Versatile Procedure for Synthesis of Janus-Type Carbon Tubes

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ABSTRACT: A bulk procedure based on bipolar electrochemistry is proposed for the generation of Janus-type carbon tubes. The concept is illustrated with carbon tubes that are selectively modified at their ends with various metals and conducting polymers. No surface or interface is required to break the symmetry and therefore this approach could be used for the mass production of Janus micro- and nano-objects. We show evidence that the technique is very versatile, allowing the choice of the kind of material that is deposited and whether the end product is mono- or bifunctionalized.

KEYWORDS: bipolar electrochemistry, carbon tubes, capillary electrophoresis, Janus particles, dumbbell structures
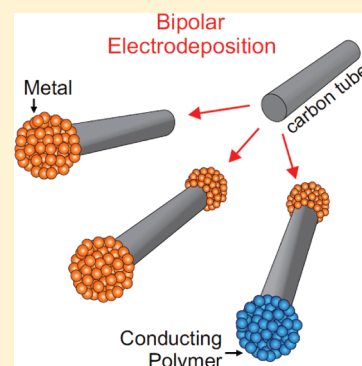
■ INTRODUCTION

Elaboration of functionalized micro- and nanoparticles, especially dissymmetrical Janus-type objects, is of enormous interest. These particles have high application potential in many areas such as sensing, new electronic devices, and catalysis.[1] Nevertheless, most processes, used to achieve the site-selective functionalization of a particle at this scale, require the use of an interface to break the symmetry.[2] This makes the preparation of large quantities rather difficult because the majority of the techniques usually leads to monolayer equivalents of material, as the modification occurs in a two-dimensional reaction space. Thus, there is an increasing interest in developing alternative truly three-dimensional techniques, allowing a scale-up of the production of dissymmetrical particles. Examples of such kind of approaches are based on the generation of charge carriers in semiconductors using light,[3] or antenna chemistry.[4] An elegant method reported by Banin et al. consists of the precipitation of HAuCl4 to grow selectively gold tips on cadmium selenide nanorods.[5]

In this context, another attractive way to selectively modify particles in a three-dimensional reaction space is based on the concept of bipolar electrochemistry, described by Fleischmann et al.[6] This appealing approach relies on the fact that when a conducting object is placed in a strong electric field between two electrodes, a polarization occurs that is proportional to the electric field and the characteristic dimensions of the object. When this polarization is strong enough, redox reactions can be carried out at the opposite ends of the object (Scheme 1a). This interesting theoretical concept[7] has recently found applications as the driving force in electrochemiluminescent reactions,[8−11] as detection mode in capillary electrophoresis,[12] for bipolar patterning,[13,14] for membrane pore functionalization,[15] as a

mechanism for propelling micro-objects,[16] and in the fields of analytical chemistry and material science in general.[11,17] The potential difference between the two ends of a conducting object under the influence of an external electric field is given by the equation

$$\Delta V = Ed \qquad (1)$$

with E being the total external electric field and d the particle size. To carry out two redox reactions at the opposite sides of the object, ΔV has to be in a first-order approximation at least equal to the difference between the formal potentials of the two redox reactions. Let us consider as an example for the dissymmetrical functionalization the formal potential (E^0) of the reduction of Ni^{II} at one side

$$Ni^{II}_{(1)} + 2e^- \rightarrow Ni^0_{(s)} \qquad (2)$$
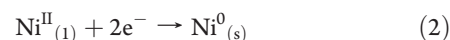
and of the oxidation of water at the opposite side

$$2H_2O_{(1)} \rightarrow 4H^+_{(1)} + O_{2(g)} + 4e^- \qquad (3)$$
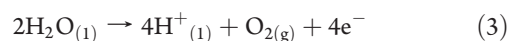
From Table 1 it immediately follows that in this case the polarization has to generate a minimum potential difference of approximately

$$\Delta V_{min} = E^0_{Ni^0/Ni^{II}} - E^0_{H_2O/O_2} = 1.5 \text{ V} \qquad (4)$$

This becomes an intrinsic problem of the approach when dealing with micro- or nanometer sized objects; as in this case E needs to

