is an organic quantum tunneling composite material.

30 12. The method according to claim 9 wherein each or all of the conductive

components are formed of the same intrinsically conductive polymer.

13. The method according to claim 9 wherein each or all of the conductive components are formed of one intrinsically conductive polymer.

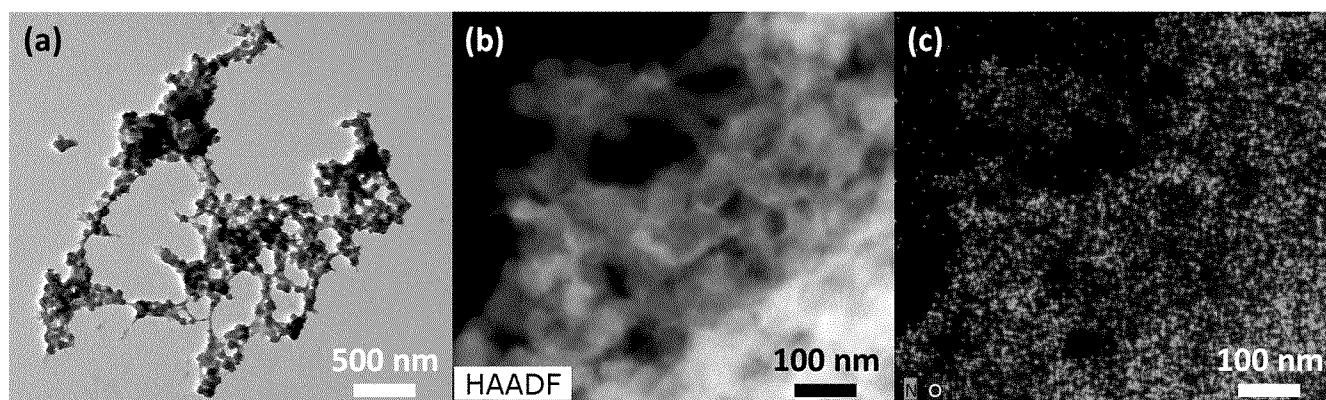


Figure 1.

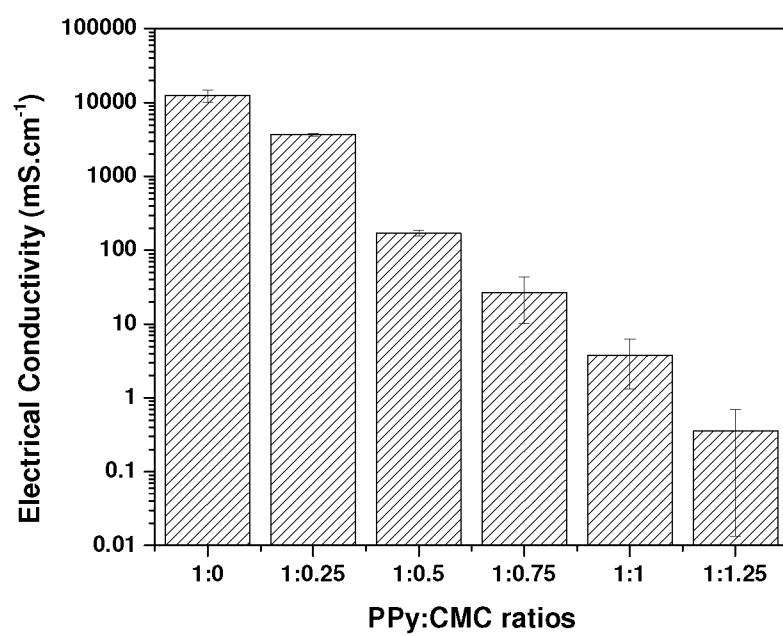


Figure 2.

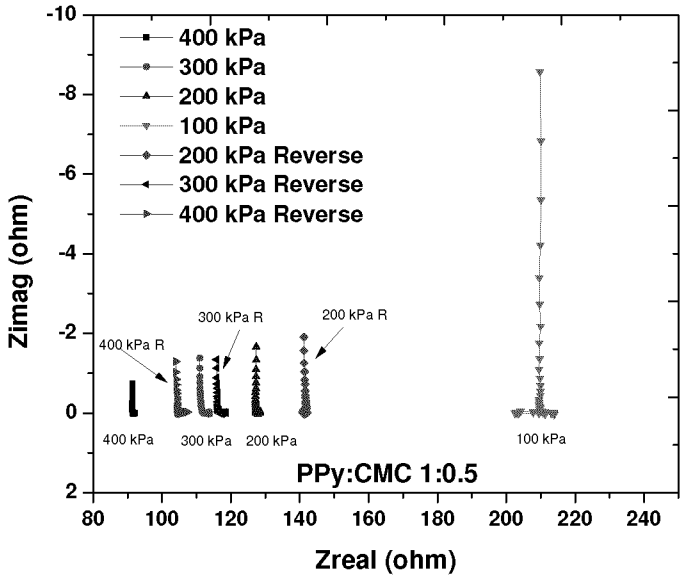


Figure 3.

