

Dissymmetric Metal Deposition on Carbon Nanotubes

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ABSTRACT

Dissymmetric nanoobjects are of enormous interest in many areas ranging from molecular electronics to targeted drug delivery. So far it has been quite difficult to synthesize dissymmetric objects at the nanoscale and most approaches have been based on using interfaces to break the symmetry. Only a few bulk procedures are known so far to produce these Janus-type objects. We report here a simple approach for the bulk generation of dissymmetric nanoobjects, especially carbon nanotubes (CNTs), based on electrochemical principles. A stabilized suspension of nanotubes is introduced in a capillary containing an aqueous metal salt solution and a high electric field is applied to orientate and polarize the individual tubes. During their transport through the capillary under sufficient polarization each nanotube is the site of water oxidation at one end, and of metal ion reduction at the other one. The method can be generalized for very different types of deposits such as other metals, semiconductors or polymers. The approach therefore opens up the way to a whole new family of experiments leading to complex nanoobjects with an increasingly sophisticated design.

Keywords: Janus particles, bipolar electrochemistry, carbon nanotubes, capillary electrophoresis

1 INTRODUCTION

Dissymmetric functionalization of micro- and nanoobjects is of major importance to study, for example, directed self-assembly, but also for many applications ranging from electronic paper to sensing and catalysis. Various approaches to generate dissymmetric particles have been reported in the recent literature. These Janus-type particles have been obtained either by protection/deprotection mechanisms [1], focused laser-induced reactions [2], co-jetting of parallel polymer solutions under the influence of an electrical field [3], anisotropic electroless deposition [4], or with microfluidic techniques [5]. However, so far most of the methods used to generate such objects need to break the symmetry by introducing interfaces like in the case of sputtering [6,7], stamp coating [8,9], and Langmuir-Blodgett-based techniques [10]. This makes the preparation of large quantities rather difficult.

Thus, there is an increasing interest in developing alternative methods to replace the two-dimensional approaches by truly three-dimensional techniques allowing a scale-up of the production of Janus objects to larger quantities by using bulk procedures [11].

In this context an attractive method that uses the concept of bipolar electrochemistry [12] has been reported by Bradley et al. and allows generating metal layers in a dissymmetric way on different substrates [13,14]. In brief, when a conducting object is placed in a strong electric field between two electrodes a polarization occurs that is proportional to the electric field E and the characteristic dimension r of the object.

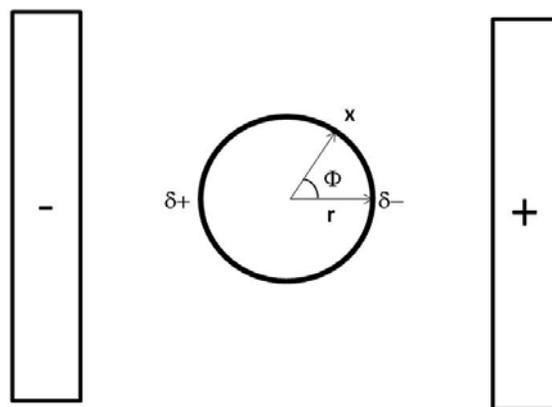


Figure 1. Polarization of a conducting spherical particle in an electric field.

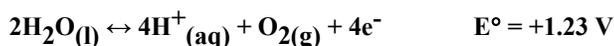
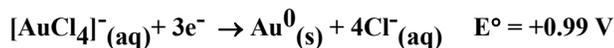
The simple equation governing this polarization also immediately illustrates the practical problems that will arise when applying this concept to nanoobjects.

$$\eta_x = E r \cos\Phi \quad (1)$$

With η_x being the polarization at a given point x at the surface of the nanoobject, one can easily calculate that the maximum potential difference between the two opposite sides of the object is given by:

$$\Delta V_{\max} = 2 E r \quad (2)$$

In order to carry out two different redox reactions at the opposite sides of the nanotube (oxidation at the left side and reduction at the right side) ΔV_{\max} has to be at least equal to the difference of the formal potentials of the two redox reactions. Two typical redox reactions that could take place in an aqueous environment might be the following ones:



It immediately follows that the polarization has to generate a potential difference of at least 0.24 V. In order to achieve this difference on an object with r in the nanometer range, E reaches values of the order of MV/m. These conditions seem to be incompatible with a normal laboratory environment and especially with an aqueous solution. This might be partly the reason why previous work has been focused on objects in the micrometer or submicrometer range and the experiments had to be carried out in organic solvents [13, 14]. We show in this contribution that the approach can be extended to nanoobjects like carbon nanotubes, modified in aqueous solutions when a capillary electrophoresis set-up is used to apply the high electric field. This capillary assisted bipolar electrodeposition (CABED) process represents, therefore, an original alternative to generate dissymmetric nanoobjects of various compositions [15].

