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PAPER

Synthesis of carbon nanospheres for the development of inkjet-printed resistive layers and sensors

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Abstract

Unitary carbon nanoparticles with a well-defined shape and a range of diameters between 50 nm and 300 nm have been synthetized from the pyrolysis of resorcinol formaldehyde copolymer. This divided solid has a molecular organization similar to carbon black with a more regular shape and a higher diameter. Thus, carbon nanospheres appear to be adapted to the development of accurate sensors. Inkjet-printable dispersion was prepared with this material and a mixture of N-methyl-2-pyrrolidone and N-cyclohexyl-2-pyrrolidone. This ink is the proof of concept that it is possible to form continuous layers on polyimide flexible substrate with resistive properties which exhibit temperature sensitivity.

1. Introduction

Deposition of nanoparticles using inkjet-printing technology enables the fabrication of electrically active thin films on large area, at low cost and with a broad choice of materials [1]. This technique is also well suited for the realization of electronic devices on a flexible substrate [2, 3]. Conductive pattern printing is a well-controlled technology especially when using silver nanoparticles inks [4, 5] and recent studies have shown that printable dispersions make it possible to obtain layers able to fulfill the task of an electronic device [1, 6]. Due to its intrinsic properties, carbon in graphitic or disordered state is an interesting material to obtain resistive layers that can be used to develop printed resistors and sensors [7].

Nowadays, carbon black is commonly used in industry or different research domains to fabricate carbon nanoparticle-based dispersions [8–10]. However, this divided solid consists of aggregated particles with an irregular shape.

Development of inks using a solid dispersed phase with a well-controlled shape and granulometry makes it possible to enhance properties of electronic devices made with the inkjet-printing technique in different ways for applications. For example, particles with a range of different diameters make it possible to increase the density of a printed layer as the smaller particles fill the gap left by the bigger ones. The shape of nanoparticles also has a significant influence on their properties [11, 12]. A spherical shape facilitates a compact arrangement.

The conductivity of the layer and of the particles plays an important role on the sensitivity of the sensor. On carbonaceous materials, this property is linked to its surface chemistry (number of dangling bonds or bonds with oxygen or sulfur), texture (density, porosity, organization of the aggregates), structure (graphitization level) and packing arrangement (aggregates or particles organization, pressure applied) [13–15]. The sol–gel method is a versatile synthesis pathway to prepare carbon nanomaterials, tailor its texture, and control the size of the beads. The pyrolysis temperature also influences the conductivity (structure and chemistry [15]) by modifying the size of the crystallites. This method permits one to obtain a range of materials with various characteristics.

This paper is a proof of concept with this type of carbon material. It describes first the fabrication of unitary carbon nanospheres having intrinsic electrical properties similar to carbon black but with a well-defined shape. Secondly, these spherical carbonaceous particles are used to formulate an ink destined to be used in printed electronics. These divided solids are
obtained by achieving a synthesis of a thermoset resorcinol/formaldehyde (RF) copolymer obtained by the sol-gel method and air drying which is subsequently pyrolyzed under nitrogen atmosphere. After the carbon nanosphere synthesis, studies have been carried out in order to develop inks able to properly feed the inkjet printer. For this goal, a formulation has been developed to obtain a medium which enables optimal dispersion and stability of carbon nanospheres and allows them to comply with the printer specifications in terms of viscosity, surface tension as well as density. Finally, the resistivity of the printed carbon films has been measured as a function of temperature.

2. Experiment

2.1. Chemical compounds

Resorcinol (99%), formaldehyde (36.5 wt.% aqueous solution with 8 wt.% methanol), calcium carbonate (99%) and N-cyclohexyl-2-pyrrolidone were purchased from Sigma-Aldrich. N-methyl-2-pyrrolidone, polystyrene and Triton X 100 (99%) was bought at Acros Company. Vulcan XC 72 (carbon black) nanoparticles were provided by Cabot. Isopropanol (VLSI standard) was obtained from Techni France. Printing on flexible substrate was carried out on polyimide apical 500 AV (125 μm) purchased at Technifilm company. All products were used as received.