Scheme 1. (a) Concept of Bipolar Electrochemistry for the Generation of Janus-Type Objects; (b) Capillary Electrophoresis Set-up Used for the Dissymmetrical Electrodeposition
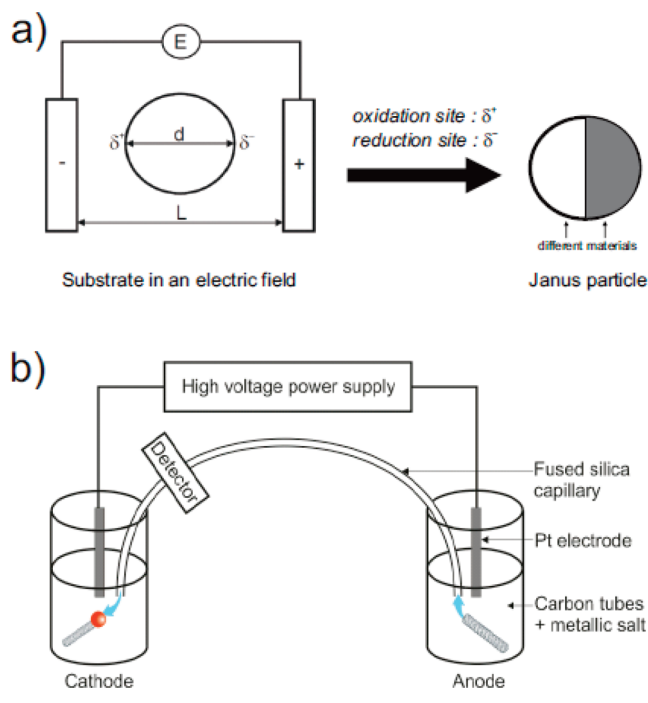

Table 1. Formal Potentials of the Redox Couples Used for the Bipolar Electrodeposition Experiments

redox couple	E^0 [V vs NHE]
$[Au^{III}Cl_4]^-/Au^0$	+0.99
Cu^I/Cu^0	+0.52
Ni^{II}/Ni^0	−0.26
Cu^{II}/Cu^I	+0.16
O_2/H_2O	+1.23

achieve values of up to $MV\,m^{-1}$ (see Eq 1), conditions that seem to be incompatible with a normal laboratory environment and especially with aqueous solutions because of the intrinsic side reactions accompanied by macroscopic bubble formation at both electrodes that disturbs the orientation of the objects in the electric field. Bradley et al. could partly circumvent the problem by using organic solvents to enlarge the potential window of the electrolyte and thus it was possible to generate metal deposits in a dissymmetrical way on different objects in the micrometer and submicrometer range.[18,19] However, it was also necessary to immobilize the objects on a surface to prevent them from rotating, which means that this is again a two-dimensional and not a bulk process. We could demonstrate that it is possible to get around these problems by using a capillary electrophoresis setup to apply the high electric field (Scheme 1b).[20] In this case the bipolar electrodeposition experiment consists of imposing a strong potential (several tens of kV) between two electrodes separated by a capillary, generating an electric field in the range of $100\,kV\,m^{-1}$. Under its influence, the conductive objects become polarized, and because of the electroosmotic flow through the

capillary, they are moving from the anodic reservoir to the cathodic one. Electrodeposition is achieved in this way and the modified substrates are detected at the outlet with a UV–vis detector. In this work, we describe a generalization of the approach and we have chosen to illustrate this with micrometer-sized carbon tubes (CTs) because they can be easily visualized with an optical microscope. However, the approach can also be used for nanosized objects, as has been shown for the particular case of gold deposition on CNTs.[20] The so-called CABED procedure (Capillary Assisted Bipolar ElectroDeposition) was restricted so far to metal deposition, and most importantly, only one side of the carbon (nano)tubes could be modified.[21,22]

In the present work we demonstrate that the concept can be applied not only to a variety of metal deposits but also to the deposition of conducting polymers. In contrast to what has been reported in our previous work, we show here that by choosing the right potential sequence including relaxation times, we can not only deposit a material selectively on one side of the tubes but also trigger in a single experiment the deposition at both ends of the tube, resulting in structures that are either modified on both sides with the same material or with two different materials. This is the first time that such symmetric or dissymmetrical dumbbell-like structures are synthesized by bipolar electrochemistry using a bulk approach without the need of interfaces or surfaces to break the symmetry.

