Top−Down Approach for the Preparation of Colloidal Carbon Nanoparticles

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Highly dispersed carbon particles are of great interest for various applications such as pigments,[1] fillers,[2] supercapacitors,[3] or high-performance electrode materials in batteries.[4] The success of these applications strongly depends on the availability of colloidal spheres with tightly controlled size and surface properties and therefore there is a continuously increasing research effort in the synthesis of colloidal carbon micro- and nanospheres. However, until now, the controlled fabrication of carbon particles with a homogeneous size in the submicrometer range is often quite complicated. They have recently been obtained essentially in a bottom−up approach, for example, by pyrolysis,[5−7] microwave plasma enhanced chemical vapor deposition,[8,9] electrolysis in molten salt,[10] graphitization of particles obtained by microemulsion polymerization,[11] or treatment in supercritical water.[12] These techniques lead to well-defined carbon particles but most of them need specific and expensive equipment. Furthermore, the so-prepared particles often have a relatively inert surface which makes surface treatment or modification necessary before using them as supports.[13] In this contribution, we present a new and very simple route to carbon particles that not only allows us to control their size down to the nanometer range but also at the same time leads to particles with a monolayer coating that makes them more reactive with respect to further modification or applications such as catalysis.[14] This top−down approach is based on the spontaneous and strong chemisorption of polyoxometalates (POM) on carbon surfaces.[15] The adsorption of these anions constitutes the driving force for the gradual division of the initially large carbon black aggregates into much smaller particles, stabilized by the negatively charged POM monolayer, finally leading to highly dispersed colloidal carbon with a quite narrow size distribution.

The adsorption of POMs on various carbon-based materials including powders and fibers has been used by several authors to elaborate on supported catalysts with promising efficiencies and high immobilization strength.[14] Nevertheless, this strong and irreversible adsorption can also be used with a completely different purpose, namely, the tailoring of carbon particles. When treating an initially very heterogeneous carbon black powder by dispersing it in an aqueous phosphomolybdic acid ($H_3PMo_{12}O_{40}$) solution (10 mM) under ultrasound, a colloidal suspension of carbon particles is obtained immediately. Quite analogous to what occurs when preparing an oil/water emulsion in the presence of an amphiphilic surfactant, the force of the ultrasound bath, together with the chemisorption of the POM anions at the carbon surface, leads to a breakdown of the carbon black clusters, and their final average size can be tuned by the duration of this treatment. After centrifugation of the obtained suspension, to remove the supernatant POM rich phase, the particles are washed several times with diluted sulfuric acid and finally redispersed in pure water. These final suspensions are stable for weeks. Neither particle sedimentation nor degradation is observed, partly due to the absence of ions in solution that could shield the electrostatic repulsion between the particles. A subsequent prolonged centrifugation however can lead to a partial sedimentation, allowing accumulation of particles of almost identical size in the remaining supernatant solution. Droplets of these samples were dried on indium tin oxide (ITO) slides or copper grids in order to visualize the particles and check their dispersity by SEM or TEM.

In Figure 1a, the mixture of particles of various sizes and shapes represents the carbon black starting material. Similar pictures were obtained after attempting dispersion of the untreated carbon powder in pure water under sonication as a blank experiment. A relatively short (a few minutes) ultrasound treatment in the presence of POM leads to particles with a characteristic

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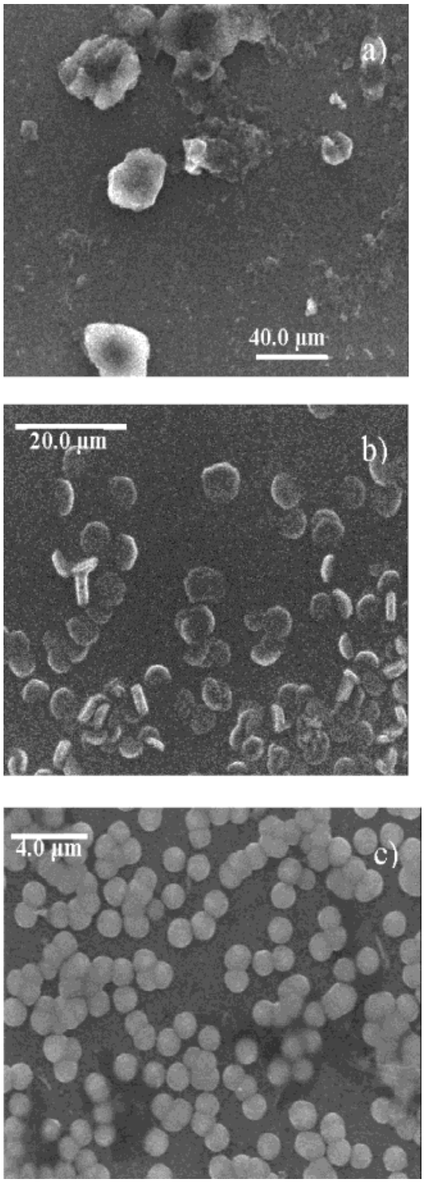