2.2. Instrumentation

Pyrolyses of the polymer were achieved using a furnace model GHA 12/300 and a temperature regulator type 3216 model P1 both from Carbolite company. Nitrogen adsorption isotherms were measured at 77 K by a MICROMERITICS ASAP 2020. Raman analyses were carried out with a Raman Lab HR 800 spectrometer (Horiba Jobin-Yvon) equipped with a 488 nm Ar laser. Transmission electron microscopy (TEM) analyses of carbon black (Vulcan XC 72) were carried out using a Philips CM12. Scanning electron microscope (SEM) images of the carbons nanospheres were recorded with a ZEISS Supra 40 or a Ultra 55 SEMs for the printed layers. Inkjet printing was performed with a Dimatix 2800-DMP from Fujifilm using 10 pl cartridges with 16 nozzles having a 21.5 μm diameter. Photonic treatments of printed layers were driven with a Pulseforge 3200 from Novacentrix company. Electrical characterizations were performed with a four-point probe analyser 4200-SCS from Keithley company.

3. Results and discussions

3.1. Synthesis of carbon nanoparticles from resorcinol/formaldehyde copolymer pyrolysis

The suitability of the products obtained with pyrolysis of RF copolymers are discussed in this part on the basis of particle size and shape, granular spreading and the presence or absence of irregular shaped structures.

The RF copolymer was given a targeted spherical nanostructure using a synthesis pathway proposed by Schedel et al. It consists in synthesis in a solution controlling reactant concentration and their ratio compared with the catalyst. In this protocol, size and shape of the synthesized solid phase only depend on relative quantities of reactant and catalyst initially introduced in the reaction medium. With a formaldehyde/resorcinol molar ratio maintained at 2, granulometric characteristic of the product is determined by 2 parameters R/C (molar ratio between resorcinol and catalyst) and M (mass fraction of resorcinol and formaldehyde on the solvent).

Individual spheres of various sizes, aggregates or monoliths can be obtained as a function of the combination of these two parameters. In order to allow good jetting of the ink and avoid printer nozzles clogging, special attention has been given to obtain a maximum diameter of the individual spheres smaller than 1 μm. Copolymerization reactions were carried out with R/C = 900 and M = 10.

In a typical synthesis, a volume of 4.1 ml of formaldehyde (36.5 wt.%) is added to 41.67 ml of deionized water, stirring at 600 RPM. Then, 3 g of resorcinol and 0.341 ml of a 0.1 M Na2CO3 solution are placed in the reaction medium. Stirring is maintained for 20 min and the mixture is placed at 85 °C in static conditions for 16 h. Finally, the product is centrifuged and dried using an oven heated at 60 °C.

Subsequently, RF copolymer nanospheres were transformed into carbon nanospheres by means of pyrolysis under nitrogen flow at 1.51 min⁻¹ and temperature equal to 1100 °C for 30 min. Pyrolysis of the RF copolymer under inert atmosphere is commonly used for the production of carbon aerogel. This treatment induces a volume shrinking with unchanged shape and is also applicable to RF divided solids.

3.2. Characterization of the carbon nanospheres after their synthesis

3.2.1. Microstructure

As can be observed in figure 1, the synthesis method led to the formation of non aggregated spherical carbon nanoparticles from 50 to 300 nm. This range of diameters enables the nanospheres to organize in compact structures where small particles fill the gap left by the bigger ones.

The obtained particles are very different, in terms of size and shape, to commercial Vulcan XC 72 carbon black as can be seen on the TEM micrograph. The particle sizes are about 50 nm with a section of smaller ones, and the shape is not totally spherical.

3.2.2. Estimation of the degree of graphitization

Carbon nanospheres obtained from RF copolymer pyrolysis were analyzed using Raman spectroscopy
Figure 1. SEM pictures of carbon nanoparticles obtained after pyrolysis treatment.

Figure 2. TEM image of Vulcan XC 72 nanoparticles.
and compared with Vulcan XC 72 carbon black as shown in Figure 3.

Both divided solids exhibit one peak at 1350 cm$^{-1}$ and 1600 cm$^{-1}$ which respectively correspond to disordered carbon and graphitic carbon\[22, 23\]. The short-range microstructure differences between these two products, which are sensitively probed by the Raman effect\[24\], have been characterized by calculating the ratio of the integrated intensities of the disordered peak ($I_D$) and the graphitic peak ($I_G$). The relative intensities ($I_D/I_G$) of the two Raman peaks of carbon nanospheres and Vulcan XC 72 are respectively equal to 2.60 and 2.01 which indicates that carbon nanospheres exhibit a lower degree of graphitization.

In order to estimate the significance of the differences observed between carbon nanospheres and Vulcan XC 72, these values have been compared with results obtained by Hauptman\ et al\ and Palomares\ et al\[25, 26\] with other commercial carbon black. Data have been reported in Table 1.

