ChemComm

Accepted Manuscript

This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the **Information for Authors**.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard **Terms & Conditions** and the **Ethical guidelines** still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

www.rsc.org/chemcomm

ChemComm

Modified nanocarbon surfaces for high performance supercapacitor and electrocatalysis applications

Mohammed Es-Souni* and Dimitri Schopf

An efficient and easy method is described which allows modification of supported nanocarbon films with carbon nanotubes (CNT) from an aqueous colloidal suspension. Subsequently CNT can be decorated with Pt-nanoparticles directly from an aqueous solution of Pt ions without need of reducing agents. High performance supercapacitor and electrocatalysts are obtained.

In a recent article Abdelaziz et al. report on using a levitated Leidenfrost drop as reactor for the nanofabrication of different functional nanostructures, including plasmonic nanoparticles, directly from the precursors without needing reducing agents.[1] As discussed by them the fascinating nanostructures are the results of complex dynamics that involve among others water self-ionization and charge separation. While this elegant method may be used to fabricate small amounts of nanomaterials, an up-scaling may not be possible to realise because of the constraints related to generating levitated Leidenfrost droplets on a hot substrate. Herein we introduce a variant of the method using the inverse process and for large area processing of thin functional films and nanocomposites. The substrate is heated slightly above the Leidenfrost temperature and directly transferred to an aqueous solution of the precursor. Thereby we could process thin films, supported nanostructures and nanocomposites of various materials. The novelty of our method lies in its easy implementation (it is as easy as described) and the ability to process large area films, in contrast to the original method where only tiny amounts of nanomaterials could be processed in a levitating Leidenfrost drop reactor from aqueous solutions of noble metal ions. Moreover, we demonstrate that the method is not only suitable for the processing of metallic nanoparticles (NP) from aqueous solutions of their ions without need of reducing agents, but is also most suitable for thin films processing from colloidal

Fig.1 SEM micrographs of nanocarbon (a), CNT-modified (b) and CNT+Pt-N modified nanocarbon films (c)

