Citation	N.K. Reddy, Lj. Palangetic, L. Stappers, J. Buitenhuis, J. Fransaer, C. Clasen Metallic and bi-metallic Janus nanofibers: electrical and self propulsion properties Journal of Materials Chemistry C 1 (2013), 3646-3650
Archived version	Author manuscript: the content is identical to the content of the published paper, but without the final typesetting by the publisher
Published version	<i>The final publication is available at Springer via</i> http://dx.doi.org/10.1039/c3tc30176a
Journal homepage	http://pubs.rsc.org/en/journals/journalissues/tc#!recentarticles&all
Author contact	your email christian.clasen@cit.kuleuven.be
IR	url in Lirias https://lirias.kuleuven.be/handle/123456789/389372

(article begins on next page)

Metallic and bi-metallic Janus nanofibers: electrical and self propulsion properties[†]

Naveen Krishna Reddy,^a Ljiljana Palangetic,^a Linda Stappers,^b Johan Buitenhuis,^c Jan Fransaer,^b and Christian Clasen^{a*}

Received Xth XXXXXXXXXX 20XX, Accepted Xth XXXXXXXXXX 20XX

First published on the web Xth XXXXXXXXXX 200X

DOI: 10.1039/b000000x

Aligned polymeric nanofibers obtained via electrospinning were sputter-coated with metals on both their front and back side. When both sides were coated with the same metal (gold, silver or platinum/palladium alloy), the nanofibers behaved as pure conductors. However, coating front and back of the fibers with different metals causes a potential difference when they are immersed in aqueous solution. This potential difference propelled the Janus fibers in the direction perpendicular to their long axis when hydrogen peroxide was present in solution.

The production of nanofibers from polymer solutions via electro, spray or forced spinning^{1–3}, has become a common practice. The most important and earliest discovered of these techniques is electrospinning, which was rediscovered by Reneker *et al.*⁴. Here a polymer solution is drawn into nanofibers by applying a high DC voltage between a dispensing needle and collector. The charged solution forms a Taylor cone that emits a jet which evolves through banding instabilities and by this stretches to nanometer dimensions. Details of the continuous production of nanofibers by electrospinning technique are given in a review by Reneker *et al.*¹. Electrospun nanofibers have been modified in different ways to incorporate metals for a variety of applications. This includes direct incorporation of gold and silver nanoparticles into the polymer solution before spinning^{5–7}, adding metal salts into the electrospinning polymer solution and a later reduction in solution to form nanoparticles^{8,9}, or electroless plating of nanofibers^{10–12}. A few researchers have used e-beam evaporation¹³ and sputtering¹⁴ techniques to coat electrospun nanofibers with gold for appli-

cations such as photocatalysis and surface-enhanced Raman scattering. To our knowledge, creating 'Janus' type coatings by sputtering two metals on opposite sides of aligned fibers obtained from electrospinning has not yet been done.

Nanofibers were produced from polymer solutions of polyethylene oxide (PEO, 1000 kDa, 3 wt% in water) and polystyrene (PS, 280 kDa, 25 wt% in DMF) in an electrospinning cabin CE IIA (IME Technologies, Eindhoven, The Netherlands). The polymer solution was dispensed from a syringe with a needle diameter of 0.25 mm at a flow rate of 0.06 ml/min for PEO and 0.13 ml/min for PS using a Harvard syringe pump. A DC voltage of 25 kV for PEO and 20 kV for PS was applied between the dispensing needle and a collector plate placed 18 cm apart, with the collector being grounded. The collector consists of two 0.2 mm thick aluminum stripes 0.7 cm wide and 1.5 cm long, placed 1 cm from each other. The space between and around the stripes was covered with a 1 mm thick polytetrafluoroethylene (PTFE) sheet¹⁵. When a DC voltage is applied the nanofibers that are formed spin across the gap between two opposing aluminum stripes and thus align parallel. Optical and transmission electron microscope images of the aligned nanofibers are shown in Fig. 1.a and b respectively.