As it is possible to observe in Table 1, carbon blacks show a greater variability in $I_D/I_G$ ratio than the difference observed between carbon nanospheres and Vulcan XC 72 (e.g. if Printex 200 and Timcal-Super P are compared) so the graphitization of carbon nanospheres is comparable with other carbon blacks. As the intrinsic conductivity of particles made of carbonaceous materials is directly linked to the graphite content\[27, 28\], this result indicates that the electrical properties of the nanospheres are, as intended, similar to those of carbon black.

3.2.3. Specific surface area and porosity measurements

Nitrogen adsorption–desorption analyses were carried out on carbon nanospheres in order to characterize their texture. Before measurements, the sample was pre-treated at 300 °C for 300 min to remove adsorbed impurities. The analysis of the N$_2$-adsorption isotherms (0.01 < p/p$_0$ < 0.3) provided the BET specific surface area, $S_{BET}$. Total pore volume ($V_t$), equals the adsorbed volume at saturation, and was determined at relative pressure of 0.995. Micropore volume ($V_{mic}$) was calculated by the Dubinin–Radushkevich equation. The type 4 nitrogen isotherms with the presence of a H1 hysteresis loop, in IUPAC classification observed in Figure 4 are often observed in resorcinol-formaldehyde based carbon xerogels or aerogels\[16, 18, 29\]. The data indicate that carbon nanospheres are essentially mesoporous with a pore distribution centred on 38 nm. The total pore volume ($V_t$) reaches 0.46 cm$^3$ g$^{-1}$ with a micropore volume of 0.26 cm$^3$ g$^{-1}$ (dramatically higher than for Vulcan XC 72 at 0.06 cm$^3$ g$^{-1}$)\[13\]. The mesopores are formed by interparticle spaces, while the micropores are due to intraparticle pores\[30\]. Their BET specific surface area measurement is equal to 528 m$^2$ g$^{-1}$ which is twice higher than carbon black XC 72 measured at 250 m$^2$ g$^{-1}$\[13, 31\].

3.3. Ink formulation

In order to be used as inkjet printable fluids, dispersions of nanoparticles must not contain agglomerates. These structures, bigger than unitary particles, would hinder the printing process inducing nozzle clogging and also have an adverse effect on ink stability because of a higher rate of sedimentation. Carbon

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**Table 1.** Ratio between integrated intensity of disordered peak ($I_D$) and graphitic peak ($I_G$).

<table>
<thead>
<tr>
<th>Material</th>
<th>$I_D/I_G$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon nanospheres</td>
<td>2.60</td>
</tr>
<tr>
<td>Vulcan XC 72</td>
<td>2.01</td>
</tr>
<tr>
<td>Printex 200</td>
<td>2.35</td>
</tr>
<tr>
<td>FW2</td>
<td>3.10</td>
</tr>
<tr>
<td>XE2-B</td>
<td>2.24</td>
</tr>
<tr>
<td>Timcal-Super P</td>
<td>1.24</td>
</tr>
<tr>
<td>Timcal-Super S</td>
<td>0.93</td>
</tr>
</tbody>
</table>
nanoparticles, as a result of the poor wettability between their surfaces and many usual solvents as well as their weak repulsive interparticle interactions are known to exhibit a strong agglomeration phenomenon when dispersed in a great number of media \[32\].

To overcome this drawback the ink has been prepared using a mixture of N-methyl-2-pyrrolidone (NMP) and N-cyclohexyl-2-pyrrolidone (CHP) as the vector liquid. NMP is often used to prepare stable dispersion with carbonaceous materials because of its good affinity with the surface of this kind of material \[7, 33\]. Furthermore, as it is possible to observe in table 2, NMP is in line with most of the specifications of the Dimatix inkjet printer; only its viscosity does not match and it is far too low.

CHP has been chosen because of its viscosity, which is suited to inkjet printing, as shown in table 2 and its chemical nature, which is very close to NMP and gives it a similar affinity with carbon nanoparticles. The surface tension of CHP is slightly above the recommended range of values, but in general, all physical properties of this compound comply with inkjet printing requirements. Thus, it has been selected as the main component of the vector liquid with a respective mass ratio of CHP/NMP equal to 7:1. This amount of NMP has been added to fulfill two objectives: firstly to reduce the surface tension of the ink and secondly to decrease the viscosity to compensate for the increase of this parameter once the nanoparticles are added. This viscosity reduction is preferable in view of the fact that pure CHP exhibits a value close to the upper limit (11.5 mPa s).

Still with the aim of achieving an ink preparation without agglomerates, Triton X 100 was added as a dispersing agent according to previous studies performed by Sharif \textit{et al} \[34\] and Kumar \textit{et al} \[35\] on carbon nanoparticles where it appeared to be the most efficient among those which are generally used.