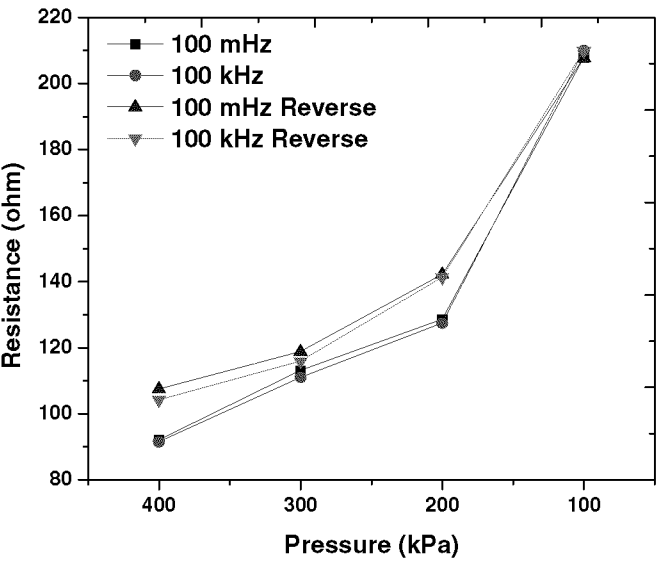


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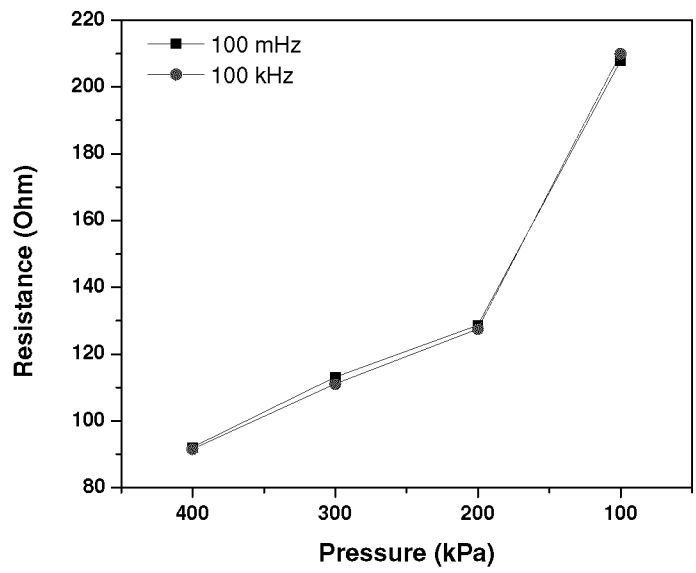


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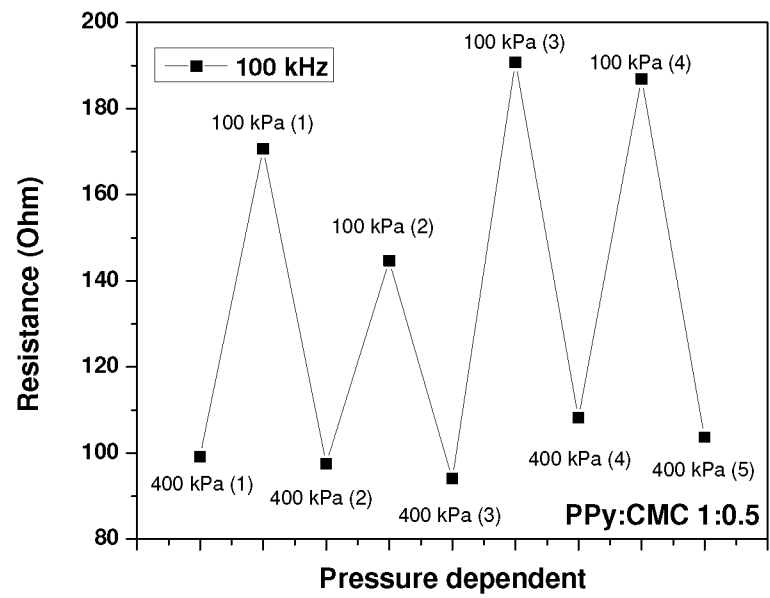


