Superior Electrochemical Performance of Carbon Nanotubes Directly Grown on Sharp Microelectrodes

Alberto Ansaldo,[†,⊥] Elisa Castagnola,[†,‡,⊥] Emma Maggiolini,[†] Luciano Fadiga,[†,§] and Davide Ricci[†,*]

[†]Robotics, Brain and Cognitive Sciences Department, Italian Institute of Technology, Genoa, Italy, [‡]Department of Informatics, Systems, Telecommunication, University of Genoa, Genoa, Italy, and [§]Section of Human Physiology, University of Ferrara, Ferrara, Italy. [⊥]These authors contributed equally to this work.

ABSTRACT We report for the first time how coatings made by directly growing carbon nanotubes (CNTs) on the tip of neural microelectrodes outperform others made by electrodeposited CNT composites. Not only do they reduce microelectrode impedance but they also are able to inject high currents without degradation and are stable in time. These results suggest that they are excellent candidates for chronic applications especially when both neural recording and stimulation have to be performed by the same microelectrode.

KEYWORDS: carbon nanotubes · chemical vapor deposition · electroplating · nanostructured composites · microelectrodes · electrochemical stability · neural recording · neural stimulation

Within brain machine interface research, which has the ambitious aim of interfacing external devices with the human central nervous system, one of the greatest technology bottlenecks resides in the lack of appropriate sensors capable of providing safe, accurate, and long lasting bidirectional access to brain signals.[1] At present, among the various approaches, intracortical microelectrode implants guarantee the best results since they allow one to obtain good quality recordings of neuronal activity and also give access to direct stimulation of neural networks. The design of intracortical electrodes has to fulfill many conflicting requirements, and there is ample room for improvement, especially on the materials side. An ideal recording electrode should be as small as possible to reduce perturbation of the local electric field and minimize tissue damage during insertion but, at the same time, should have low impedance to enhance signal quality during recordings.[2,3] Moreover, for neural stimulation, electrodes should be capable of injecting relatively large currents while minimizing electrode degradation due to faradaic effects, requirements generally satisfied by increasing the electrode size. In order to allow long-term operation, the surface of the microelectrodes should be able to facilitate charge transport and minimize inflammatory reaction and gliosis.[4] The vast majority of electrodes commonly used rely on metals as interface material for recording and stimulation and fall short in satisfying such conflicting requirements.

In the past few years, research has been directed to introduce new electrode materials such as iridium oxide,[5,6] conductive polymers,[7−9] and carbon nanotubes (CNTs)[10−13] and develop methods for creating a new generation of implantable devices which can help overcoming aforementioned problems.

CNTs have attracted special attention for the purpose as they possess attractive properties such as high surface area, high electrical conductivity, and mechanical strength, as testified in recent years by an increasing amount of published work mainly related to *in vitro* neural applications. A variety of methods for the deposition of CNTs as electrode material have been proposed, such as solution casting,[14−17] chemical vapor deposition,[10,13,18−21] electrochemical deposition,[11,22−25] covalent bonding,[11] and layer-by-layer deposition.[26,27] Even if CNTs are always present in composition of the electrode material, care must be taken in correlating results as the final properties of the devices strongly depend on the treatments that CNTs have undergone, that is, their chemical functionalization, their interaction with other chemical compounds used, and the electrode coating process.

Solution casting of appropriately functionalized CNTs on glass coverslips followed by high-temperature defunctionalization resulted in large area planar electrodes that act as good growth substrates for neurons[14] and show intimate contact between CNTs

* Address correspondence to davide.ricci@iit.it.

Received for review December 14, 2010 and accepted February 14, 2011.

Published online February 22, 2011
10.1021/nn103445d

and the cell membranes[15] promoting electrical coupling.[16] Direct synthesis of multiwalled CNT (MWCNT) pillars *via* chemical vapor deposition (CVD) onto micromachined substrates has allowed preparation of a multielectrode array (MEA)[10] where the superior properties in charge injection of the exposed carbon surface of CNTs have been successfully demonstrated through stimulation of a cultivated network of primary hippocampal neurons. Islands of MWCNTs assembled having a different morphology (*i.e.*, "fluffy" mats) have been directly synthesized on the active area of MEAs and a comparison with the uncoated device has been made.[13] The CNT mats induced preferential adhesion of neural cells anchored *via* dendrite entanglement to the carbon nanotubes and allowed superior signal recording.[18,19] The same substrates were successfully employed also on retina slices,[20] indicating how such three-dimensional CNT coatings have a great potential for signal recording also on organotypic cultures of neural tissue.

Electrochemical techniques for the co-deposition of CNTs and conductive polymers,[11,12,24,25] gold,[11,22,23] and polyethylene glycol,[23] where the CNTs act as nanoscaffolds for increasing the porosity and total surface area of the composite, have been applied on a variety of *in vitro* and *in vivo* electrodes with different shape and made from different materials, demonstrating that such nanostructured coatings enhance both recording and electrical stimulation of neurons by decreasing electrode impedance and increasing charge transfer capability. Layer-by-layer techniques[26,27] involving functionalized CNTs and polyelectrolytes show similar results, with superior performance compared to other nanofillers or pure conductive polymers.[27]

While the corpus of published results for both *in vivo* and *in vitro* experiments strongly encourages pursuit of the use of CNTs for manufacturing superior neural electrodes, a direct comparison of the performance of the different CNT-based composites and *in situ* grown CNTs on *in vivo* microelectrodes is still lacking.

RESULTS AND DISCUSSION

By using sharp metal microelectrodes insulated by quartz glass, we show that it is possible to set up a comparison between an ample variety of CNT deposition methods obtaining coatings to be tested in one of the most demanding applications for electrodes (*i.e.*, intracortical neural recording and stimulation). Quartz-insulated platinum/tungsten wires of 80 μm outer shank diameter and 20 μm metal core diameter (Thomas Recording, Giessen, Germany) were ground using a tip grinding machine (DIECKL-ST, Thomas Recording), obtaining sharp tips with a typical geometric area of $\sim$1000 μm^2 and with an impedance value at 1 kHz ranging from 0.5 to 0.7 MΩ. These sharpened wires are used to build what are usually considered excellent quality intracortical microelectrodes.

Such quartz-insulated wires are capable of withstanding high temperatures and have thus allowed us, for the first time, to report a direct comparison of the performance of *in situ* CVD grown CNT coatings (CVD-CNT) and of polypyrrole CNT (PPy-CNT) and gold CNT (Au-CNT) composites prepared by electrochemical co-deposition methods on identical devices.