* Institute for Materials & Surface Technology, University of Applied Sciences, Kiel, Germany. E-mail: mohammed.es-souni@fh-kiel.de
† Electronic Supplementary Information (ESI) available. See DOI: 10.1039/x0xx00000x
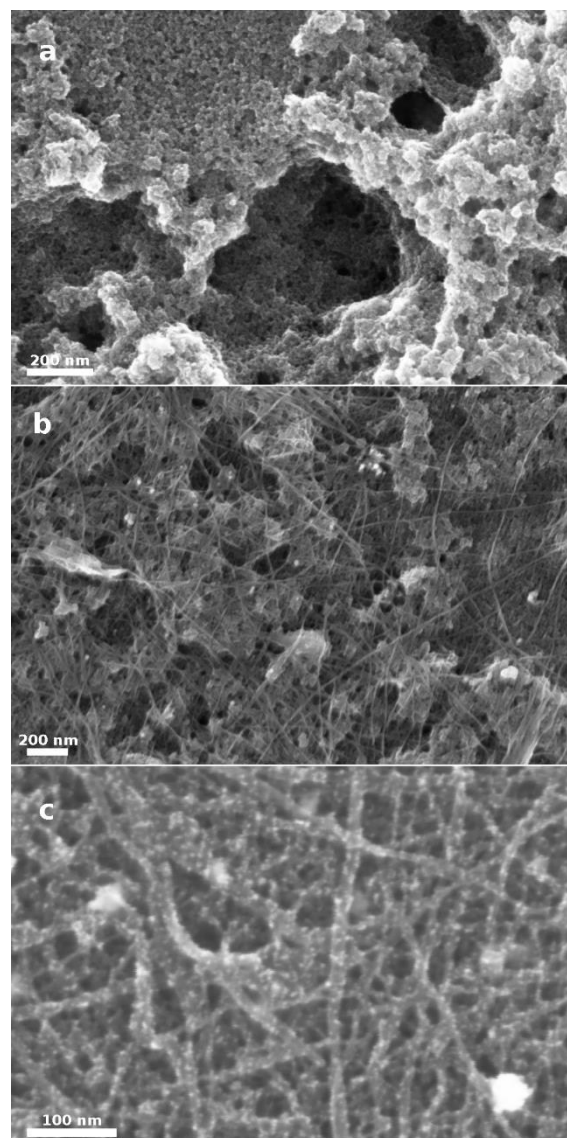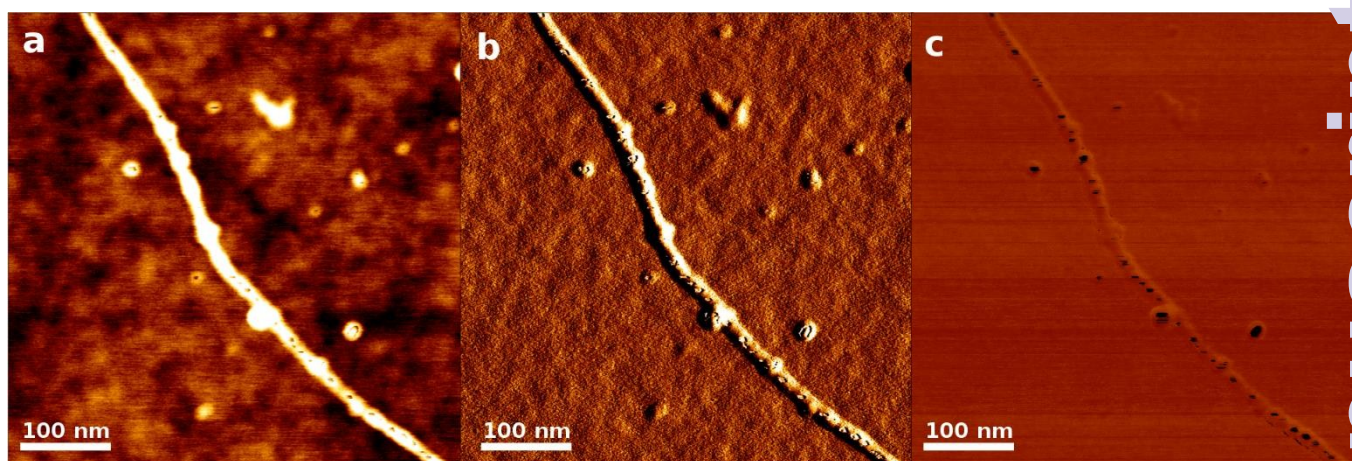
COMMUNICATION

Fig. 2 AFM micrographs of Pt-decorated CNT using the frequency force modulation mode that traces differences in the elastic properties of the participating materials. (a) Topography, (b) amplitude micrograph and (c) phase micrograph. The micrographs suggest that the Pt-NPs are well anchored to CNT.

suspensions of nanomaterials in aqueous solutions, a result that was not reported before. In this communication we will concentrate on carbon nanomaterials revealing interesting structures of carbon nanotube (CNT) thin films and noble metal nanoparticles decorated CNT. The thin films are applied as supercapacitors and electrocatalysts, respectively.

The processing route for supported nanocarbon thin films starts from porous PVDF that is subsequently pyrolysed and has been described in detail in our previous publications.[2,3] The microstructure is exemplary shown in Fig. 1a, with a distribution of macro and mesopores. When the nanocarbon film is heated on hot plate to a temperature slightly above 290 °C and directly transferred to an aqueous solution of PEG functionalized single walled CNT (SWCNT) a thin and adherent layer of CNT bundles forms on the nanocarbon surface. This is illustrated in Fig. 1b. Thicker layers may be obtained by repeating the procedure. In the same manner when the CNT covered films are heated and transferred to an aqueous solution containing 2 mM of H_2PtCl_6 the CNT upper layer appears to be fully decorated with a high density of Pt-nanoparticles (NP) as illustrated in Fig. 1c (see also EDS analysis, Fig. 1S, and grazing incidence XRD, Fig. 2S, supplementary information). The AFM amplitude and phase micrographs of Fig. 2 show that Pt-NPs are not just loosely decorating the CNT but that they rather tightly adhere to them. Using image analysis software Pt-NPs in the size range between 5 and 8 nm are obtained corresponding to particle density of 4.3×10^{11} particle/cm². This corresponds to a total Pt mass of approximately 3 μg in the active area assuming homogeneously distributed spherical particles of 8 nm diameter and taking into account the density of Pt (21.45 g/cm³).