■ EXPERIMENTAL SECTION

Preparation of Carbon Tube Suspensions. The CTs used in this study were produced by chemical vapor deposition with a porous aluminum oxide membrane serving as a template. After acid digestion of the template, the quite homogeneous tubes were recovered as a powder. For the suspensions containing Au^{III} and Ni^{II}, about 0.1 mg of CTs was added to absolute ethanol (1.5 mL). To accelerate the formation of a suspension, the mixture was sonicated, but only for a short time (1 min), to avoid excessive breaking of the tubes. After 3 h of sedimentation, 0.5 mL of the supernatant was taken and added to 0.5 mL of 10 mM $NiSO_4$ or 10 mM $HAuCl_4$ in ultrapure water. The suspension with Cu^I was prepared by adding about 0.1 mg of CTs to a solution of 10 mM CuI in acetonitrile. Suspensions with CuI and pyrrole were prepared by adding the same amount of CTs to a mixture of 10 mM CuI and freshly distilled 50 mM pyrrole in acetonitrile.

Bipolar Electrodeposition on Carbon Tubes. For electrodeposition experiments, all solutions or suspensions were introduced into the capillary by filling it manually with a syringe. The capillary used here is a fused silica capillary with a length of 24 cm and an inner diameter of $100\,\mu m$. The applied voltage was 30 kV for 5 min and the temperature was maintained at 25 °C. The CE experiment was first performed by rinsing the capillary with ultrapure water or acetonitrile. Then the CT suspension was introduced into the capillary. Because the addition of salt increases the ionic strength, it can result in the aggregation of the CTs, and therefore the suspensions were sonicated for a short time in an ultrasound bath before introduction into the capillary. For such salt concentrations, the typical currents in the electrophoresis setup were around $1\,\mu A$. The sample leaving the capillary at the cathodic side was collected directly at the outlet and transferred onto a TEM grid or another substrate, rinsed, and dried. The objects were then characterized by optical microscopy and scanning electron microscopy (SEM).
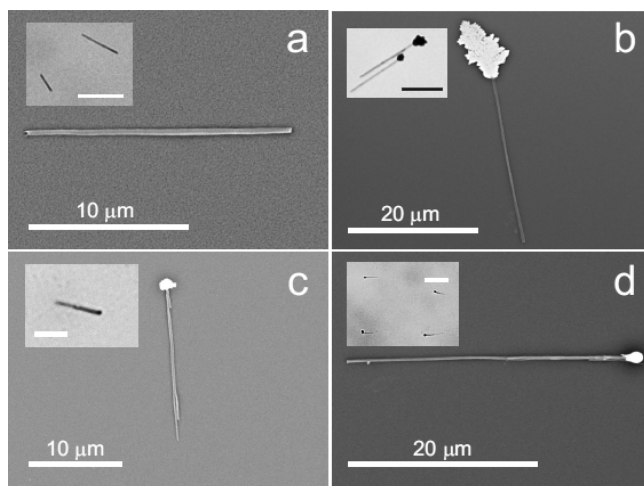
Figure 1. SEM images of CTs (a) without modification; modified at one side with (b) copper, (c) gold, and (d) nickel. Inset: optical microscope image of the modified CTs; scale bars are:(a), (b), and (d) 20 μm; (c) 10 μm.

■ RESULTS AND DISCUSSION

The Janus-type CTs are obtained from raw carbon tubes synthesized by chemical vapor deposition into pores of an aluminum oxide membrane. The thickness of the collected tubes is 200 nm and their length is 20–30 μm (Figure 1a). The modified CTs are collected at the outlet of the capillary after bipolar electrodeposition. Samples shown in Figure 1b–d were obtained using carbon tube suspensions in solutions of Cu^I (10 mM) in acetonitrile, Au^{III} (5 mM) in water, and Ni^{II} (5 mM) in water, respectively. Since copper modification was achieved in a non-aqueous solution, the reactions that occur at the tube ends are

$$Cu^I + e^- \rightarrow Cu^0_{(s)} \qquad (5)$$

at one side and:

$$Cu^I \rightarrow Cu^{II} + e^- \qquad (6)$$
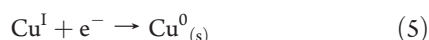
at the opposite side. Using the E^0 values given in Table 1, one can easily see that the overall reaction resulting from a combination of eqs 5 and 6 should occur spontaneously via a dismutation. However, the Cu^I species seem to be sufficiently stabilized because of the presence of I^- ions so that a potential difference is still needed between the two ends of the tube to drive the reaction.