For the *in situ* CNT CVD growth, we have used an ad-hoc process based on ethanol CVD on nickel-plated electrodes.[28] Among all other possible CNT coatings, we have chosen, as one benchmark, PPy-CNT composites as they have been presented as excellent materials for electrodes by several research groups,[11,12,24,25] thanks to their very low impedance and large charge injection limit. In our case, polypyrrole (PPy) and chemically functionalized multiwalled CNT nanocomposites were co-electrodeposited in potentiostatic mode from an aqueous suspension of 1 mg$\cdot$mL^{-1} COOH-MWCNTs containing 0.5 M of pyrrole and 0.4 wt % of poly(sodium 4-styrene sulfonate) (PSS). The other chosen benchmark, Au-CNT, has the interesting feature of being derived from standard metal plating techniques usually available in neurophysiology laboratories.[11,23] Starting from a 10 mM potassium dicyanaurate(I) (Sigma-Aldrich) aqueous solution containing 1.5 mg$\cdot$mL^{-1} of partially dispersed MWCNTs, Au-CNT nanocomposites were co-electrodeposited by applying monophasic voltage pulses.

We have chosen two different CNT composites, one based on a conductive polymer and the other based on a noble metal, in order to help discriminate the effects due to the CNT-induced surface nanostructure from those derived from the nature of the material that ultimately acts as the electrode−solution interface. As the final aim is to select the most appropriate material to be used for intracortical microelectrodes, we have extended our analysis beyond the electrical and electrochemical performance of the coatings and investigated also their mechanical sturdiness and stability in time. In fact, it is of the utmost importance that the coatings are capable of withstanding the mechanical stress they undergo while piercing the *dura mater* to reach the brain *cortex* without losing their properties. The electrochemical behavior of the different CNT coatings was studied by cyclic voltammetry (CV) and galvano electrochemical impedance spectroscopy (GEIS) in a physiological aqueous solution (NaCl 0.9%). For CVs, the potential on the working electrode was swept between 0.6 and −1.0 V *vs* Ag/AgCl at a scan rate of 100 mV/s, starting at open-circuit potential and sweeping in the positive direction first. The total charge transfer capability (CTC_{tot}) was calculated as the time integral of a whole CV cycle and the cathodic charge transfer capability (CTC_c) as the time integral of the cathodic current of a CV cycle. For GEIS measurements, a sine wave of 300 nA rms amplitude was used. The impedance of all electrodes was measured over the

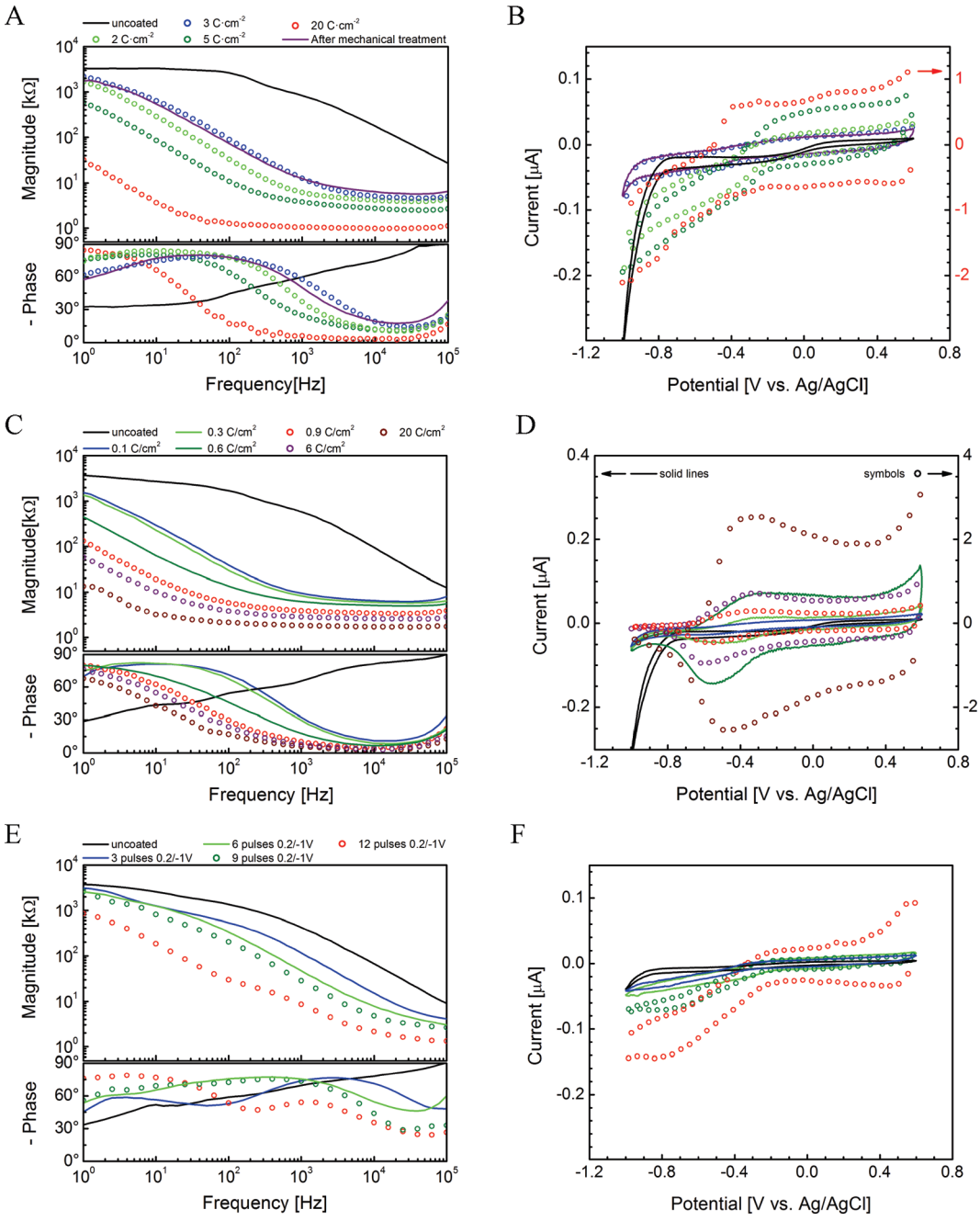

Figure 1. Examples of impedance spectra and cyclic voltammograms (CV) of uncoated and CNT-coated microelectrodes. In all panels, the black solid line corresponds to an uncoated electrode, solid lines correspond to electrodes that are mechanically stable, and circles correspond to electrodes that are not viable due to mechanical instability of the coating. (A) Impedance spectra and (B) cyclic voltammetry of electrodes coated with carbon nanotubes grown by chemical vapor deposition varying the charge used to deposit the catalyst (nickel). Almost all electrodes become usable only after a mechanical pretreatment (purple solid line); in CVs, red circle plot refers to the scale on the right; (C) impedance spectra and (D) cyclic voltammetries of electrodes coated with different amounts (*i.e.*, deposition charge) of polypyrrole-CNT composite; in CVs, all of the plots of unstable electrodes (circle plot) refer to the right scale; (E) impedance spectra and (F) cyclic voltammetries of electrodes coated with different amounts (*i.e.*, deposition charge) of gold-CNT composite.

range of $1-10^5$ Hz. All of the electrochemical depositions and characterizations were carried out using a potentiostat/galvanostat (Parstat 2273, Princeton Applied Reasearch, Oak Ridge, TN, USA) connected to a standard electrochemical cell used in a three-electrode configuration with a platinum counter electrode (area of 35 mm^2) and a Ag/AgCl reference electrode.