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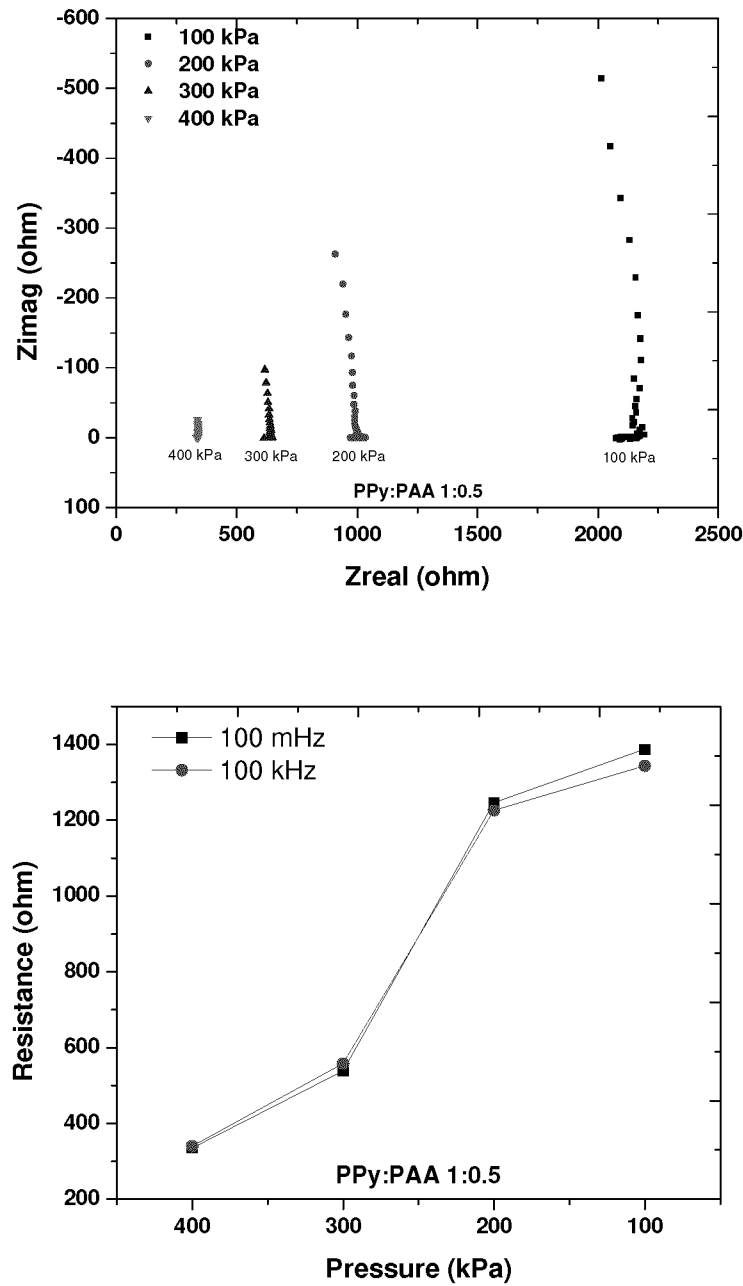


Figure 7.