Gold deposition was carried out in aqueous solution, involving the following reactions:

$$[Au^{III}Cl_4]^- + 3e^- \rightarrow Au^0_{(s)} + 4Cl^- \qquad (7)$$

and

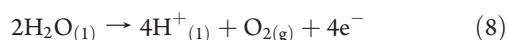$$2H_2O_{(l)} \rightarrow 4H^+_{(l)} + O_{2(g)} + 4e^- \qquad (8)$$
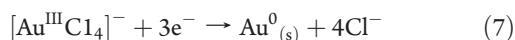
Table 1 indicates that in this case the combination of eqs 7 and 8 is not a spontaneous reaction and therefore a minimum potential difference between the two tube ends has to be generated to achieve dissymmetrical deposition:

$$\Delta V_{min} = E^0_{Au^0/AuCl_4^-} - E^0_{H_2O/O_2} = 0.24\ V \qquad (9)$$

Obviously, because the experiments are carried out in far from standard conditions in terms of pH, concentrations, and partial gas pressures, deviations from the theoretical values of the potential threshold are expected. For all these experiments the same external electric field value $E = 125$ kV m^{-1} was applied, which gives typically for a 30 μm object a $\Delta V = 3.75$ V. This value is definitely high enough, compared to the theoretical ΔV_{min} values previously calculated, to drive all these redox reactions. Looking at the SEM pictures of CTs collected at the capillary outlet (Figure 1b–d), it is obvious that the corresponding metal has been deposited. Because we used the same E, the same capillary length, and an identical experiment time, the variation in deposit size can be understood via the different growth kinetics which depend essentially on (i) the required ΔV_{min} and (ii) the salt concentration. Nickel modification, which requires the highest driving force ($\Delta V_{min} = 1.5$ V), results in the smallest deposit size because for the given overall electric field the driving force is smaller and therefore the reaction proceeds more slowly. As stated above, copper deposition should occur almost spontaneously and therefore the required minimum voltage is certainly the smallest one compared to the other metals. This means that in this case the external field generates the highest driving force and leads to the biggest deposit. Another parameter that is important for the apparent deposit size is the growth morphology and its density. Copper is growing in a much more ramified structure, which leads for the same amount of reduced metal to a much bigger deposit compared to what is obtained for nickel and gold. This new family of monofunctionalized dissymmetric particles can be used for the localized functionalization of carbon tubes with organic molecules, for binding carbon tubes to a surface and for the development of nanodevices such as nanomotors because the orientation of tubes modified with a ferromagnetic material can be controlled with a magnetic field,[21] or a decomposition reaction can be driven by a catalytically active metal present at one tube end.[22]