Impedance spectra and cyclic voltammograms obtained using the three different coatings are reported in Figure 1. The electrode impedance can be lowered by many orders of magnitudes, but thick coatings are usually not stable when a mechanical stress is applied (circles). As our final goal is to prepare electrodes suitable for *in vivo* recordings in rats, we have

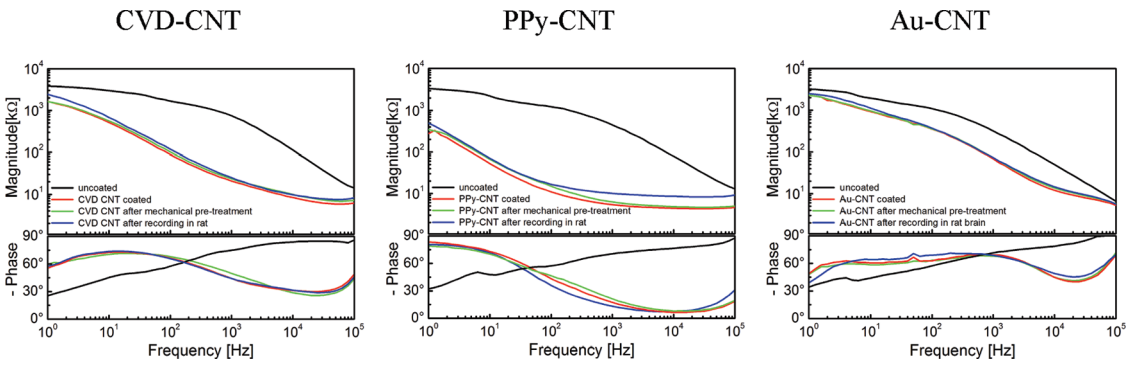

Figure 2. Impedance spectra of viable electrodes withstanding rat dura mater penetration. Coated electrodes (red), after a mechanical pretreatment (green), and after recording sessions in rat brain (blue) *versus* an uncoated one (black).

systematically subjected all electrodes to mechanical tests simulating the penetration through the dura mater of a rat brain. The electrodes were repeatedly passed through a sheet of Parafilm M (Pechiney Plastic Packaging) wet with physiological solution and kept in tension (but not stretched) through the opening of a beaker; after each penetration, they were electrochemically and morphologically characterized. Initially, there is a loss of excess material, but after 3−5 penetrations, the coating left is stable and performance is satisfactory. The electrodes that have been pretreated in this way are capable of withstanding *dura mater* penetration: a clear evidence is that even after an acute intracortical recording session "viable electrodes" present an impedance spectrum that does not change significantly (Figure 2).

Special care must be taken in presenting "dramatic" changes in impedance and charge transfer capability that may be valuable when electrodes are used in other application fields but cannot be employed for intracortical neural recording and stimulation.

All data reported are based on an average of five electrodes for each different condition. With all three coatings, we achieved a significant decrease of magnitude and phase of the impedance while increasing frequency, with behaviors that strongly depend on the amount of material and the deposition process.

For CVD-CNT electrodes, nanotube growth is roughly proportional to the amount of nickel deposited,[28] that is, the charge density applied during the electrodeposition (ranging from 2 to 20 $C \cdot cm^{-2}$), and gives rise to a quite remarkable volume of woven CNT material for larger nickel quantities (Figure S1 in Supporting Information). The impedance decreases down to 1.1 ± 0.1 kΩ at the biologically relevant frequency of 1 kHz, with a CTC_{tot} of 2630.1 ± 122.2 $mC \cdot cm^{-2}$ and a CTC_c of 1743.4 ± 161.7 $mC \cdot cm^{-2}$. After mechanical treatment, quite independently from the initial amount of CNTs, the final viable electrode has typically an impedance of 16.3 ± 4.8 kΩ and −47.4° ± 0.9° phase at 1 kHz, with a 70.8 ± 1.1 $mC \cdot cm^{-2}$ CTC_{tot} and 56.9 ± 0.8 $mC \cdot cm^{-2}$ CTC_c still significantly better than the uncoated electrode (typically 600 kΩ and 20 $mC \cdot cm^{-2}$ CTC_{tot}). An example of a viable CVD-CNT electrode is shown in Figure 3A,B.

In the case of PPy-CNT-coated electrodes, the final impedance frequency response and CTC can be accurately predetermined by controlling the charge density applied during deposition, which is proportional to the amount of PPy-CNT formed on the electrode surface (Table S2 in Supporting Information). Coatings obtained using a high deposition charge density, 20 $C \cdot cm^{-2}$ (an example of such an electrode is shown in Figure S2 in Supporting Information), result in an impedance modulus of 1.9 ± 0.2 kΩ with a huge 5486.6 ± 77.4 $mC \cdot cm^{-2}$ CTC_{tot} and 2920.3 ± 191.4 $mC \cdot cm^{-2}$ CTC_c. These values compare well with those reported in literature,[11,24] but it must be said that such electrodes do not pass the mechanical test without performance degradation (*i.e.*, loss of material). Viable electrodes are made using charge densities between 0.1 $C \cdot cm^{-2}$ (impedance magnitude 12.3 ± 2.2 kΩ @1 kHz, CTC_{tot} 59.4 ± 16.5 $mC \cdot cm^{-2}$, and CTC_c 40.8 ± 10.9 $mC \cdot cm^{-2}$) and 0.6 $C \cdot cm^{-2}$ (impedance magnitude 5.7 ± 0.3 kΩ @1 kHz, CTC_{tot} 212.3 ± 23.9 $mC \cdot cm^{-2}$, and CTC_c 118.2 ± 5.6 $mC \cdot cm^{-2}$) where the coatings stay stable during insertion in the brain tissue. An example of a viable PPy-CNT electrode is shown in Figure 3C,D.