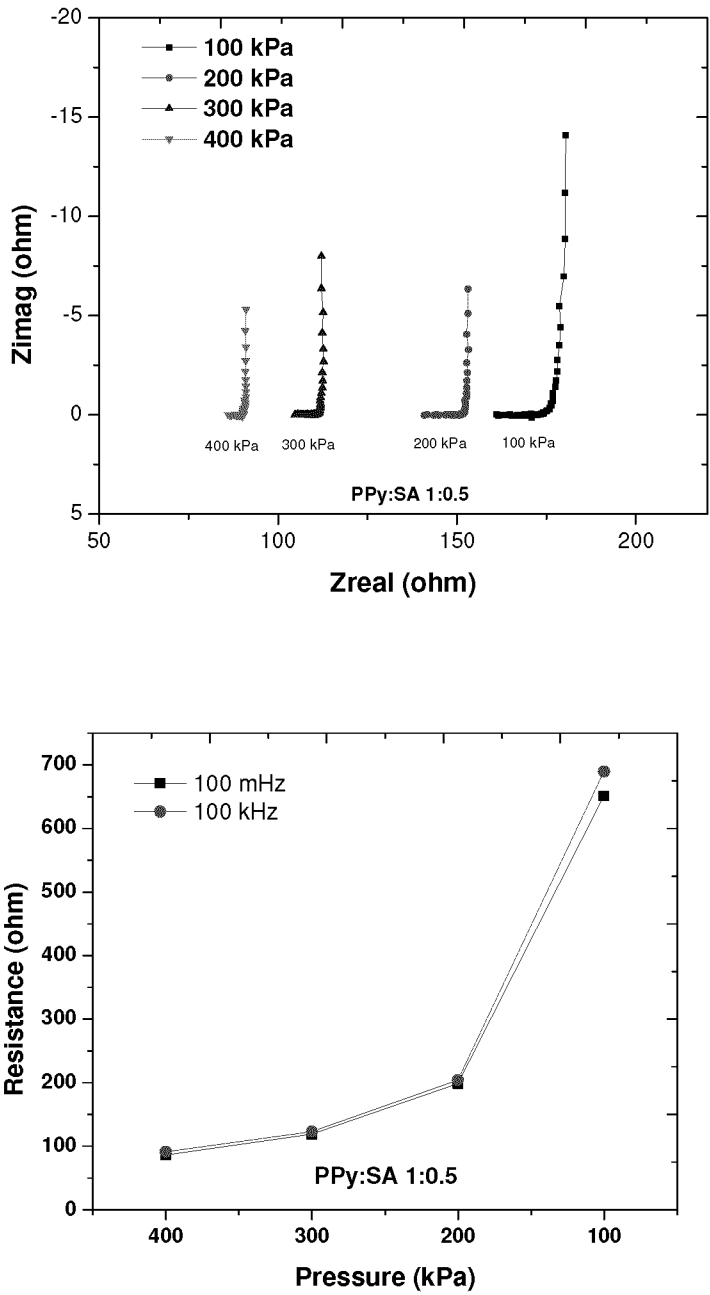


Figure 8.

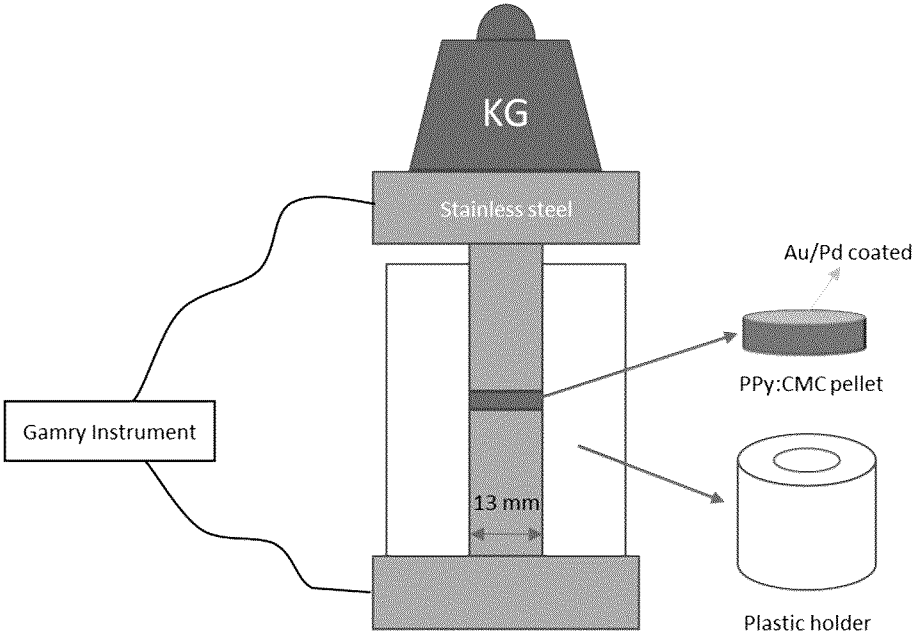


Figure 9.