The aligned nanofibers held between the aluminum stripes provide an easy access to both sides of the fibers. By coating two sides of the nanofibers with one or different types of materials, a whole variety of composite materials can be produced; examples include transparent conductors, optically and magnetically active nanofibers or self propelling nanofibers. As a proof of concept, we will demonstrate two applications: metallically conducting nanofibers and Janus nanofibers. To produce these two materials the aligned nanofibers were coated with different metals using a sputtering technique. For this, the target coating (gold, silver or platinum/palladium) acts as the cathode and the fiber specimen to be coated is grounded. Creating a discharge between the cathode and the anode separated by 8 cm (in an argon environment at 20 kV), the ion bombardment causes the cathode to erode and the eroded material sputter coats the anode. Figs. 1.c

[†] Electronic Supplementary Information (ESI) available: See DOI: 10.1039/b000000x/

^a Department of Chemical Engineering, KU Leuven, W. de Croylaan 46, B-3001 Leuven, Belgium. Fax: +32 16 32 29 91; Tel: +32 16 3 22354; E-mail: christian.clasen@cit.kuleuven.be

^b Department of Metallurgy and Materials Engineering, KU Leuven, Kasteelpark Arenberg 44, B-3001 Leuven, Belgium. Fax: +32 16 3 21990; Tel: +32 16 3 21239

^c Institute of Complex Systems, Forschungszentrum Jülich, Wilhelm-Johnen-Strasse, 52425 Jülich, Germany. Fax: +49 2461 61 2280; Tel: +49 2461 61 3146

Fig. 1 a) Electrospun aligned nanofibers of polyethylene oxide; b) transmission electron micrographs of aligned nanofibers coated with gold on a copper grid; c) high magnification images of gold coated nanofibers and d) platinum/palladium coated nanofibers, showing the grainy structure of metals.

and d show transmission electron microscopy (TEM) images (Philips CM200 operating at 200 kV) of nanofibers coated with gold (Au) and platinum/palladium (Pt/Pd) on both sides (for TEM image of silver coating see ESI Fig. S1†). Controlling the sputtering time allows to adjust the coating thickness on each side, in the current case a 30 s exposure produced a thickness of 5–7 nm of the metal half-shells around the nanofibers. Gold sputtering produced an interconnected granular coating with a grain size of around 5 nm as shown in Fig. 1.c. The Pt/Pd coating on the other hand gave a much smoother coating with smaller grain size of the order of less than 1 nm (Fig. 1.d).

The electrical conductivity of the metal coated fibers was determined from a linear sweep voltammogram recorded using a Solartron SI 1287 electrochemical interface. Two electrodes were attached to the aluminum foil next to the fibers and the current was allowed to pass through the nanofibers. There was no influence of the aluminum and PTFE to the measured values of current. The current-voltage (I-V) plots of aligned metal coated nanofibers are shown in Fig. 2. For a linear voltage sweep ranging from -1 to 1 V between both ends of the fibers, a linear current response was observed for all metal coated fibers which corresponds to a true ohmic behavior. Nanofibers coated with gold gave the lowest current for the applied voltage (on the order of nano amperes, see inset in Fig. 2). This result can be correlated to the granular structure

of the gold coating (Fig. 1.c). The smooth surface structure of the nanofibers coated with Pt/Pd and silver (Fig. 1.d and S1†) led to much higher currents (order of milli amperes) as shown in Fig. 2. A rough estimation of the electrical resistivity from the measured resistance (from the I-V curve), the area through which current flows (from the cross-sectional area of the metal coating) and the length of the fibers give $1.10^{-8} \Omega\text{m}$ for Ag, $5.10^{-8} \Omega\text{m}$ for Pt/Pd and $5.10^{-4} \Omega\text{m}$ for Au. The electrical resistivity of Ag and Pt/Pd are in good agreement with known values but for Au the estimation is off by 4 orders of magnitude. This is likely due to the fact that the Au layers are not continuous but consists of Au islands that are electrically connected by point-contacts.