Our results show that adherent CNT layers are transferred to the nanocarbon films from an aqueous suspension, and that the CNT layer can subsequently be decorated with Pt-NP without need of a reducing agent. At this moment we can only speculate that adherence of the CNT layer on nanocarbon is via mechanical retention that is favoured by the porous surface, although other mechanisms may also be operating. For instance covalent bonding between CNT and nanocarbon surface is quite possible if we consider that the surface of the carbon film may contain defects that originate during pyrolysis of the polymeric

film, e.g. hydroxyl groups. The Raman spectrum of the nanocarbon film (Fig. 3) indeed shows the predominance of the D band which is indicative of the presence of defects in graphite materials.[4] Taking this into account it is then straightforward to stipulate -C-O-C- bonding between the hydroxylated CNT and nanocarbon with the elimination of water. It should be pointed out that the adhesion of the CNT layer to the surface is so high that their subsequent decoration with Pt-NPs by transferring the modified hot substrate into the aqueous solution of Pt ions does not lead to their detachment from the surface. The reduction of Pt-NPs may follow the mechanism described by Abdelaziz et al.[1] where charge separation is stipulated in a Leidenfrost drop consequently leading to the reduction of metallic ions without need of reducing agents. Although in-depth investigations of the mechanisms underlying both the formation of the CNT-coating and the decoration of the CNT with metallic NP of narrow size in the range of 5 to 8 nm are still to be conducted, the method presented here is nonetheless a versatile and quite rapid one for the fabrication of functional
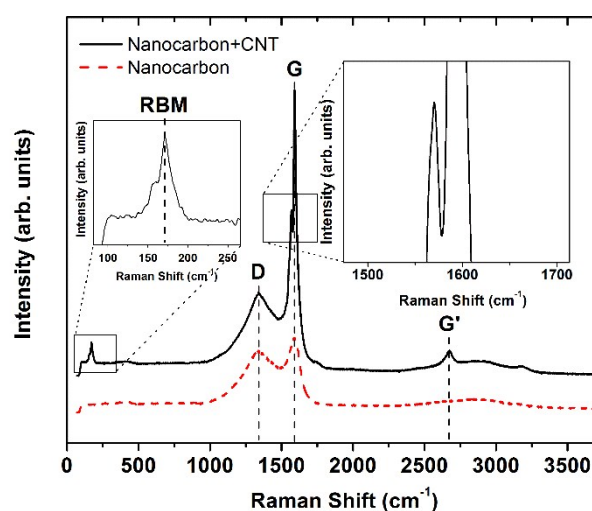