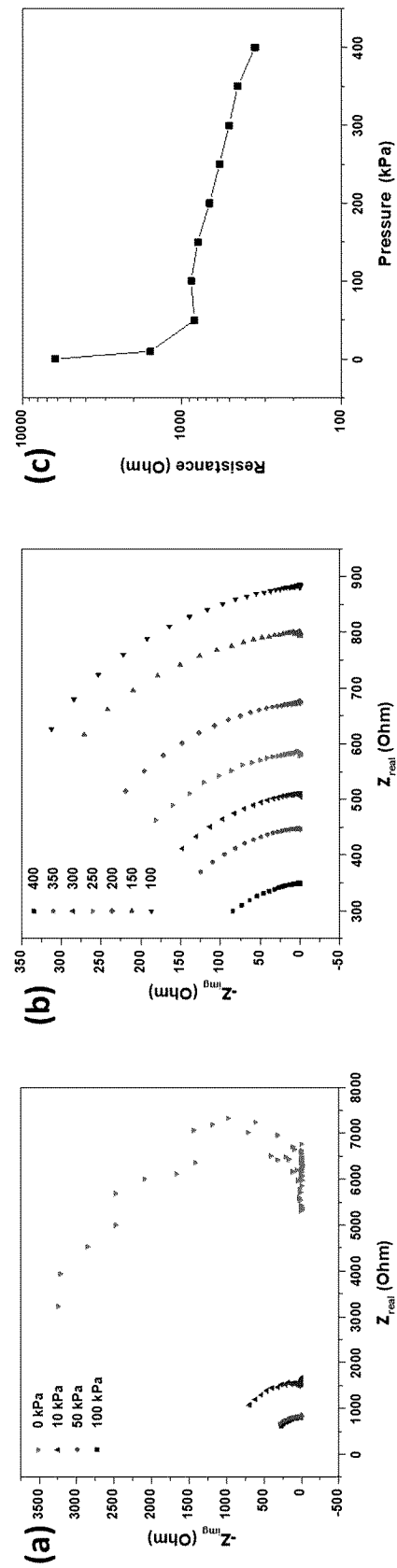


Figure 10

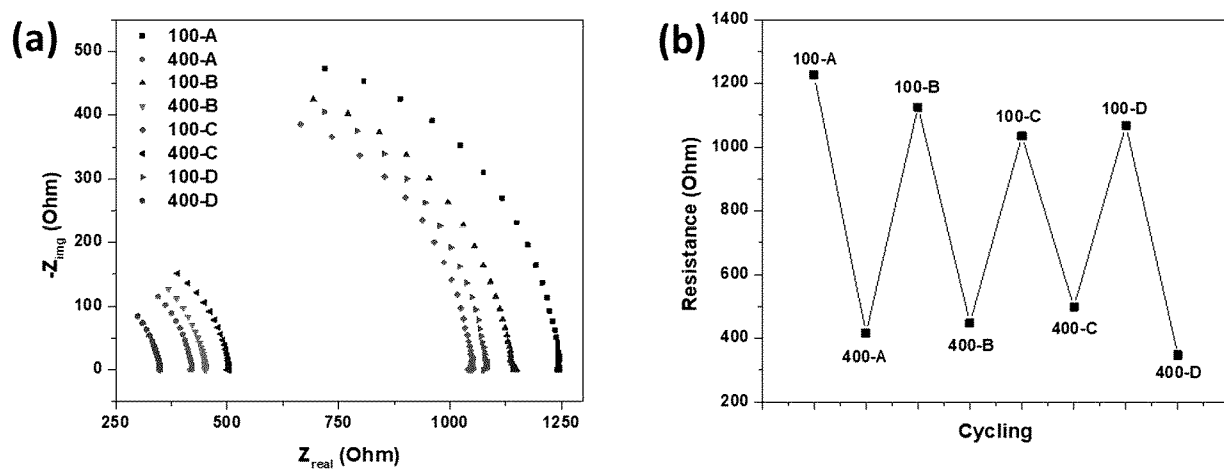


Figure 11.