Fig. 2 Current-voltage characteristics of aligned polyethylene oxide nanofibers coated with gold, silver and platinum/palladium. Transmission electron micrographs of the corresponding metal coated nanofibers are shown in Fig. 1.c, d and S1†.

Coating two different metals on opposite sides of the fiber creates an anisotropy (a ‘Janus’ fibers) that causes the fibers to develop self propulsion properties. Self propulsion has been gaining much attention in recent years due to its advantages over Brownian motion such as faster and directed motion of nanoparticles^{16,17}. The self propulsion of spherical particles in hydrogen peroxide (H_2O_2) has been achieved by coating one half of a sphere with Pt¹⁶ as a catalyst to reduce H_2O_2 . The addition of Au to cover the bare side gives an extra reaction mechanism which increases the propulsion even further^{16,18,19}. Non-spherical self propellers such as nanorods, carbon nanotubes, helical structures and other complex shapes have also been investigated^{20–22}. All of the self propelling nanorods have been designed such that the propulsion is in the direction along the rods long axis, or in some cases one end of the nanorods is anchored to the substrate and the other is free to rotate thus producing a rotational motion¹⁸. In contrast

to this, using a Janus coating on different sides along the long axis, the self propulsion can be directed along the short axis of the rod. In this communication, as a proof of concept, we show the self propelling nature of nanofibers coated on one side with Pt/Pd and on the other side with Au, suspended in a H_2O_2 solution. A dark field and bright field TEM image (Carl Zeiss Libra, operating at 120 kV) of a single Janus nanofiber is shown in Fig. 3. The TEM images show a clear distinction between the two different half-shells. In Fig. 3 the Au coated side of the fiber (right side) has a granular structure whereas the Pt/Pd coated side of the fiber (left side) is smooth as has been also seen for the fully coated fibers in Figs. 1.c and d. A schematic of this coating as well as the mechanism proposed¹⁶ for the reaction of H_2O_2 on the Janus particle coating is shown in Fig. 4. The propulsion of the rod is due to the movement of H^+ ions created at the Pt side across the outside of the fiber to the Au side. The momentum created by this movement, as well as the drag that the H^+ ions exert on the surrounding fluid, propels the rod in the opposite direction, i.e. perpendicular to the long axis of the rod¹⁶.

Fig. 3 Dark field (a) and bright field (b) transmission electron micrograph of a Janus fiber with Au (right side of the fiber) and Pt/Pd coating (left side of the fiber) on the same nanofiber along its long axis.

To monitor the self propulsion, the aligned Janus nanofibers were ultrasonicated (550 W Elmasonic S100H, Elma, Germany) in water so as to produce short nanorods. The nanofibers when dropped in water initially exhibit aggregation. However, after ultrasonication for 30 min the nanofibers were broken into shorter (polydisperse) rods and were well dispersed in water. 50 μl of water containing Pt/Pd-Au coated nanofibers was mixed with 1 ml of 7.5 vol% H_2O_2 and placed

Fig. 4 Schematic representation of the self propulsion of nanorods coated with gold on one side and platinum/palladium on the other in H_2O_2 solution. The reaction mechanism of H_2O_2 with Pt and with Au is also indicated¹⁶.

in a closed glass bottom culture dish (MatTeck corporation, U.S.A.) to reduce disturbance from the surroundings. All the fibers sink in water to the bottom plate due to the higher density of polystyrene, and the Pt/Pd-Au coating. Movies of self propulsion of fibers were captured using an Olympus (IX71) optical microscope and a Hamamatsu digital camera (C4742-95) at a frame rate of ~ 3 fps. Movie 1 (see electronic supplementary information, movie M1†, 50X) shows three fibers self propelling in 7.5 vol% H_2O_2 solution. Of the three fibers in movie 1, the large aspect ratio (long) fiber exhibits a constant directional motion along the surface. In contrast to this, the low aspect ratio (short) fiber moves more erratic (due to increased rotational Brownian motion). The intermediate length fiber interacts with a dirt particle which is stationary prior to interaction with the fiber. The fiber is able to ‘wipe’ away the dirt by carrying it along the surface (see ESI movie M1†). Since the nanofibers are in the same image and are performing motions in different directions, erroneous effects such as convection and sedimentation can be ruled out²³. Since the fibers are close to the bottom plate they experience a larger frictional drag due to the interaction with the wall. Furthermore, the fibers moving perpendicular to the long axis expe-