2 EXPERIMENTAL

2.1. Preparation of the nanotube suspensions

Aqueous suspensions of CNTs can be produced analogous to what has been reported for other types of carbon [16, 17]. The raw sample of carbon nanotubes used for this study was multi-wall carbon nanotubes produced by catalytic chemical vapor deposition (ARKEMA). About 0.1 mg of MWNTs was added to a polyoxometalate (POM) solution (10 mM $\text{H}_3\text{PMo}_{12}\text{O}_{40}/0.1 \text{ M H}_2\text{SO}_4$). This solution was prepared from phosphomolybdic acid hydrate, $\text{H}_3\text{PMo}_{12}\text{O}_{40} \cdot x\text{H}_2\text{O}$ (FLUKA) in 0.1 M H_2SO_4 . The suspension was sonicated with a high intensity ultrasonic processor. After 1 hour of sonication a stable suspension of shortened CNTs is formed that can be further processed by fractionated centrifugation in order to select nanotubes with a quite narrow size distribution [18].

2.2. Bipolar gold deposition on carbon nanotubes

The starting solution used for the capillary electrophoresis (CE) experiment is an aqueous CNT/ HAuCl_4 (1 mM) suspension. For CE 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 45 cm and an inner diameter of 100 μm . The distance from the capillary inlet (left side in Figure 2) to the detection window (right side) in this case was 41 cm. The applied voltage was 30 kV whilst the temperature was maintained at 25°C. The CE experiment was first performed by rinsing the capillary with ultrapure water. Then the diluted aqueous suspension of the shortened, POM-modified carbon nanotubes was introduced into the capillary. The reason for using a diluted suspension for the CE experiment is due to the narrow capillary (100 μm). Introducing suspensions that are too concentrated leads to clogging of the capillary. The combination of migration and electroosmotic flow determines the transport of the CNTs through the capillary. The flow characteristics were determined by recording the absorbance variations in the UV detector (254 nm) as a function of time.

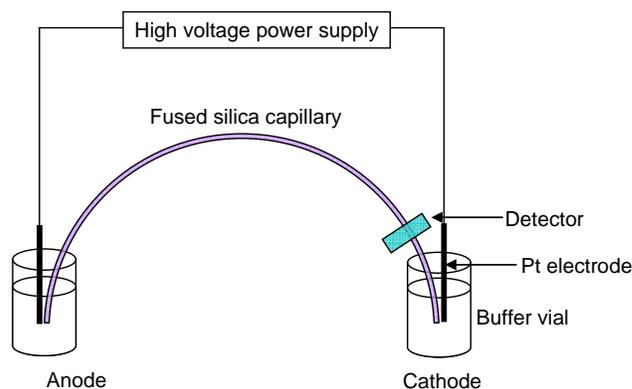


Figure 2. Schematic illustration of the capillary electrophoresis set-up.

The bipolar electrochemical gold deposition on CNTs is achieved by introducing the CNT/ HAuCl_4 (1mM) suspension into the capillary at the anodic side. Because the addition of acid (HAuCl_4 here) can result in the aggregation of the POM-modified CNTs, the suspension has to be sonicated for 1 minute in an ultrasound bath in order to maintain the CNTs being well dispersed before introduction into the capillary.

The sample leaving the capillary at the cathodic side was collected directly at the outlet. This collected sample drop was put on a TEM grid and dried. Because the suspension still contains the gold salt (AuCl_4^-), drying of the suspension on the grid leads to gold salt crystallization

which extremely disturbs the further TEM analysis. Therefore, after the suspension was dropped onto the TEM grid, the solution still containing HAuCl_4 was soaked through the grid by placing a cleaning tissue under the grid. After that, the remaining particles on the grid were washed three times with ultrapure water using the same procedure. The washed particles were then characterized by TEM.

3 RESULTS AND DISCUSSION

The potentials given in the above redox equations are standard potentials and as the experiment is carried out far from standard conditions in terms of concentrations and partial gas pressures, large deviations from the threshold value of 0.24 V can be expected. This also means that the calculated electric fields in the MV range might be different, especially when somewhat longer objects like the CNTs are used. Using carbon nanotubes for this proof-of-principle experiment also has the advantage that, due to their anisotropy the polarization induces at the same time an orientation parallel to the electric field, that the nanotubes preserve during their whole journey through the capillary. Thus, it will be easier to perform such a bipolar electrochemical deposition with CNTs compared to spherical objects that might change their orientation during the experiment and in this way lead to random metal deposition at the object's surface.

The experiment has been carried out at the maximum potential difference that can be delivered by the capillary electrophoresis set-up, which is 30 kV. When this potential difference is applied between the two ends of a capillary with a total length of 45 cm, an electric field of 67 kV/m is generated in the capillary. The nanotube pieces obtained by the above mentioned sonication procedure have an average length of 500 nm [18]. One can therefore easily calculate that the maximum polarization that can be obtained between the two ends of a nanotube is of the order of 50 mV. This value is smaller than the minimum potential difference necessary for driving the two redox reactions when the calculation is based on the standard potentials and, therefore, no bipolar electrodeposition should occur under these conditions. Performing the experiment shows, however, striking evidence for a dissymmetric deposition of gold nanoparticles at one end of the nanotubes (see Figure 3). We explain this not only by the conditions that are far from the standard conditions used to define the E° values, but most likely the presence of adsorbed polyoxometalate molecules at the CNT surface has also an influence on the potential values as they can undergo complexation reactions with metal ions [19].