Fig. 3 Raman scattering of the nanocarbon, lower pattern, and the nanocarbon-CNT nanocomposite film, upper pattern. The characteristic vibrations of CNT are highlighted. RBM: radial breathing mode.
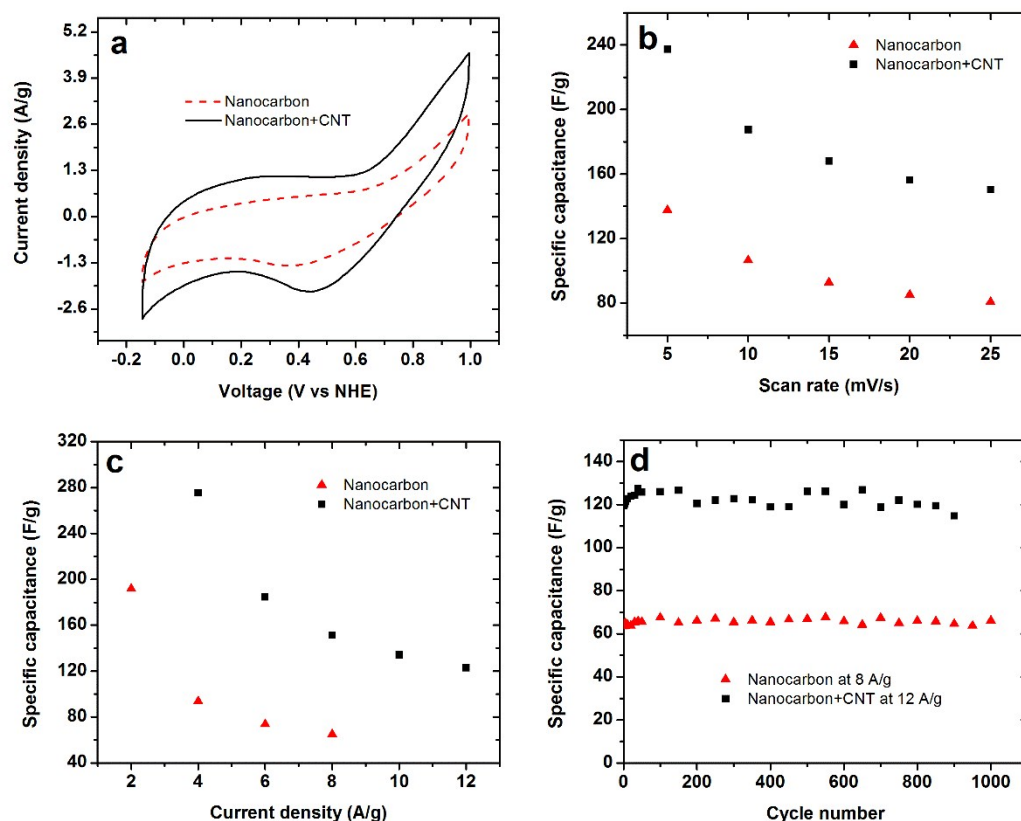
Fig. 4 Comparative electrochemical measurements in 0.5M H_2SO_4 of bare nanocarbon film and CNT coated film. (a) Cyclic voltammetry (CV) curves at 5 mV/s; (b) specific capacitance at different scan rates; (c) specific capacitance at different current densities; (d) long term cycling behaviour at indicated current densities. Specific capacitance is calculated using the total mass of nanocarbon and CNT.

surfaces. Below we show that CNT coated nanocarbon can be used as high performance supercapacitor while nanocarbon films with Pt-NPs decorated CNT coatings show outstanding electrocatalysis properties.

Figs. 4a-d compare the capacitive performance of the nanocarbon films with and without CNT upper layer. The results show that specific capacitance is doubled when the films are modified with CNT both using CV and galvanostatic measurements. The specific capacitance obtained outperform the values known for carbon nanotube structures reported in literature, e.g. Chen and Dai[5] and Bose et al.[6], and match those obtained for the best of activated carbon that undergoes complex high temperature treatments in KOH atmosphere for its activation.[7] The long term cycling behaviour is also outstanding, Fig. 4d, with no performance loss even at the high current density and the large voltage window employed (see also Figs. 3S and 4S, electronic supplementary information). The increase in performance may be discussed in terms of the high surface area imparted to the films by the CNT layer that should afford a huge density of sites for double layer capacitance both on the CNT layer itself and the carbon layer underneath. Furthermore the wetting behaviour is largely improved with the
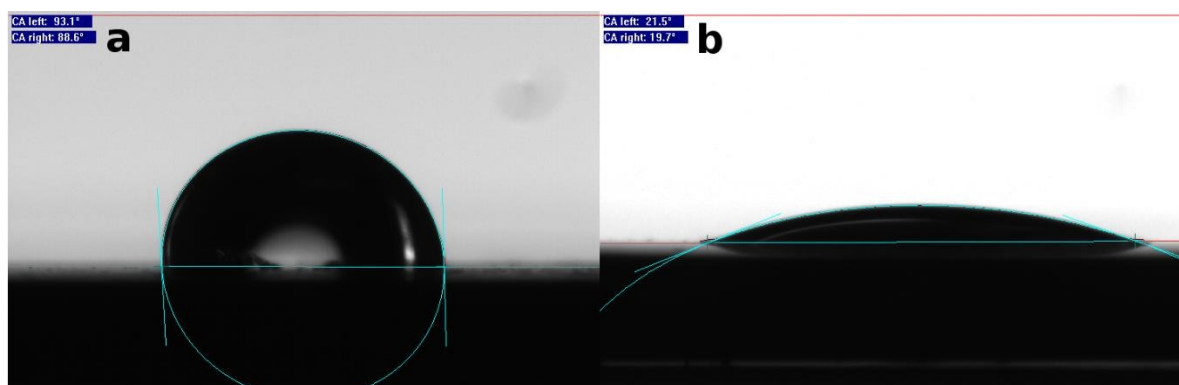