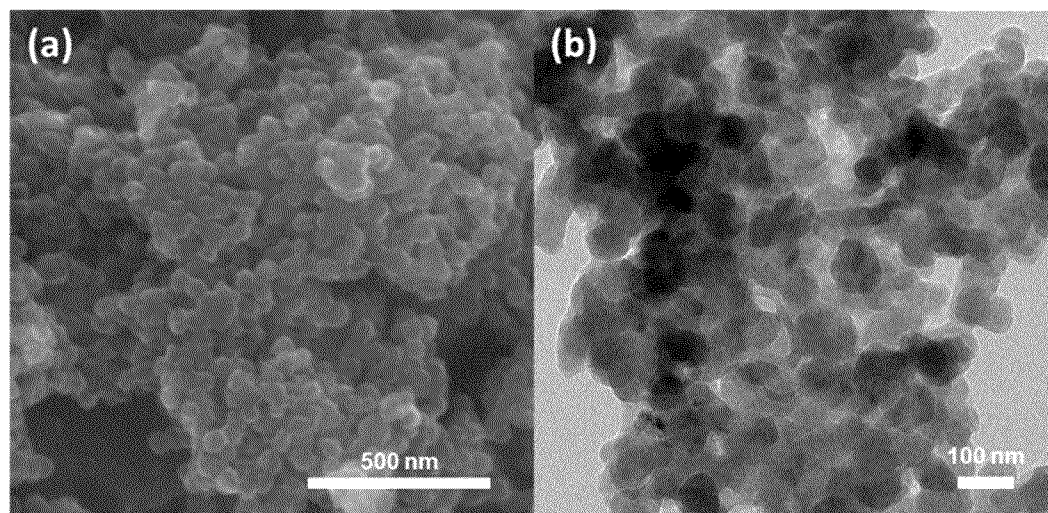


Figure 12.