The pictures of Figure 3 are representative of the majority of the nanotubes reaching the capillary outlet; however, not 100% are modified. There are several possible origins for a non-quantitative modification. First of all, the

gold deposit can detach from the tube during the collection and rinsing procedure, as seems to be the case for the small particles that can be seen in Figure 3A. Second, nanotubes can be more or less conducting depending on their morphology and defects. In the extreme case of an isolating tube, no deposition can occur and even for conducting tubes the conductivity has to be better than that of the surrounding electrolyte to induce a sufficient potential difference. The third reason is that the potential drop scales with the length of the tube, and therefore shorter tubes might experience a potential difference between the two ends that is below the threshold value.

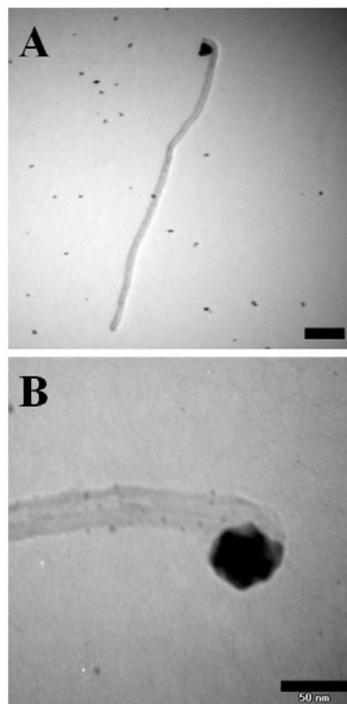


Figure 3. Site selective bipolar electrodeposition of gold at one end of a carbon nanotube **A)** TEM image of a selected nanotube from a very diluted sample **B)** Magnification of the modified end of a nanotube; scale bars are 100 and 50 nm respectively.

It is important to note that, in contrast to the former experiments [13, 14], in this set-up the high voltage is not a problem, although we don't use organic solvents but water, because the electrodes are positioned at the outside of the capillary. This means that an eventual macroscopic hydrogen or oxygen evolution at the cathode or anode respectively doesn't perturb the experiment as it takes place in the bulk solution and not in the capillary. Furthermore the currents are in the nA range because there is no supporting electrolyte present and thus the total amount of developed gas is rather low.

4 CONCLUSION

In summary, the concept of bipolar electrochemistry has been adapted to modify in a dissymmetric way multiwall carbon nanotubes with a gold cap as illustrated in Figure 4. The method employed to create these Janus-type objects is based on a slightly modified capillary electrophoresis experiment, (i) allowing the application of the mandatory high voltages (ii) without having to use organic solvents and (iii) especially avoiding gas bubble formation in the reaction chamber, which otherwise would completely prevent the alignment of the nanotubes in the electric field.

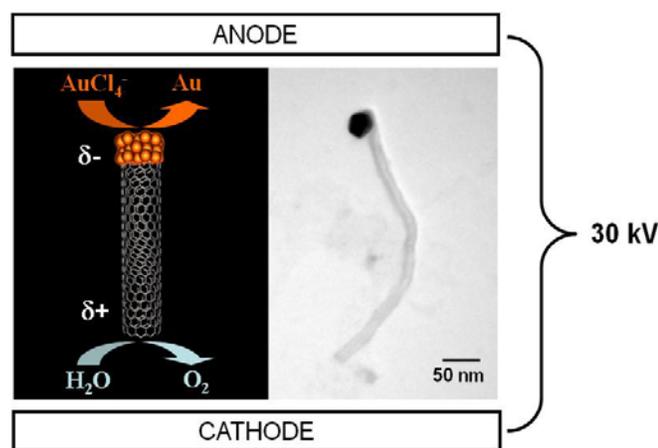


Figure 4. Reaction scheme for the site selective generation of a metal cluster (left) and TEM image of a MWCNT, modified at one end with a gold cluster(right).

Most importantly, the procedure uses a real bulk-phase reaction in contrast to most of the literature methods based on interfaces to break the symmetry. This makes the method very attractive to scale-up the production of such dissymmetric objects.

Looking to the future, the CABED process can be generalized to other types of nanoobjects and also deposits of a very different nature such as other metals, semiconductors, or polymers. The approach therefore opens up the way to a whole new family of experiments leading to complex nanoobjects with an increasingly sophisticated design allowing original applications. In addition, the procedure reported here could also be adapted to sort conducting, semiconducting, and insulating carbon nanotubes, as the latter ones will not be modified with metal, whereas the first two categories of species will undergo a potential-dependent metal modification.

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