Fig. 5 Water contact angle of (a) Nanocarbon and (b) Nanocarbon+CNT films.
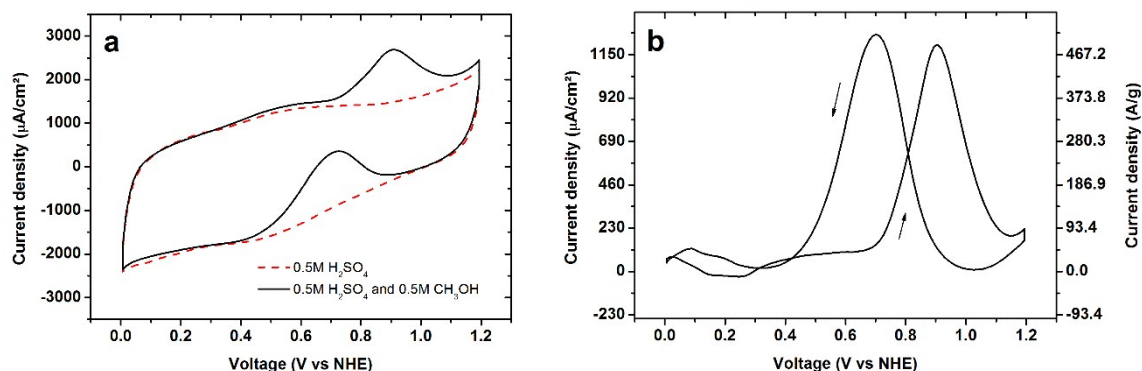
Fig. 6 CV-behaviour of the Nanocarbon-CNT-Pt-nanocomposite film; (a) CV curves in 0.5 M H_2SO_4 (dashed-line curve) and in 0.5 M H_2SO_4+0.5 M CH_3OH (full-line curve); (b) shows the difference between the two curves in (a). Scan rate: 50 mV/s.

CNT coating due to the presence of –OH groups (see Fig. 5S for the FTIR spectra, supplementary information) as illustrated in Fig. 5 where the water contact angle (WCA) decreases from approximately 90° for the bare nanocarbon film to 21° that should lead to better access of the electrolyte to the surface sites. It is thought that both effects, i.e. increasing the surface area and wetting, are complementary for imparting the high capacitive performance observed in this work.