perience a larger drag compared to a movement along the long axis^{20–22}. Despite this, the nanofibers shown in Fig. 5 are able to propel themselves.

To better visualize the directed side-ways motion of the Janus rods, Fig. 5 shows a sequence of color coded optical images from a second movie (see ESI movie M2†). The rods labeled 1–4 show translational motion perpendicular to their long axis and their mean squared displacement (MSD) as a function of time is shown in Fig. 6.a. For a purely Brownian motion of a rod-like particle one would expect MSD to show a linear dependence on time $(\Delta L)^2 = 4Dt$, where $(\Delta L)^2$ is the MSD, $D = (2D_{\parallel} + D_{\perp})/3$ the diffusion coefficient and t the time. This Brownian MSD is calculated for the selected particles 1–4 and is also shown in Fig. 6.a. In comparison to this the observed MSD of the self propelling rods is much larger and furthermore shows a squared dependence on time at time scales smaller than rotational Brownian motion which is a hallmark of self propulsion^{16,23}. Fig. 6.a also gives the velocity of each particle obtained by fitting $(\Delta L)^2 = v^2 t^2$, where v the velocity and t the time. On an average the velocity of the particles are 1–2 $\mu\text{m/s}$ for particles of 10–20 μm long. To achieve propulsion at this velocity the rods must create forces to overcome viscous drag in the perpendicular direction²⁴ which for rods of 20 μm length and 3 μm diameter is of the order of 1.10^{-16} N.

Clustering of two or more rods, or, an asymmetric coating can lead to a rotation rather than linear propulsion. Examples are particles 5 and 6 in Fig. 5. The orientation angle θ of particles 5 and 6 with respect to the x-axis as a function of time is shown in Fig. 6.b. Again, the directed motion of the rotating particles indicates a self propulsion, rather than a Brownian motion. Furthermore, the average rotational velocity of these 20 μm long particles is 0.5–1.5 rad/s , with at least two orders of magnitude larger than the rotational Brownian diffusion of particles with similar dimensions ($5\text{--}7 \cdot 10^{-3}$ rad/s). Unlike particle 6 which shows a smooth rotation, particle 5 shows a faster rotation however with a few collisions with other particles that are crossing its path.

To conclude, we have shown a simple and versatile method to produce aligned nanofibers that are easy to coat with metals on two different sides of the fiber. The current-voltage curves show that these nanofibers behave like pure conductors, with their conductivity depending on the type of metal as well as the roughness of the coating. Janus nanofibers coated with two metals (Pt/Pd and Au) on opposite sides along their long axis show self propulsion perpendicular to the the long axis of the fiber when placed in a H_2O_2 solution. These fibers, in spite of being long ($\gg 1$ μm) and of larger density than the surrounding medium, are able to self propel even at the boundary of the glass plate.

Fig. 5 Color coded optical microscope images of self propelling Janus Pt/Pd-Au coated polystyrene fibers in 7.5 vol% H_2O_2 . For clarity only a part of the image with four time steps that are approximately 17 s apart are shown. The corresponding movie is given in the electronic supplementary information (see ESI movies M2†).

Acknowledgments

Financial support from the ERC-2007-StG starting grant 203043 NANOFIB is gratefully acknowledged. Authors would like to acknowledge Raf De Dier and Pavlik Lettinga for useful discussion.