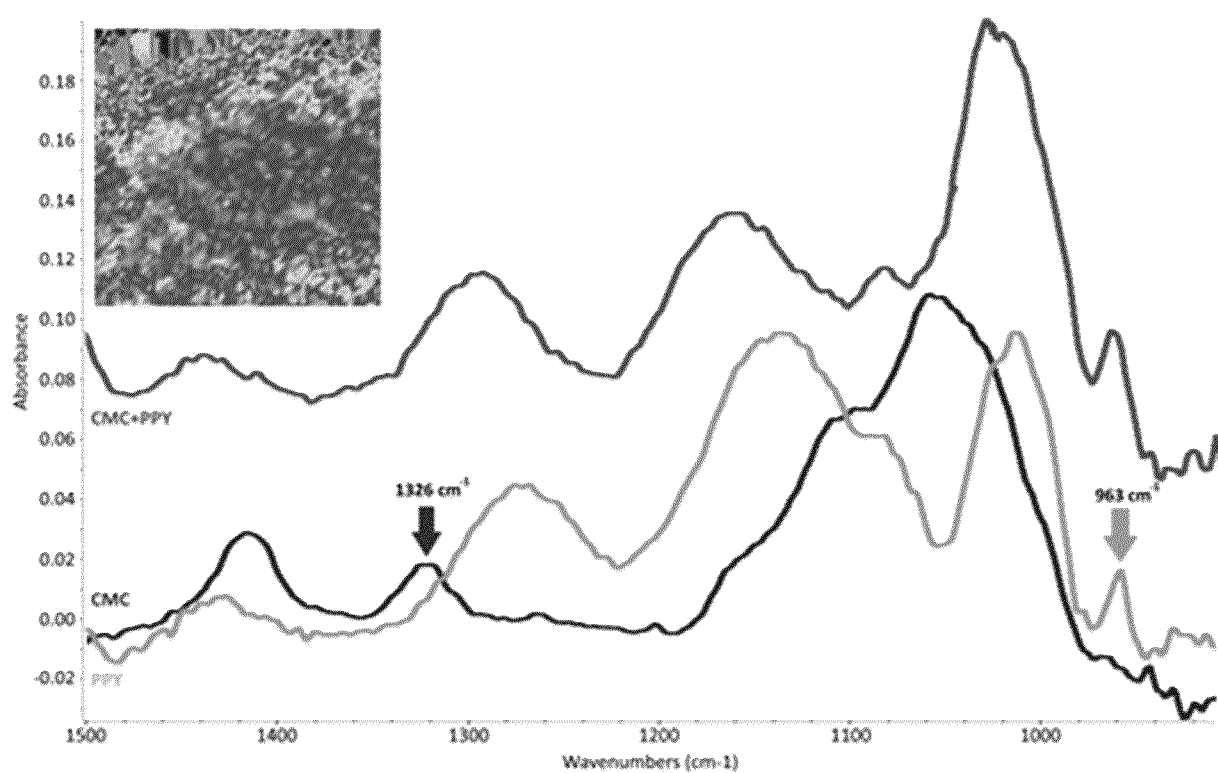


Figure 13

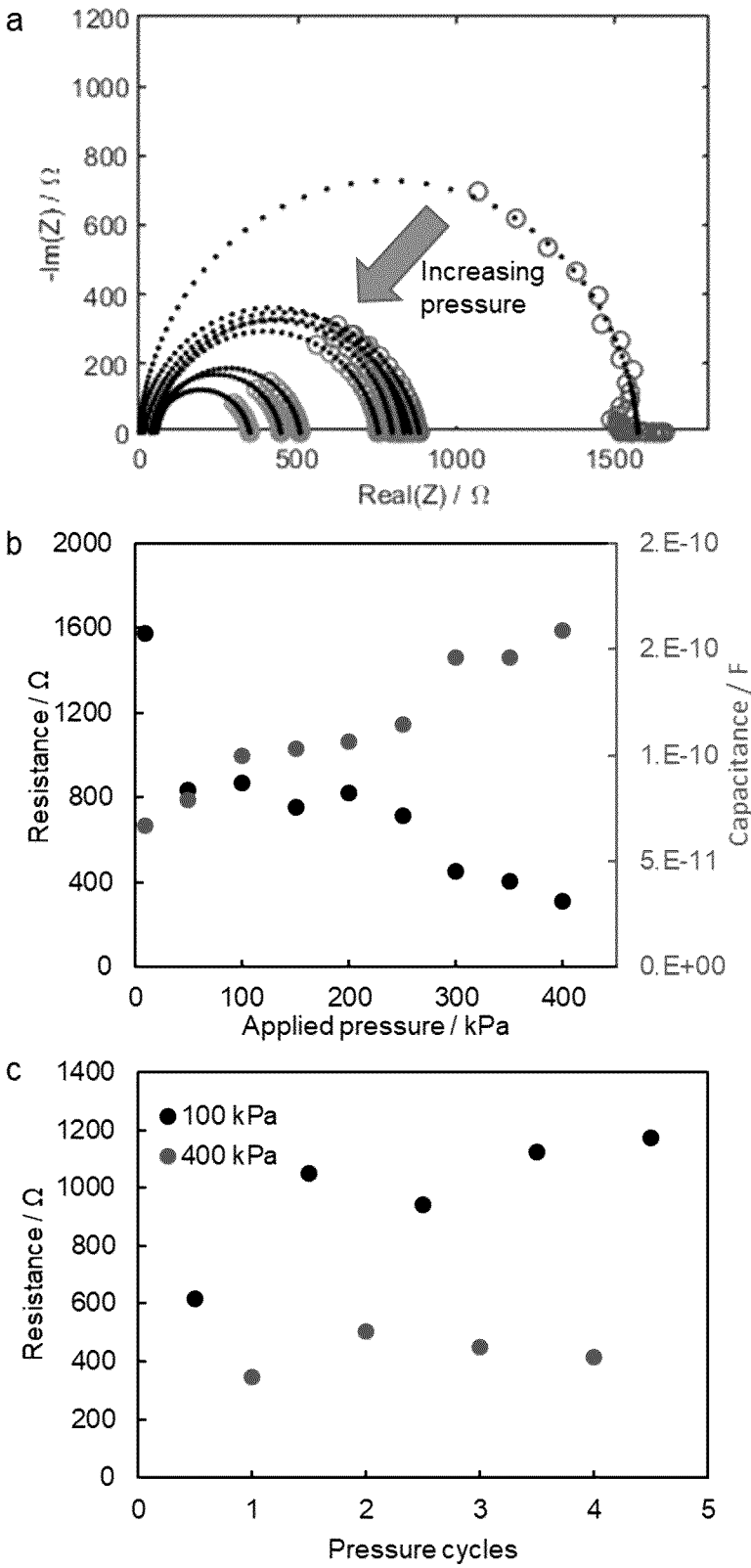


Figure 14.