The electrocatalytic behaviour of the Pt-modified nanocarbon-CNT film in an aqueous solution containing 0.5 M H_2SO_4 and 0.5 M CH_3OH is displayed in Fig. 6. It shows a forward anodic peak at approximately 0.9 V and a backward anodic peak at 0.7 V corresponding to the electro-oxidation of methanol and removal of carbonaceous species, respectively. With the onset voltage in the range of 0.65 to 0.7 V the Pt-CNT composite nanostructure displays a high electrocatalytic activity with rather high resistance to poisoning by oxidation products that is reflected in the high ratio of the forward peak intensity, J_f, to that of the reverse peak, J_r, that amounts to 0.96.[8] Maximum current densities of the order of 1200 µA/cm^2 are obtained which lead with the Pt mass of 3 µg determined above to a specific current density of approximately 470 A/g. This reflects a high electrocatalytic performance that surpasses reported values for Pt-decorated MWCNT[9,10] as well as values of Pt-nanostructures obtained using ZnO nanotubes[11] and nanorods[12] as templates. Also reported values of Pt in combination with other catalysts on carbon materials are better only in exceptional cases.[13] The reason for the high electrocatalytic activity of the present structure may first lie in the high surface area offered by the CNT forest structure for the Pt-NPs and the suitable size range of the latter. Secondly, high electrical conductivity is expected for the CNT-Pt-NP-composite. McAndrew and Baxendale report that the presence of metal-NP at CNT nano-junctions leads to increase in conductivity of CNT films.[14] Taking a closer look at Fig. 1c it should be rather easy to see that most of the CNT junctions are indeed decorated by Pt-NPs. Both the densely and homogeneously distributed Pt-NPs and the higher conductivity of the composite network are thought to be at the origin of the excellent electrocatalytic activity obtained in this work.

In conclusion a versatile and efficient method for surface modification with nanomaterials has been proposed. It is based on transferring a preheated substrate into an aqueous solution of the desirable material, and is exemplary shown to be successful with CNT and Pt-nanoparticles modification of a nanocarbon surface. The formation of narrow-size distribution of metal nanoparticles is achieved directly from the aqueous precursor solution without need of reducing agents. Further advantage of the method lies in its suitability for large area surface functionalization. The films can be advantageously applied for electrochemical energy storage and as electrodes for direct methanol fuel cells, but other applications such as chemical sensors are fully conceivable.

Notes and references

1 R. Abdelaziz, D. Disci-Zayed, M. K. Hedayati, J-H.Pöhls, A. U. Zillohu, B. Erkartal, V.S. Kiran Chakravadhanula, V. Duppel,L. Kienle, M. Elbahri, *Nature Communications*, 2013, **4**, 2400.
2 M. Es-Souni, D. Schopf, C.-H. Solterbeck and M. Dietze, *RSC Adv.*, 2014, **4**, 17748.
3 M. Es-Souni, Ma. Es-Souni and M. Dietze, *RSC Adv.*, 2011,**1**, 579-583.
4 M. A. Pimenta, G. Dresselhaus, M. S. Dresselhaus, L. G. Cançado, A. Jorio and R. Saito, *Phys. Chem. Chem. Phys.*, 2007, **9**, 1276–1291.
5 T. Chen and L. Dai, *Materials Today*, 2013, **16**, 272-280.
6 S. Bose, T. Kuila, A. K. Mishra, R. Rajasekar, N. H. Kim and J. H. Lee, *J. Mater. Chem.*, 2012, **22**, 767-784.
7 K. Kierzek, E. Frackowiak, G. Lota, G. Gryglewicz, J. Machnikowski, *Electrochimica Acta*, 2004, **49**, 515–523.
8 E. Yoo, T. Okata, T. Akita, M. Kohyama, J. Nakamura and I. Honma, *Nano Lett.*, 2009, **9**(6), 2255-2259.
9 C.-T. Hsieh, Y.-S. Chang and K.-M. Yin, *J. Phys. Chem. C*, 2013, **117**, 15478–15486.
10 S. Zhang, Y. Shao, G. Yin, Y. Lin, *J. Mater. Chem.*, 2010, **20**, 2826–2830.
11 R. Minch and M. Es-Souni, *Chem. Commun.*, 2011, **47**, 6284-6286.
12 R. Minch and M. Es-Souni, *J. Mater. Chem.*, 2011, **21**, 4182–4188.
13 H. Huang and X. Wang, *J. Mater. Chem. A*, 2014, **2**, 6266-6291.
14 C. F McAndrew and M. Baxendale, *Nanotechnology*, 2013, **24**, 305202.