In the case of Au-CNT coatings, the improvements in impedance and CTC are limited by the behavior of gold that produces nanorough surfaces rather that nanoporous ones. It has been reported that the surface morphology of electroplated gold can be controlled both by varying density and waveform of the deposition current[29,30] and by adding to the plating solution additives such as poly(ethylene glycol) or CNTs.[23] In our experience, using CNTs as additive, morphologies vary from lamellae with a thickness of 20−50 nm to globular structures of 100 nm to 2 μm in diameter (Figure 4). Such globular structures tend to form large arborizations that usually correspond to lower impedance and higher CTC but are mechanically unstable: we have therefore focused our attention to coatings that are made of lamellar structure. Limiting the analysis to viable electrodes, in the best case, they present an impedance of 59.6 ± 11.2 kΩ @1 kHz, a CTC_{tot} of 65.6 ±

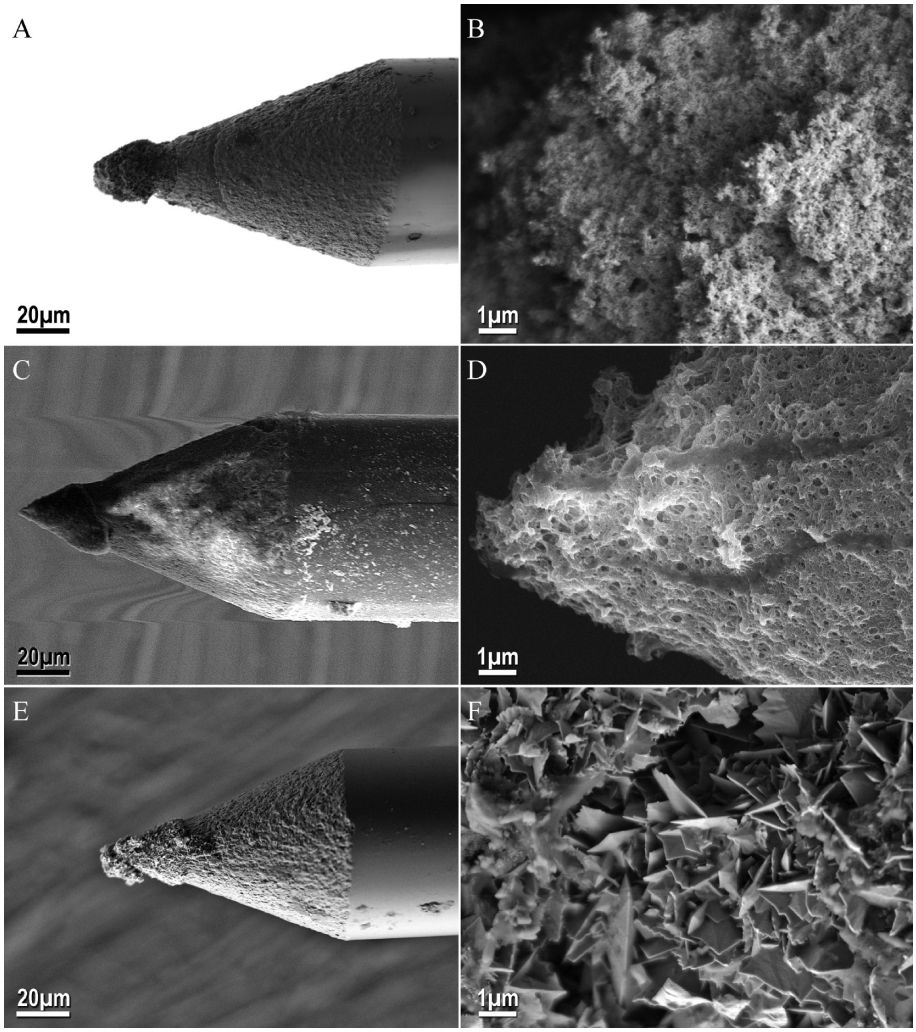

Figure 3. Scanning electron microscopy images of microelectrodes coated with (A,B) carbon nanotubes grown by chemical vapor deposition, (C,D) polypyrrole-CNT composite, and (E,F) gold-CNT composite.

13.6 mC·cm^{-2}, and a CTC$_c$ of 58.5 ± 10.6 mC·cm^{-2}. An example of the morphology of such an electrode is shown in Figure 3E,F.

These electrochemical data demonstrate that all the three CNT-based coatings allow, to a different degree, the wanted impedance decrease that opens the route to better signal-to-noise ratio in single neuron and multiunit recordings.

The voltammograms show how this effect arises from an increased exchange of charges between electrode and solution due to the increased effective area of the nanostructured material. The enhanced CTC is an essential feature that makes these electrodes suitable not only for recording but also for stimulation, a very sought-after property in BMI applications. This, combined with their low impedance, opens the possibility to safely use these electrodes for stimulation maintaining excellent recording performance. In particular, all three coatings enhance the cathodic CTC of the electrodes, which is well-known to initiate more efficiently cellular action and is typically used to stimulate neural tissues.[27,31,33]

To fully assess this possibility, we have estimated the charge injection limit for a set of typical electrodes, using cathodic-first charge-balanced biphasic symmetric current pulses, commonly used in electrophysiology experiments.[3,31,32] The charge injection limit is defined as the maximum quantity of charge an electrode can inject before reaching the water electrolysis potential that was determined experimentally by cyclic voltammetry and is reported in Table 1. The charge density injection limit (Q_{inj}) was calculated as the time integral of the current in the loading phase normalized by the geometric area of the uncoated microelectrode. Q_{inj} was obtained using pulses with total period of 2 ms and a cathodic duration of 500 μs. Values of the charge injection limit calculated for uncoated and coated electrodes are reported in Table 1 together with their maximum current intensity and impedance at 1 kHz.