References

- 1 D. H. Reneker, A. L. Yarin, E. Zussman and H. Xu, *Adv. Appl. Mech.*, 2007, **41**, 43.
- 2 S. Srinivasan, S. S. Chhatre, J. M. Mabry, R. E. Cohen, G. H. McKinley, *Polymer*, 2011, **52**, 3209.
- 3 P. Mellado, H. A. McIlwee, M. R. Badrossamay, J. A. Goss, L. Mahadevan, and K. K. Parker, *Appl. Phys. Lett.*, 2011, **99**, 203107.
- 4 J. Doshi and D. H. Reneker *J. Electrostat.*, 1995, **35**, 151.
- 5 D. He, B. Hu, Q.-F. Yao, K. Wang and S.-H. Yu, *ACS Nano*, 2009, **3**, 3993.
- 6 K. E. Roskov, K. A. Kozek, W.-C. Wu, R. K. Chhetri, A. L. Oldenburg, R. J. Spontak and J. B. Tracy, *Langmuir*, 2011, **27**, 13965.
- 7 K. Gries, H. Vieker, A. Götzhäuser, S. Agarwal and A. Greiner, *Small*, 2012, **8**, 1436.
- 8 S. Park, S. C. Moon, D. Chen, R. J. Farris and T. P. Russell, *J. Mater. Chem.*, 2010, **20**, 1198.
- 9 V. G. Pol, E. Koren and A. Zaban, *Chem. Mater.*, 2008, **20**, 3055.

Fig. 6 Mean square displacements (a) and rotation angle with respect to x-axis (b) of particles labeled 1-6 in Fig.5 are shown as a function of time. In (a) the velocity of the particles 1-4 is shown next to each curve and the dashed lines show the theoretical mean square displacements of particles 1-4 solely due to the Brownian motion.

- 18 S. Fournier-Bidoz, A. C. Arsenault, I. Manners and G. A. Ozin, *Chem. Commun.*, 2005, 441.
- 19 W. F. Paxton, K. C. Kistler, C. C. Olmeda, A. Sen, S. K. St. Angelo, Y. Cao, T. E. Mallouk, P. E. Lammert and V. H. Crespi, *J. Am. Chem. Soc.*, 2004, **126**, 13424.
- 20 S. Sengupta, M. E. Ibele and A. Sen, *Chem. Int. Ed.*, 2012, **51**, 8434.
- 21 J. Wang and W. Gao, *ACS Nano*, 2012, **6**, 5745.
- 22 G. Loget and A. Kuhn, *J. Mater. Chem.*, 2012, **22**, 15457.
- 23 G. Dunderdale, S. Ebbens, P. Fairclough and J. Howse, *Langmuir*, 2012, **28**, 10997.
- 24 B. J. Berne and R. Pecora, *Dynamic light scattering: with applications to chemistry, biology, and physics*, Dover Publications, 2000.

- 10 B. Guo, S. Zhao, G. Han and L. Zhang, *Electrochim. Acta*, 2008, **53**, 5174.
- 11 S. Marx, M. V. Jose, J. D. Andersen and A. J. Russell, *Biosens. Bioelectron.*, 2011, **26**, 2981.
- 12 L. Zhang, X. Gong, Y. Bao, Y. Zhao, M. Xi, C. Jiang, and H. Fong, *Langmuir*, 2012, **28**, 14433.
- 13 S. J. H. Fathima, J. Paul, and S. Valiyaveetil, *Small*, 2010, **6**, 2443.
- 14 C. Pan, L. Dong, Z.-Z. Gu, *Int. J. Appl. Ceram. Technol.*, 2010, **6**, 895.
- 15 D. Li, Y. Wang and Y. Xia, *Adv. Mater.*, 2004, **16**, 361.
- 16 S. J. Ebbens and J. R. Howse, *Soft Matter*, 2010, **6**, 726.
- 17 J. Wang and K. M. Manesh, *Small*, 2010, **6**, 338.