![Figure 4. Nitrogen isotherms of carbon nanospheres at 77 K and pore size distribution.](image)

**Table 2.** Specifications required by the Dimatix DMP-2800 printer and physical properties of NMP and CHP.

<table>
<thead>
<tr>
<th>Physical property</th>
<th>Dimatix specifications</th>
<th>NMP</th>
<th>CHP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Viscosity</td>
<td>10–12 mPa s</td>
<td>1.8 mPa s</td>
<td>11.5 mPa s</td>
</tr>
<tr>
<td>Surface tension</td>
<td>28–42 mN m⁻¹</td>
<td>40.79 mN m⁻¹</td>
<td>43.2 mN m⁻¹</td>
</tr>
<tr>
<td>Boiling point</td>
<td>&gt;100 °C</td>
<td>202 °C</td>
<td>284 °C</td>
</tr>
<tr>
<td>Density</td>
<td>&gt;1 g cm⁻³</td>
<td>1.028</td>
<td>1.007</td>
</tr>
</tbody>
</table>
Finally, as the melting point of carbon is far too high, to make it possible to obtain sintering without deterioration of the polymer substrate a small amount of polystyrene was added with the aim of enhancing interparticle and particle/substrate adhesion once the vector liquid is evaporated.

In a typical ink formulation, 5 mg of polystyrene is dissolved in a mixture composed of 7 g of CHP and 1 g of NMP. Subsequently, several drops of Triton X 100 are poured in the mixture. Then, carbon nanoparticles are added until 5% wt. of dispersed solid phase in the ink is reached. Finally, the medium is then placed in an ultrasound bath for 30 min and stirred at 800 RPM for 12 h.

At the end of this protocol, the ink exhibited a viscosity and a surface tension respectively equal to 10.2 mPa s and 41.3 mN m$^{-1}$. The boiling point of each liquid and density of each component is sufficiently high to be certain that our formulation meets the specification of the Dimatix regarding these two parameters.

### 3.4. Printing process and post-printing treatment

Printing tests were carried out on polyimide foil because of its wide use in the domain of flexible printed electronics. The substrate underwent a pretreatment phase during which it has been straightened at 100 °C for 10 min, cleaned with isopropanol and dried using blown compressed nitrogen. Layer depositions were performed using the printing conditions described in table 3 and the waveform represented in figure 5.

The level (in ordinate) indicates the percentage of the firing voltage applied. The duration of each segment and the different slew rates (SR) which led to each plate are indicated in the waveform graphical representation. The non-jetting state consists in a constant percentage of firing voltage equal to 40% which corresponds to the end and the beginning of the jetting waveform. This indicates that when the ink is not ejected it does not undergo any shearing. This would be necessary with volatile solvents in order to avoid nozzle clogging due to evaporation. As NMP and CHP both exhibit a high boiling point and a low vapor pressure this precaution is not relevant. As a side note, it was still possible to print one week after it had been placed in the cartridge and no sedimentation phenomenon in a period exceeding 70 days was observed.

A photonic pulse treatment was needed to freeze particles in position on the substrate and obtain a rapid solvent evaporation in order to avoid a marked particle migration leading to inhomogeneities once the drying step was achieved. The settings of this photonic treatment are summarized in the table 4.

With these parameters, each pulse corresponded to 320 mL cm$^{-2}$, so during the entire photonic treatment, the sample was exposed to an energy of 32 J cm$^{-2}$.

As shown in figure 6, post-printing photonic treatment made it possible to obtain macroscopically continuous dry layers with a conservation of shape and dimensions of the printed pattern.

### 3.5. Characterization of printed layers

#### 3.5.1. Microstructure

The nanostructure of the printed layers was observed using SEM (figure 7). A stacking of the small granulometric class of particles can be observed through the samples with a trend of channel forming as illustrated in right the part of the micrograph 6B. This phenomenon is presumably caused by the solvent evaporation. However, the gathering of the smaller particles does not create defects in the layers, so, SEM observations confirm their continuity at the microscopic scale.

#### 3.5.2. Thermal–electrical coupling

Electrical properties of the carbon nanospheres layers were studied using a four-point probe in contact with the printed layer surface after the drying step under photonic pulses. A significant resistivity was measured and a marked correlation between sheet resistance and temperature was pointed out (figure 8).