As it could be expected from the lower impedance, the highest Q_{inj} (7 mC·cm^{-2}) was achieved using PPy-CNT coating, a value very close to the ones previously reported for similar electrodes.[25] In the case of

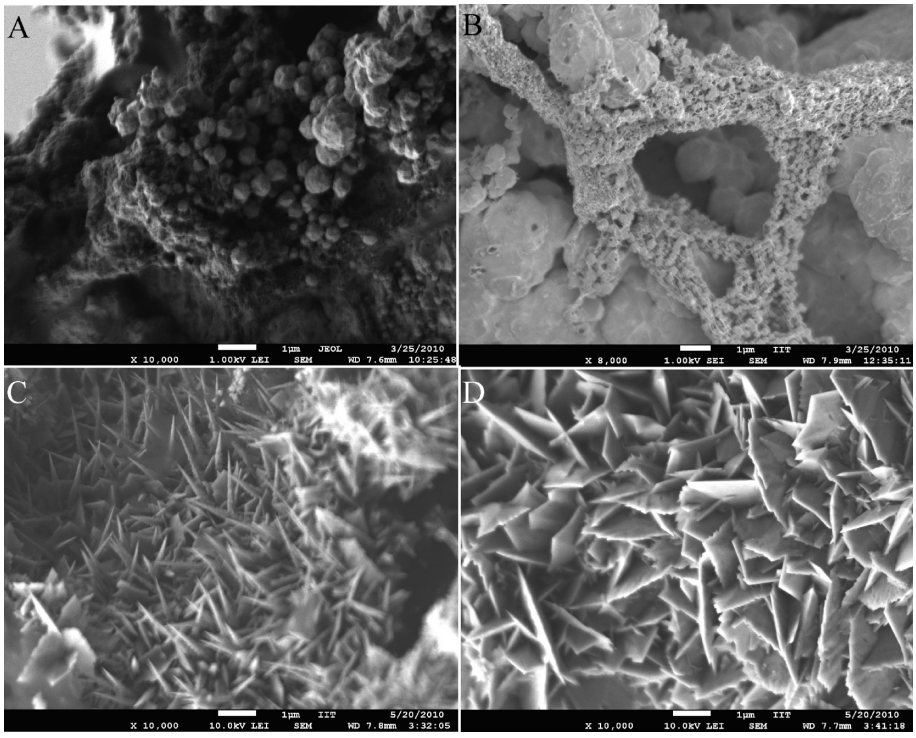

Figure 4. Different morphologies of Au-CNT coatings. Globular structures obtained applying (A) monophasic voltage pulses of 0.2−1 V, 50% duty cycle, 10 s, and −0.4 V bias potential, (B) monophasic voltage pulses of 0.2−1 V, 50% duty cycle, 60 s, and −0.4 V bias potential. (C,D) Different size lamellar crystals obtained applying monophasic voltage pulses of 0.2−1 V, 50% duty cycle, 120 s, and 0 V bias potential and varying the solution stirring and the dispersion of the CNTs.

TABLE 1. Examples of Values of Charge Injection Limit Calculated for Differently Coated Electrodes

	potential limit (V *vs* Ag/AgCl)	charge injection limit Q_{inj} (mC·cm^{-2})	cathodic current (μA)	impedance magnitude @1 kHz (kΩ)	mechanism
uncoated	−0.8−0.6	0.3	6	600	capacitive
CVD-CNT	−1−1.15	4	80	15	capacitive
PPy-CNT	−1−0.6	7	140	7	pseudocapacitive
Au-CNT	−1−0.6	0.8	16	50	capacitive

CVD-CNT, the value achieved is 4 mC·cm^{-2}, superior to previously reported 1−1.6 mC·cm^{-2} for vertical pillars, thanks to the larger exposed CNT surface of our coating morphology.[10] Au-CNT electrodes do not achieve high values of Q_{inj} (0.8 mC·cm^{-2}) but still ensure at least a factor of 2 improvement with respect to uncoated electrodes (0.2−0.4 mC·cm^{-2}).

Limiting the analysis to these results, the coatings based on the electrochemical co-deposition of a conductive polymer (such as PPy) and CNTs appear to be the ones that show the best performance. As long as our aim is to establish whether these electrodes could be used for long-term signal acquisition (chronic) and neural stimulation, we investigated their stability over time and under prolonged stimulation use.

To understand the ability to withstand a sustained stimulation activity, we have compared the impedance of typical usable electrodes prior and after having subjected them to series of cathodic-first charge-balanced biphasic current pulses varying the pulse duration between 2 and 3 ms, charge density between 0.4 and 1.6 mC·cm^{-2}, and cathodic pulse duration between 100 and 500 μs. As it can be clearly seen in Figure 5, while CVD-CNT-coated electrodes are stable and withstand a million 500 μs pulses without degradation whatsoever, all of the other coatings show different degrees of impedance variation upon stimulation.

PPy-CNT coatings rapidly degrade after a few thousands pulses at 1.6 mC·cm^{-2}, and even if the current density is reduced down to 0.4 mC·cm^{-2}, after a number of pulses on the order of 10 000, they again start degrading (Figure S3 in Supporting Information), in good agreement with previous reports[24] that show how carbon nanotubes have a positive effect reducing but unfortunately not avoiding polypyrrole degradation under current flow.

Au-CNT composite coatings are nearly as stable as CVD-CNTs, being able to sustain a million pulses too, but the maximum charge density is limited to 0.8 mC·cm^{-2}, which corresponds to its charge injection limit, in order to avoid faradaic reactions.

Another important feature not to be overlooked while assessing microelectrode performance is that

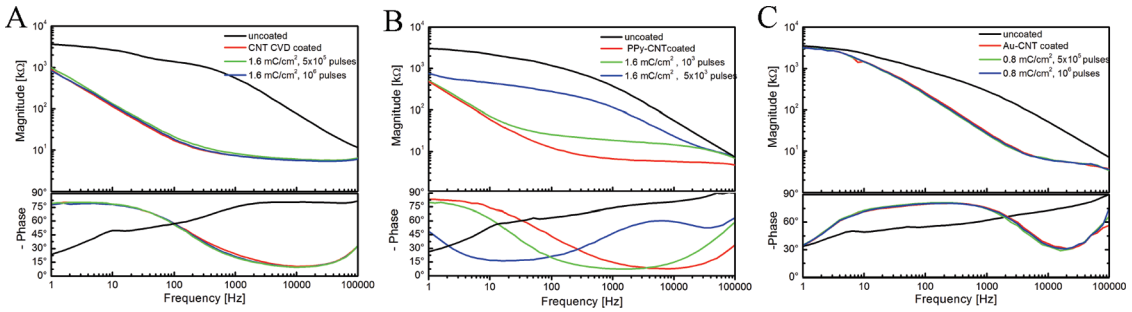

Figure 5. Impedance spectra, before and after stimulation experiments, of electrodes coated with (A) carbon nanotubes grown by chemical vapor deposition, (B) polypyrrole-CNT composite, and (C) gold-CNT composite. In all panels, the black line corresponds to an uncoated reference electrode.