During these bipolar electrodeposition runs, the end of the tube opposite to the one where the metal deposition takes place is positively polarized and therefore cannot be a site of reduction. If one wants to modify in a single experiment both ends with the same metal, polarization has to be reversed after the first deposition step so that the side that was the oxidation site becomes the reduction site. Since a classic electrophoresis set-up does not allow reversal of the polarization between the electrodes, we employed another approach consisting of the introduction of a relaxation time after the first polarization (without applied potential) to induce a statistical reversal of the CTs in the capillary. The optical microscope pictures in Figure 2 were obtained with the same carbon tube dispersion and the same electric field value as for the previous dissymmetrical deposition of copper, but with a regular interruption of the potential. When the potential is continuously applied or when the relaxation time between the pulses is short (Figure 2b,d), the CTs do not have the possibility to turn around in the capillary. Actually, once these anisotropic objects are polarized in the electric field, it would cost too much energy for them to flip in the opposite direction. This means that the tubes are all aligned parallel to the electric field and will not tumble or turn during their journey through the capillary. Therefore, this results exclusively in dissymmetrical deposits. In contrast, when the pulses are sufficiently separated in time (Figure 2a,c), the tubes are no longer polarized during the relaxation period without applied field and therefore have time to statistically change their orientation, thus leading to a symmetric deposition. In this case, after the first pulse, only one end of the tube is modified with Cu^0, but during the 5 minutes
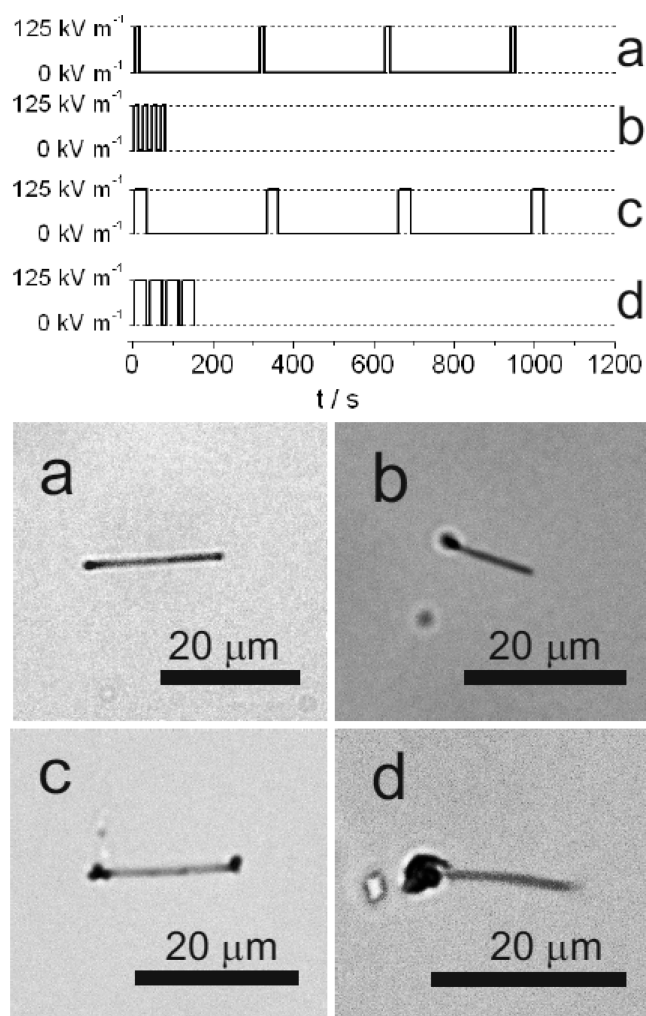
Figure 2. Pulsed bipolar electrodeposition with a suspension of CTs in 10 mM CuI in acetonitrile. The electric signal imposed between the electrodes is reported at the top and the corresponding optical microscope images of the modified carbon tubes at the bottom. The electric field was 125 kV·m. Time of potential pulses are 12 s (a and b) and 30 s (c and d); the time between the pulses are 5 min (a and c) and 10 s (b and d).

Figure 3. SEM pictures of modified dumbbell-like CTs. (a) Symmetric dumbbell-like object with copper deposits on both sides. (b) Dissymmetrical dumbbell-like object with one copper end (square 1) and one polypyrrole end (square 2). (c) EDX spectra recorded for the copper end (1) and for the polypyrrole end (2).

without polarization the tubes are allowed to reorientate in the capillary. Statistically, half of them will do so. Therefore, when the second pulse is applied, for half of the tubes the end where previously the oxidation of Cu^I into Cu^{II} took place becomes the reduction site where metal is formed. For these tubes, the counter reaction, which is the oxidation of Cu^I into Cu^{II}, now takes place at the end of the tube that had been already modified with copper during the first potential pulse. Another possible counter reaction could be the oxidation of the already present copper deposit. However, it is more difficult to oxidize Cu^0 than Cu^I because the oxidation potential is more positive (see Table 1) and therefore the dominating counter reaction is $Cu^I \rightarrow Cu^{II}$, thus preserving the already existing metal deposit.