Figure 1. Particle size as a function of sonication time. (a) Inhomogeneous untreated carbon black powder. (b) After sonication in POM solution for 10 min and (c) after 1-h sonication.

size around 7 μm (Figure 1b). Further sonication (1 h) decreases the particle size down to 1 μm (Figure 1c). A treatment over several hours in the presence of POM allows the production of particles with a homogeneous shape and size in the nanometer range (Figure 2a,b) and no lower limit could be established so far. During prolonged sonication, the POM solution has to be renewed several times after intermediate centrifugation because a significant change from the characteristic yellow color of oxidized POM to green-blue was noticed, indicating that these anions not only adsorb but also oxidize the carbon surface and diffuse back into solution as reduced heteropolyblue species. However, this color change becomes less and less prominent as the treatment goes on and can be used as a rough indicator with respect to the end of the particle splitting reaction.

Light diffusion experiments with the noncentrifuged samples also illustrate the evolution of the size distribution as a function of sonication time (Figure 3a). Not only does the maximum of the initially quite broad distribution shift gradually to lower values but also the distribution itself is becoming more narrow and is characterized by a very good autocorrelation curve ($R = 0.9996$). Statistical evaluation of the particle size by counting and measuring on the images gives values in good agreement with those obtained by light diffusion. This indicates the formation of a homogeneous colloidal suspension. No agglomeration seems to occur after stopping the ultrasound treatment. This high stability is essentially due to the irreversible chemisorption of a layer of POM ions on the carbon surface, playing thus the role of a permanent “inorganic surfactant” that leads to negatively charged particles. The repulsive interaction between these like-charged objects finally allows the formation of the colloid, sufficiently stable that even prolonged centrifugation does not lead to a complete settling of the particles. A similar effect has been observed recently by other authors who succeeded in stabilizing metal nanoparticles by the adsorption of POM on their surface.[16,17]

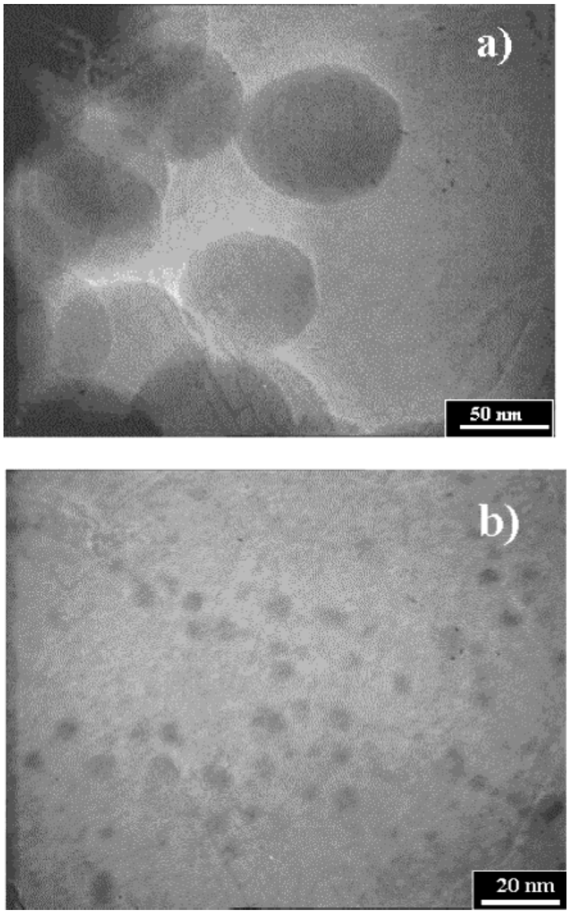

Figure 2. Transmission electron microscopy of the carbon particles. After prolonged sonication in polyoxometalate solution (several hours), the particle size can be decreased further down to the nanometer range.