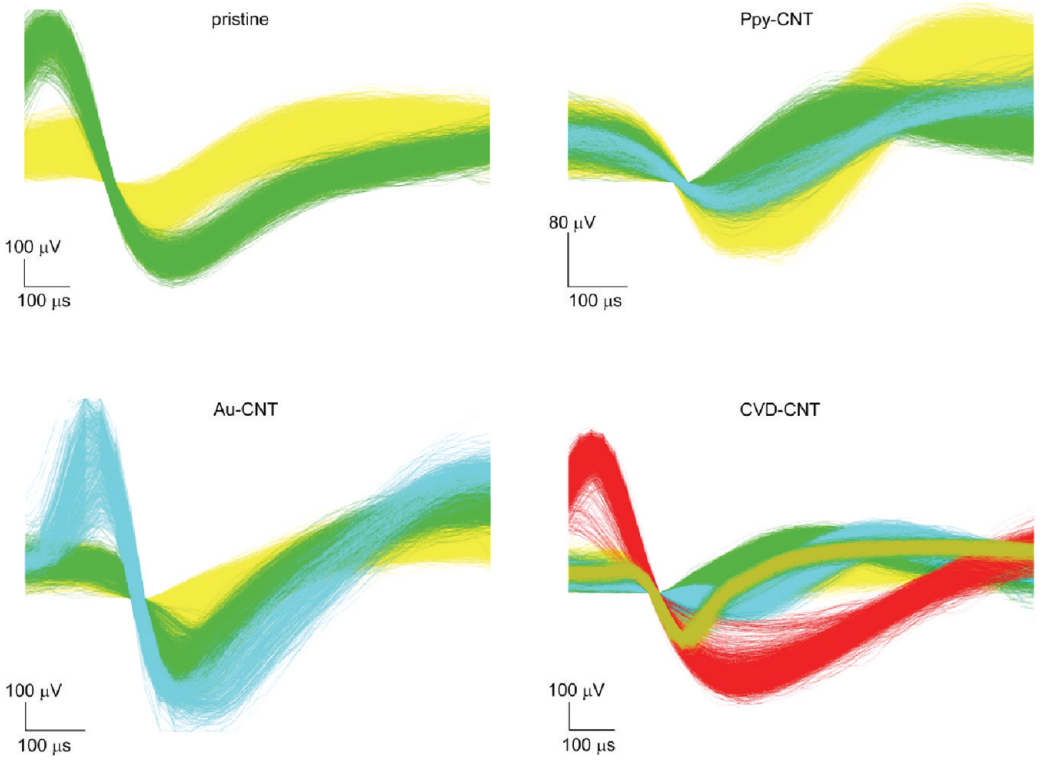

Figure 6. Sorted single neurons recorded during acute session, using noncoated and coated microelectrodes. Each color represents the discharge of a single unit. Action potential amplitudes ranged from approximately 300 to 1200 μV.

they should possess a reasonable stability in time upon storage, the so-called "shelf life". When the impedance spectra of electrodes are checked immediately after preparation and after 2 months, it emerges that the CVD-CNT coatings are significantly more stable than the other two (Figure S4 in Supporting Information). In fact, while the impedance at 1 kHz of PPy-CNT coatings increases 220% and that of Au-CNT coatings 60% after 2 months, CVD-CNT-coated electrodes maintain an identical impedance spectrum over all the measured frequency ranges even after 1 year (<2% variation of impedance magnitude at 1 kHz). These results also give an indication for the viability of the electrodes in chronic implants, as stability in ambient condition is a minimal requirement to be fulfilled for any long-term application. Naturally this does not imply that other phenomena, both chemical and biological, could not limit the operability of the microelectrodes during their use in chronic applications, which needs to be verified by long-term *in vivo* implants.

A first validation that these microelectrodes are suitable for *in vivo* use has been obtained by acute intracortical recording sessions in rats. Examples of intracortical neural signals recorded using the three differently coated and uncoated electrodes are shown in Figure 6. To our knowledge, this is the first time that signals recorded *in vivo* using *in situ* grown carbon nanotube coated wire microelectrodes are reported. The experiments were carried out on Long-Evans rats, under anesthesia. A small craniotomy in the parietal bone was made, and then microelectrodes were lowered perpendicularly into the cortex through dura

mater. Off-line PCA-based sorting procedure was performed on the recorded data.

CONCLUSION

In summary, we have compared the performance of pure carbon nanotube coatings selectively synthesized by chemical vapor deposition directly on the tip of sharp microelectrodes with that of a choice of electrodeposited composites, recently reported in literature, where CNTs act as nanofillers. This was made possible through an appropriate choice of electrode materials, capable of withstanding the high temperature necessary for CNT growth. All coatings have been designed and tested to comply with the requirements set by intracortical neural recording and stimulation applications. The main advantage of the electrodeposited coatings is that the deposition is performed at room temperature and can be applied to an unconstrained variety of materials; PPy-CNT coatings allow one to achieve lower impedance, but their electrical properties degrade with time, while, on the contrary, Au-CNT coatings have shown a remarkable mechanical toughness and stability, but do not allow one to achieve impedance values as low as the other coatings. The electrochemical characterization clearly demonstrates that pure carbon-coated microelectrodes outperform the other CNT coatings, especially from the point of view of stability and reliability in time. CVD-CNT-coated microelectrodes retain unaltered the same impedance values after 1 year storage or after being used to deliver one million current pulses at their charge injection limit. This result bears the promise of a superior performance in long-term implants. Finally, we have demonstrated for the first time that CVD-CNT electrodes are capable of recording single unit neural signal *in vivo* using standard neurophysiology recording setup.

METHODS

Microelectrode Preparation. Microelectrodes were produced by mechanically ground (ThomasRecording GmbH DIECKL-ST) quartz-coated platinum/tungsten (95:5) fibers of 80 μm outer shank diameter and 20 μm metal core diameter (ThomasRecording GmbH EF8025). The tip angle was estimated to be between 36° and 44° by optical microscopy, meaning that the active area is 923 $\pm$ 70 μm^2. The electrodes were cleaned by cycling three times the voltage between −0.25 and 1.55 V *vs* Ag/AgCl at a scan rate of 0.1 $V \cdot s^{-1}$ in a 1 M solution of sulfuric acid.

In Situ Chemical Vapor Deposition of CNTs on Microelectrodes. Nickel was electroplated from an aqueous solution containing 300 $g \cdot L^{-1}$ nickel(II) sulfate hexaydrate ($NiSO_4 \cdot 6H_2O$, CAS 10101-97-0, puriss. p.a. Riedel-de Haën), 90 $g \cdot L^{-1}$ nickel chloride hexaydrate ($NiCl_2 \cdot 6H_2O$, CAS 7791-20-0 purum, p.a.; >99.0% Fluka), and 45 $g \cdot L^{-1}$ boric acid (H_3BO_3, CAS 10043-35-3, puriss. p.a. Riedel-de Haën). The electrodepositions were performed in potentiostatic mode at −0.9 V *vs* Ag/AgCl reference electrode. The solution acidity was kept at pH 4, and the temperature was kept constant (45 °C). The depositions were carried out under inert atmosphere. The amount of material deposited onto the electrode was controlled by the charge passed during the deposition.