If this long relaxation is repeated many times, statistically all tubes have turned around several times and consequently are modified on both sides. Striking evidence for the symmetric deposition of copper at both ends of the CT is shown in the SEM image of Figure 3a. The symmetric dumbbell-like functionalization of CTs can be extended to metals other than
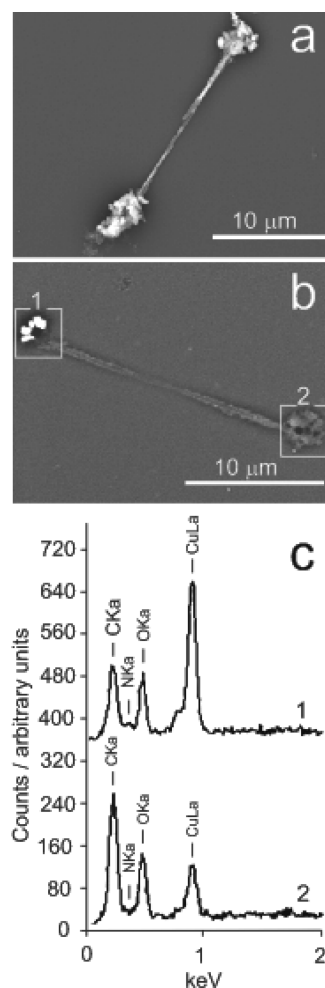
copper and these new materials can find exciting applications for self-assembly.

In the above experiments, the oxidation that occurs at the anodic end of the CTs produces gas or other oxidation products, but the involved reactions do not lead to a modification. We were therefore looking for an additional strategy, which would make use of this oxidation reaction to deposit also a material on the positively polarized side, concomitant with the reductive metal deposition on the negatively polarized side. One obvious type of material that can be obtained by oxidation is a conducting polymer. Because of their intrinsic reactivity, the metal salt and the monomer have to be chosen carefully. A mixture of Cu^I and pyrrole was found to be stable in acetonitrile for at least 12 h. For longer times a brownish color that was due to the spontaneous polymerization of pyrrole appeared. CTs were added to this freshly prepared solution and bipolar electrodeposition was achieved using the same parameters that were applied for the dissymmetrical deposition of Cu^0. A SEM picture of a typical CT is shown in Figure 3b, the metallic end being clearly visible since the color contrast between metal and the carbon tube is very important. The polypyrrole (Ppy) end is less conductive than copper and thus exhibits a weaker contrast with respect to the

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carbon tube. To make sure that the type of deposit at both ends is different, we performed, in addition, EDX experiments. The analysis has been carried out at the two opposite ends of the carbon tube. Figure 3c shows that the upper left end of the tube is characterized by a strong Cu signal around 1 keV compared to a much weaker carbon signal which originates most likely from the underlying carbon tube and the supporting grid. At the other end of the tube the carbon signal is much more prominent due to the presence of the conducting polymer. When both peaks are compared to the background oxygen signal, it becomes clear that their ratio is significantly different for the two ends of the tube, demonstrating the presence of the two different materials. However, on the Ppy side there is still a small contribution of Cu. This signal can be assigned to ionic copper species that become trapped in the polymer matrix during the pyrrole oxidation, it being known that copper forms stable complexes with polypyrrole, based on a Cu−N bond.[23]

This result opens up the way to a new family of bifunctional Janus-type materials that can be created by bipolar electrodeposition. Indeed, one can easily imagine that various metal-conducting polymer combinations can be deposited, leading to structures that could show interesting features. The pictures of Figures 1, 2, and 3 are representative of the majority of the tubes reaching the capillary outlet; however, in a more general sense, not 100% of the tubes are modified. The percentage of modified tubes obviously depends on the experimental parameters and there are several possible origins for a nonquantitative modification. The deposits might for example detach from the tube during the collection and rinsing procedure. Also, the tubes can be more or less conducting depending on their morphology and defects, which will lead to differences in polarization. When this kind of problem is minimized by careful sample handling, quantitative modification can be achieved.

CONCLUSION

In summary, we present the generalization of a new bulk method based on bipolar electrochemistry that allows the highly controlled and localized functionalization of CTs. For the first time we could synthesize with one and the same process Janus-type carbon tubes that can be divided into three families, as a function of the used experimental parameters: (i) monofunctionalized dissymmetrical tubes, (ii) symmetric dumbbell-like tubes, and (iii) dissymmetrical dumbbell-like tubes. The deposit size and location can be very easily tuned by changing the strength and time variations of the electric field. Various materials can be deposited, assigning localized features to carbon tubes, thus leading to promising materials in domains such as sensing, electronic devices, self-assembly, and catalysis. Because this process is a true bulk process, one can imagine a scale-up of the production. Although we demonstrated the validity of the approach for the particular example of carbon tubes, this technique might be adapted to a large range of other micro- and nanoparticles of various size and shape.