Sheet resistance was equal to 40.5 kΩ at room temperature and increased up to 47.8 kΩ at 180 °C indicating that the ink formulated in this work is compatible with the development of inkjet resistors and temperature sensing devices. This variation can be fitted adequately by a linear regression and the equation of the corresponding straight line enables the calculation of the temperature coefficient of resistance ($\alpha$). This variation can be fitted adequately by a linear regression with a coefficient of determination $R^2$ equal to 0.924 which indicates a very moderate scattering of the measurements. This suggests that printed layers made of carbon nanospheres are well adapted to the development of accurate sensors. The equation of the corresponding linear function enables the calculation of the temperature coefficient of resistance ($\alpha$) that establishes the correlation between the sheet resistance and the temperature as described in the equation (1) with $T$ the temperature, $R_{\text{sh}}$ the sheet resistance at a given temperature, and $R_{\text{sh}(25)}$ the sheet resistance at room temperature (25 °C).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Drop spacing</td>
<td>30 μm</td>
</tr>
<tr>
<td>Number of printing passes</td>
<td>4</td>
</tr>
<tr>
<td>Firing voltage</td>
<td>40 V</td>
</tr>
<tr>
<td>Nozzle temperature</td>
<td>Room temperature</td>
</tr>
<tr>
<td>Substrate temperature</td>
<td>Room temperature</td>
</tr>
<tr>
<td>Meniscus vacuum</td>
<td>2 inches H$_2$O</td>
</tr>
<tr>
<td>Cartridge height</td>
<td>0.8 mm</td>
</tr>
</tbody>
</table>
The absolute value of $\alpha$ is directly linked to the sensor sensitivity and must be as high as possible. The inkjet-printed carbon nanosphere layers exhibit a value of $\alpha$ equal to $1.26 \times 10^{-3}^\circ C^{-1}$. This result is of the opposite sign and has an absolute value 2.5 times higher than $\alpha$ measured on the bulk graphitic carbon, which is equal to $-5 \times 10^{-4}^\circ C^{-1}$ [35]. These differences could be explained by the nanostructure of the inkjet printed film. When temperature increases the dilatation of the device would tend to separate the nanospheres from each other which hinders electron flow through the layer. Thus, the resistivity of the printed layers increases with temperature even if the intrinsic resistivity of each particle exhibits an opposite behavior.

Compared with the $\alpha$ coefficient of platinum ($3.92 \times 10^{-3}$) [36] which is one of the most commonly used materials to measure temperature in industry through the Pt100 probe [37], carbon nanosphere layers exhibit values 3 times lower. Sensors made with the ink developed in this work will not be as sensitive as platinum thermometers but they can be printed on flexible substrates in order to fabricate devices enabling one to perform measurements in hard to reach places or facilities with a complex geometry. Furthermore, considering only the domain of printed sensors, unlike metal nanoparticles, carbon nanospheres, owing to the very high melting point of the bulk carbon, will not be likely to undergo any sintering phenomena at high temperatures and thus avoid measurements of drift in these conditions.

4. Conclusions

The pyrolysis of resorcinol-formaldehyde thermoset copolymer allowed fabrication of non-aggregated carbon nanospheres with a well-defined shape. The product exhibits a granulometric distribution which makes it possible to form dense layers in spite of a noticeable migration of the smaller population during the drying step. The maximum diameter of nanospheres does not exceed 1 $\mu m$ and their minimum size is above 50 nm.

The formulation based on N-methyl-2-pyrrolidone (NMP) and N-cyclohexyl-2-pyrrrolidone (CHP) and Triton X 100 led to an easily printable ink that made it possible to prepare cartridge ink that is reusable over one week. Furthermore, inks contained in the vials in which they were prepared did not exhibit...
any naked-eye observable clarification or sedimentation phenomena over a period exceeding 70 days.

Raman spectroscopy analysis shows that products obtained with resorcinol-formaldehyde pyrolysis are composed of a proportion of graphitic crystallites and amorphous and disordered carbon with a molecular configuration quite similar to carbon black.

Electrical measurements confirmed the resistive nature of the printed carbon nanospheres layers and have demonstrated the interdependence between this
property and the temperature. The ink developed with carbon nanospheres is, thus, suited for the realization of inkjet-printed resistors. This preliminary study is a proof of concept that carbon nanospheres based on sol-gel synthesis are suited to creating thermometers. (fl) The authors thank Suzanne Jacomet (MINES ParisTech CEMEF) for SEM image and Nanomines for the financial support of the project.

Acknowledgments

The authors thank Suzanne Jacomet (MINES Paris-Tech CEMEF) for SEM image and Nanomines for the financial support of the project.

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