The CVD process was performed using a reactor formed by a quartz tube of 120 cm length and 25 mm inner diameter through a Lenton PSC 12/--/600H split furnace. The catalyst was reduced for 20 min by flowing an argon−hydrogen mixture (Ar 95 sccm, H_2, 5 sccm, ambient pressure) while heating the samples up to 650 °C; the carbon feedstock was then introduced into the reaction chamber by bubbling the same gas mixture through absolute ethanol at room temperature in a Drechsel washing bottle with glass filter disk. Growth time was 15 min.

Polypyrrole-CNT Microelectrode Coating. Polypyrrole and chemically functionalized multiwalled CNT nanocomposites were co-electrodeposited from an aqueous suspension of 1 $mg \cdot mL^{-1}$ COOH-MWCNTs (Nanocyl 3151, <4% of −COOH functional groups) containing 0.5 M of pyrrole monomer (Sigma-Aldrich) and 0.4 wt % of poly(sodium 4-styrene sulfonate) (PSS) (Sigma-Aldrich). As-purchased COOH-MWCNTs were suspended in ultrapure water (Milli-Q, Millipore) by horn sonication (6 s at 66% duty cycle pulses, 4 $W \cdot mL^{-1}$) for 30 min while keeping the solution cooled with an ice bath. PSS and pyrrole were added to the suspension immediately afterward, and the solution was kept deoxygenated by bubbling with nitrogen. The electrochemical deposition was carried out under an inert atmosphere in potentiostatic mode. The polymerization potential was set to 0.55 V *vs* Ag/AgCl reference electrode.

Gold-CNT Microelectrode Coating. Starting from a 10 mM potassium dicyanaurate(I) (Sigma-Aldrich) aqueous solution containing 1.5 $mg \cdot mL^{-1}$ of partially dispersed MWCNTs (Nanocyl 3100, thin MWCNT 95+% carbon purity), Au-CNT nanocomposites were co-electrodeposited by applying monophasic voltage pulses (0.2−1.0 V, 240 s, duty cycle 50%).

Extracellular Recording Sessions. The extracellular recording sessions were carried out on Long-Evans rats. An anesthetic mixture of Zoletil (30 mg/kg) and Xylazine (5 mg/kg) was delivered intraperitoneally. Under anesthesia, rats were placed in a stereotaxis apparatus (myNeuroLab) and a small craniotomy in the parietal bone was made. Each type of coated microelectrodes was lowered perpendicularly into the cortex, using a hydraulic micropositioner (Kopf, 2650). Dura mater remained intact. The extracellular signals were amplified, digitalized, and recorded using a multichannel recording system (MAP, Plexon Inc., 40 kHz sampling frequency per channel with a 12 bit resolution), and off-line PCA-based sorting procedure was performed using commercially available software (RASPUTIN, Plexon Inc.). The experimental plan was designed in compliance with the Italian law regarding the care and use of experimental animals (DL116/92) and approved by the Italian Ministry of Health.

Acknowledgment. This work was supported by the BMI project of the Robotics, Brain and Cognitive Sciences Department, Italian Institute of Technology.

Supporting Information Available: SEM pictures of CVD-CNT and PPy-CNT-coated microelectrodes with excess material, electrochemical properties of CVD-CNT electrodes depending on amount of catalyst and of PPy-CNT electrodes depending on deposition charge, GEIS of PPy-CNT-coated electrodes before and after been subjected to current pulses, GEIS of ready-made and aged coated electrodes. This material is available free of charge *via* the Internet at http://pubs.acs.org.

REFERENCES AND NOTES

1. Andersen, R. A.; Musallam, S.; Pesaran, B. Selecting the Signals for a Brain−Machine Interface. *Curr. Opin. Neurobiol.* **2004,** *14*, 720–726.
2. Ludwig, K. A.; Uram, J. D.; Yang, J.; Martin, D. C.; Kipke, D. R. Chronic Neural Recordings Using Silicon Microelectrode