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REFERENCES

(1) Walther, A.; Muller, A. H. E. *Soft Matter* **2008**, *4*, 663–668.

(2) Pradhan, S.; Xu, L.; Chen, S. *Adv. Funct. Mater* **2007**, *17*, 2385–2392.

(3) Reiche, H.; Dunn, W. W.; Bard, A.J. *J. Phys. Chem.* **1979**, *83*, 2248–2251.

(4) Duque, J. G.; Pasquali, M.; Schmidt, H. K. *J. Am. Chem. Soc.* **2008**, *130*, 15340–15347.

(5) Mokari, T.; Sztrum, C. G.; Salant, A.; Rabani, E.; Banin, U. *Nat. Mater.* **2005**, *4*, 855–863.

(6) Fleischmann, M.; Ghoroghchian, J.; Rolison, D.; Pons, S. *J. Phys. Chem.* **1986**, *90*, 6392–6400.

(7) Duval, J.; Kleijn, J. M.; Van Leeuwen, H. P. *J. Electroanal. Chem.* **2001**, *505*, 1–11.

(8) Mavré, F.; Chow, K.-F.; Sheridan, E.; Chang, B.-Y.; Crooks, J. A.; Crooks, R. M. *Anal. Chem.* **2009**, *81*, 6218.

(9) Chow, K.-F.; Mavré, F.; Crookes, J. A.; Chang, B.-Y.; Crooks, R. M. *J. Am. Chem. Soc.* **2009**, *131*, 8364–8365.

(10) Chow, K.-F.; Mavré, F.; Crooks, R. M. *J. Am. Chem. Soc.* **2008**, *130*, 7544–7545.

(11) Mavré, F.; Anand, R. K.; Laws, D. R.; Chow, K. F.; Chang, B. Y.; Crooks, J. A.; Crooks, R. M. *Anal. Chem.* **2010**, *82*, 8766–8774.

(12) Ordeig, O.; Godino, N.; Del Campo, J.; Munos, F. X.; Nikolajeff, F; Nyholm, L. *Anal. Chem.* **2008**, *80*, 3622–3632.

(13) Ulrich, C.; Andersson, O.; Nyholm, L.; Björefors, F. *Anal. Chem.* **2009**, *81*, 453–459.

(14) Ramakrishnan, S.; Shannon, C. *Langmuir* **2010**, *26*, 4602–4606.

(15) Bouquet, A.; Deschamp, E.; Maillet, P.; Livache, T.; Chatelain, F.; Haguet, V. *Small* **2009**, *5*, 2297–2303.

(16) Loget, G.; Kuhn, A. *J. Am. Chem. Soc.* **2010**, *132*, 15918–15919.

(17) Loget, G.; Kuhn, A. *Anal.Bioanal.Chem.* **2011**, in press, DOI 10.1007/s00216-011-4862-1.

(18) Bradley, J.-C.; Chen, H.-M.; Crawford, J.; Eckert, J.; Ernazarova, K.; Kurzeja, T.; Lin, M.; Nadler, W.; Stephens, S. G. *Nature* **1997**, *389*, 268–271.

(19) Bradley, J.-C.; Ma, Z. *Angew. Chem., Int. Ed.* **1999**, *38*, 1663–1666.

(20) Warakulwit, C.; Nguyen, T.; Majimel, J.; Delville, M.-H.; Lapeyre, V.; Garrigue, P.; Ravaine, V.; Limtrakul, J.; Kuhn, A. *Nano Lett.* **2008**, *8*, 500–504.

(21) Loget, G.; Larcade, G.; Lapeyre, V.; Garrigue, P.; Warakulwit, C.; Delville, M.-H.; Ravaine, V.; Kuhn, A. *Electrochim. Acta* **2010**, *55*, 8116–8120.

(22) Fattah, Z.; Loget, G.; Lapeyre, V.; Garrigue, P.; Warakulwit, C.; Limtrakul, J.; Bouffier, L.; Kuhn, A. *Electrochim. Acta* **2011**, in press, 10.1016/j.electacta.2011.01.048.

(23) Inoue, M. B.; Nebesny, K. W.; Fernando, Q.; Castillo-Ortega, M.; Inoue, M. *Synth. Met.* **1990**, *38*, 205–212.

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