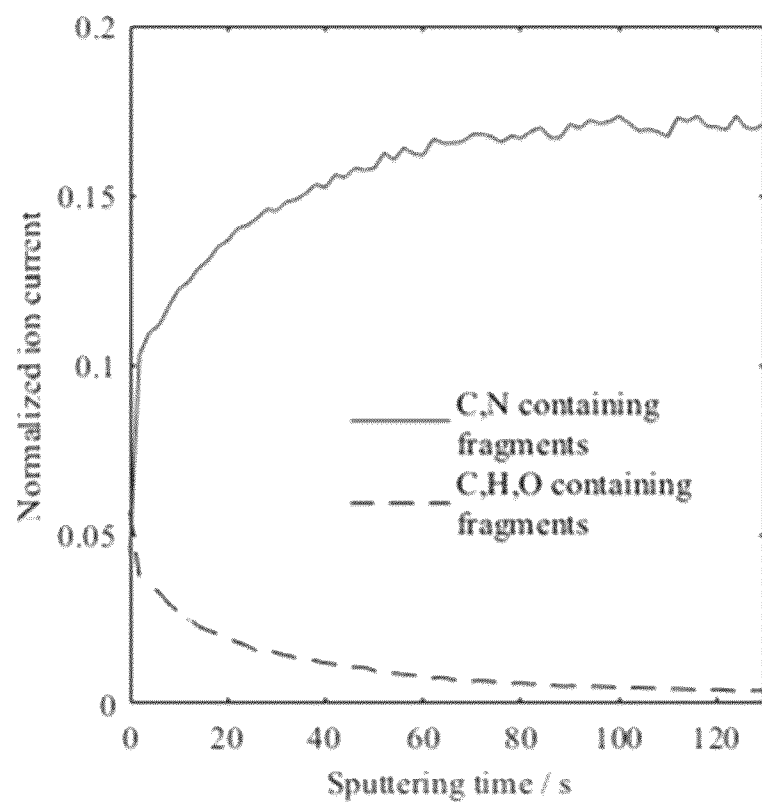


Figure 15.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/CA2022/050211

A. CLASSIFICATION OF SUBJECT MATTER

IPC: **H01L 29/12** (2006.01), **B82Y 30/00** (2011.01), **G01L 1/18** (2006.01)CPC: **H01L 29/12** (2020.01), **B82Y 30/00** (2020.01), **G01L 1/18** (2020.01)

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC: **H01L 29/12** (2006.01), **B82Y 30/00** (2011.01), **G01L 1/18** (2006.01)CPC: **H01L 29/12** (2020.01), **B82Y 30/00** (2020.01), **G01L 1/18** (2020.01)

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic database(s) consulted during the international search (name of database(s) and, where practicable, search terms used)

Database: Questel Orbit | Keywords: quantum tunnelling, quantum tunneling, polymer, matrix, conductive, polypyrrole, polythiophene, polyaniline, polyacetylene, carboxymethyl cellulose, polyacrylate, alginate, adjacent conductive component, aqueous dispersion, carboxy methyl, composite material, conductive component, conductive matrix material, conductive polymer, derivative, electron conduction pathway, intrinsically conductive polymer, matrix material, nonconductive matrix material, polymer matrix, pressure, structural element conduction

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US9490045 B2 (TEE et al.) 08 November 2016 (08-11-2016) *whole document*	1-13
A	US2018/0159092 A1 (BARENBERG et al.) 07 June 2018 (07-06-2018) *whole document*	1-13
A	WO2020/039216 A2 (LUSSEY) 27 February 2020 (27-02-2020) *whole document*	1-13

☐ Further documents are listed in the continuation of Box C.☒ See patent family annex.

* "A" "D" "E" "L" "O" "P"	Special categories of cited documents: document defining the general state of the art which is not considered to be of particular relevance document cited by the applicant in the international application earlier application or patent but published on or after the international filing date document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) document referring to an oral disclosure, use, exhibition or other means document published prior to the international filing date but later than the priority date claimed	"I" "X" "Y" "&"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art document member of the same patent family
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Date of the actual completion of the international search
12 May 2022 (12-05-2022)Date of mailing of the international search report
13 May 2022 (13-05-2022)

Name and mailing address of the ISA/CA
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Authorized officer

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INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.

PCT/CA2022/050211

Patent Document Cited in Search Report	Publication Date	Patent Family Member(s)	Publication Date
US9490045B2	08 November 2016 (08-11-2016)	US2016049217A1 CN104919626A WO2014116335A2 WO2014116335A3 WO2014116335A9	18 February 2016 (18-02-2016) 16 September 2015 (16-09-2015) 31 July 2014 (31-07-2014) 23 October 2014 (23-10-2014) 12 February 2015 (12-02-2015)
US2018159092A1	07 June 2018 (07-06-2018)	EP3292581A1 EP3292581A4 WO2016179501A1	14 March 2018 (14-03-2018) 05 December 2018 (05-12-2018) 10 November 2016 (10-11-2016)
WO2020039216A2	27 February 2020 (27-02-2020)	WO2020039216A3 CN112601789A EP3841171A2 GB201912281D0 GB2581223A GB201813857D0 GB201911813D0 US2021225552A1	26 March 2020 (26-03-2020) 02 April 2021 (02-04-2021) 30 June 2021 (30-06-2021) 09 October 2019 (09-10-2019) 12 August 2020 (12-08-2020) 10 October 2018 (10-10-2018) 02 October 2019 (02-10-2019) 22 July 2021 (22-07-2021)