Arrays Electrochemically Deposited with a Poly(3,4-ethylenedioxythiophene) (PEDOT) Film. *J. Neural Eng.* **2006,** *3*, 59–70.
3. Cogan, S. F. Neural Stimulation and Recording Electrodes. Annual. *Rev. Biomed. Eng.* **2008,** *10*, 275–309.
4. Marin, C.; Fernández, E. Biocompatibility of Intracortical Microelectrodes: Current Status and Future Prospects. *Front. Neuroeng.* **2010,** *3*, 1–6.
5. Cogan, S. F.; Guzelian, A. A.; Agnew, W. F.; Yuen, T. G. H.; McCreery, D. B. Over-Pulsing Degrades Activated Iridium Oxide Films Used for Intracortical Neural Stimulation. *J. Neurosci. Methods* **2004,** *137*, 141–150.
6. Gawad, S.; Giugliano, M.; Heuschkel, M.; Wessling, B.; Markram, H.; Schnakenberg, U.; Renaud, P.; Morgan, H. Substrate Arrays of Iridium Oxide Microelectrodes for *In Vitro* Neuronal Interfacing. *Front. Neuroeng.* **2010,** *2*, 1–6.
7. Cui, X.; Lee, V. A.; Raphael, Y.; Wiler, J. A.; Hetke, J. F.; Anderson, D. J.; Martin, D. C. Surface Modification of Neural Recording Electrodes with Conducting Polymer/Biomolecule Blends. *J. Biomed. Mater. Res.* **2001,** *56*, 261–272.
8. Cui, X.; Martin, D. C. Electrochemical Deposition and Characterization of Poly(3,4-ethylenedioxythiophene) on Neural Microelectrode Arrays. *Sens. Actuators, B* **2003,** *89*, 92–102.
9. Yang, J.; Martin, D. C. Impedance Spectroscopy and Nanoindentation of Conducting Poly(3,4-ethylenedioxythiophene) Coatings on Microfabricated Neural Prosthetic Devices. *J. Mater. Res.* **2006,** *21*, 1124–1132.
10. Wang, K.; Fishman, H. A.; Dai, H.; Harris, J. S. Neural Stimulation with a Carbon Nanotube Microelectrode Array. *Nano Lett.* **2006,** *6*, 2043–2048.
11. Keefer, E. W.; Botterman, B. R.; Romero, M. I.; Rossi, A. F.; Gross, G. W. Carbon Nanotube Coating Improves Neuronal Recordings. *Nat. Nanotechnol.* **2008,** *3*, 434–439.
12. Kmecko, T.; Hughes, G.; Cauller, L.; Lee, J. B.; Romero-Ortega, M. I. *Mater. Res. Soc. Symp. Proc.* **2006,** *926*, 0926-CC04-06.
13. Gabay, T.; Ben-David, M.; Kalifa, I.; Sorkin, R.; Abrams, Z. R.; Ben-Jacob, E.; Hanein, Y. Electro-chemical and Biological Properties of Carbon Nanotube Based Multi-electrode Arrays. *Nanotechnology* **2007,** *18*, 035201.
14. Lovat, V.; Pantarotto, D.; Lagostena, L.; Cacciari, B.; Grandolfo, M.; Righi, M.; Spalluto, G.; Prato, M.; Ballerini, L. Carbon Nanotube Substrates Boost Neuronal Electrical Signaling. *Nano Lett.* **2005,** *5*, 1107–1110.
15. Mazzatenta, A.; Giugliano, M.; Campidelli, S.; Gambazzi, L.; Businaro, L.; Markram, H.; Prato, M.; Ballerini, L. Interfacing Neurons with Carbon Nanotubes: Electrical Signal Transfer and Synaptic Stimulation in Cultured Brain Circuits. *J. Neurosci.* **2007,** *27*, 6931–6936.
16. Cellot, G.; Cilia, E.; Cipollone, S.; Rancic, V.; Sucapane, V.; Giordani, S.; Gambazzi, L.; Markram, H.; Grandolfo, M.; Scaini, D.;*et al.*Carbon Nanotubes Might Improve Neuronal Performance by Favouring Electrical Shortcuts. *Nat. Nanotechnol.* **2008,** *4*, 126–133.
17. Gabriel, G.; Gómez, R.; Bongard, V.; Benito, N.; Fernández, E.; Villa, R. Easily Made Single-Walled Carbon Nanotube Surface Microelectrodes for Neuronal Applications. *Biosens. Bioelectron.* **2009,** *24*, 1942–1948.
18. Sorkin, R.; Greenbaum, A.; David-Pur, M.; Anava, S.; Ayali, A.; Ben-Jacob, E.; Henein, Y. Process Entanglement as a Neuronal Anchorage Mechanism to Rough Surfaces. *Nanotechnology* **2009,** *20*, 015101.
19. Shein, M.; Greenbaum, A.; Gabay, T.; Sorkin, R.; David-Pur, M.; Ben-Jacob, E.; Hanein, Y. Engineered Neuronal Circuits Shaped and Interfaced with Carbon Nanotube Microelectrode Arrays. *Biomed. Microdevices* **2009,** *11*, 495–451.
20. Shoval, A.; Adams, C.; Davide-Pur, M.; Shein, M.; Hanein, Y.; Sernagor, E. Carbon Nanotube Electrodes for Effective Interfacing with Retinal Tissue. *Front. Neuroeng.* **2009,** *2*, 1–8.
21. Sauter-Starace, F.; Bibari, O.; Berger, F.; Caillat, P.; Benabid, A. L. ECoG Recordings of a Non-human Primate Using Carbon Nanotubes Electrodes on a Flexible Polyimide Implant. Proceedings of the 4th International IEEE EMBS Conference on Neural Engineering; Antalya, Turkey, April 29−May 2, 2009; pp 112−115.
22. Keefer, E. W. Coating Neural Electrodes with Carbon Nanotubes and Variations. WO/2009/023579, Feb 2, 2009.
23. Ferguson, J. E.; Boldt, C.; Redish, A. D. Creating Low-Impedance Tetrodes by Electroplating with Additives. *Sens. Actuators, A* **2009,** *156*, 388–393.
24. Green, R. A.; Williams, C. M.; Lovell, N. H.; Poole-Warren, L. A. Novel Neural Interface for Implant Electrodes: Improving Electroactivity of Polypyrrole through MWNT Incorporation. *J. Mater. Sci.: Mater. Med.* **2008,** *19*, 1625–1629.
25. Lu, Y.; Li, T.; Zhao, X.; Li, M.; Cao, Y.; Yang, H.; Duan, Y. Y. Electrodeposited Polypyrrole/Carbon Nanotubes Composite Films Electrodes for Neural Interfaces. *Biomaterials* **2010,** *31*, 5169–518.
26. Gheith, M. K.; Pappas, T. C.; Liopo, A. V.; Sinani, V. A.; Shim, B. S.; Motamedi, M.; Wicksted, J. P.; Kotov, N. A. Stimulation of Neural Cells by Lateral Currents in Conductive Layer-by-Layer Films of Single-Walled Carbon Nanotubes. *Adv. Mater.* **2006,** *18*, 2975–2979.
27. Jan, E.; Hendricks, J. L.; Husaini, V.; Richardson-Burns, S. M.; Sereno, A.; Martin, D. C.; Kotov, N. A. Layered Carbon Nanotube-Polyelectrolyte Electrodes Outperform Traditional Neural Interface Materials. *Nano Lett.* **2009,** *9*, 4012–4018.
28. Castagnola, E.; Ansaldo, A.; Fadiga, L.; Ricci, D. Chemical Vapour Deposited Carbon Nanotube Coated Microelectrodes for Intracortical Neural Recording. *Phys. Status Solidi B* **2010,** *247*, 2703–2707.
29. Cui, X.; Martin, D. Fuzzy Gold Electrodes for Lowering Impedance and Improving Adhesion with Electrodeposited Conducting Polymer Films. *Sens. Actuator, A* **2003,** *103*, 384–394.
30. Lin, K.; Weil, R.; Desai, K. Effects of Current Density, Pulse Plating, and Additives on the Initial Stage of Gold Deposition. *J. Electrochem. Soc.* **1986,** *133*, 690–692.
31. Brummer, S. B.; Robblee, L. S.; Hambrecht, F. T. Criteria for Selecting Electrodes for Electrical Stimulation: Theoretical and Practical Considerations. *Ann. N.Y. Acad. Sci.* **1983,** *405*, 159–171.
32. Merrill, D. R.; Bikson, M.; Jefferys, J. G. R. Electrical Stimulation of Excitable Tissue: Design of Efficacious and Safe Protocols. *J. Neurosci. Methods* **2005,** *141*, 171–198.
33. Stieglitz, T.; Meyer, J.-U. Neural Implants in Clinical Practice. In *BioMEMS*; Urban, G., Ed.; Springer: The Netherlands, 2006; pp 41−70.