To demonstrate the presence of POM clusters on the carbon surface, fractions of the particles were collected by centrifugation of the aqueous suspension, after addition of some salt or acid in order to screen the

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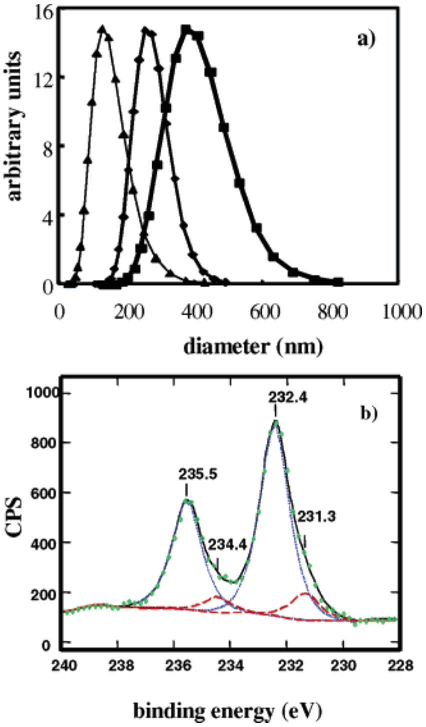

Figure 3. Characterization of the particles by light diffusion (LD) and X-ray photoelectron spectroscopy (XPS). (a) LD: a continuous decrease of the mean particle diameter and the width of size distribution is observed upon sonication for (■) 5 min, (◆) 1 h, and (▲) 3 h. (b) XPS: after washing and isolating the particles, XPS studies reveal the presence of Mo(V) and Mo(VI) on the carbon surface: (green ◇), experimental data; dashed red and blue lines, simulated contributions of Mo(V) and Mo(VI), respectively. Their addition leads to the solid black line, fitting the experimental data.

electrostatic repulsion. The dried powder was analyzed by XPS and Figure 3b illustrates a typical pattern obtained in the binding energy region corresponding to Mo(VI) and Mo(V). A closer look at the experimental data (green diamonds) reveals that not only is molybdenum present in the fully oxidized +6 state but also a certain fraction is in the partially reduced +5 state (shoulders at 234.4 and 231.3 eV, respectively). Control XPS experiments with either pure POM powder or a mechanical mixture of POM and carbon black powder did not exhibit these shoulders (data not presented). A simulation of the individual contributions of the different redox states (dotted blue line for Mo(VI), dashed red line for Mo (V)), adding up to the global simulated signal (solid black line), fits the experimental data very well. Calculation of the area of the different contributions by integration indicates that approximately 1 out of 10 molybdenum atoms is in the +5 state. This is in agreement with the strong chemisorption of the POM involving a partial charge transfer from the carbon surface to the LUMO of the clusters, leading to a mixed valence compound.[18] The present result suggests that roughly one electron is transferred per anion. From these measurements it cannot be completely excluded that during the adsorption on the carbon surface the POM is partly hydrolyzed; however, as the treatment is performed in phosphomolybdic acid, the pH is quite low and therefore this effect should be of minor importance.

We can conclude that during ultrasound treatment the presence of POM anions leads to a maximization of exposed surface by dividing an initial carbon black agglomerate into smaller and smaller units in order to benefit from the free energy related to the chemisorption. The final particles are therefore composed of a pure carbon core and a POM shell that, according to previous studies,[15,19−24] is a monolayer.

In summary, the suggested top−down approach is a so far unexplored low-cost route to carbon particles with a characteristic size ranging from the micrometer to the nanometer scale. Inherent to the procedure is the modification of the particles with monolayers of charged polyoxometalates having well-known catalytic and electrochemical activity and this opens applications for these well-defined particles ranging from catalysis to energy storage. Furthermore, the here presented procedure might be easily adapted to the formation of stabilized suspensions of other carbon nanostructures such as single-walled carbon nanotubes. Several methods to obtain individual nanotubes or at least well-dispersed assemblies of nanotubes have been proposed very recently in the literature,[25] but some of them severely damage the tube walls. In this context, the reaction with POM represents a milder and more promising alternative. The POM functionalized carbon nanostructures obtained in this way might be used as building blocks in well-characterized network films analogous to what has been recently described for dendrimers[26] and metal nanoparticles.[27]

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Supporting Information Available: Details of particle preparation and characterization (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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