Interaction of highly charged ions with carbon nano membranes

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Abstract. Charge state and energy loss measurements of slow highly charged ions (HCIs) after transmission through nanometer and sub-nanometer thin membranes are presented. Direct transmission measurements through carbon nano membranes (CNMs) show an unexpected bimodal exit charge state distribution, accompanied by charge exchange dependent energy loss. The energy loss of ions in CNMs with large charge loss shows a quadratic dependency on the incident charge state, indicating charge state dependent stopping force values. Another access to the exit charge state distribution is given by irradiating stacks of CNMs and investigating each layer of the stack with high resolution imaging techniques like transmission electron microscopy (TEM) and helium ion microscopy (HIM) independently. The observation of pores created in all of the layers confirms the assumption derived from the transmission measurements that the two separated charge state distributions reflect two different impact parameter regimes, i.e. close collision with large charge exchange and distant collisions with weak ion-target interaction.

1. Motivation

Since its discovery, single layer graphene has attracted enormous attention due to its unique electronic properties [1, 2]. It is considered as the ultimately thin membrane made of sp²-hybridized carbon atoms with possible applications in future nanoelectronics. Ion or energetic electron irradiation of this 2D material affects the electronic structure and opens the possibility to modify and tailor its properties. Studies on collisions between ions and free standing single graphene or other thin membranes, like carbon nano membranes [3], are of fundamental interest too because they may close the gap between atomic collisions in gaseous and in solid targets. Thereby, highly charged ions are an ideal tool to probe interaction processes in these thin materials due to their potential energy deposition in a shallow surface region via multiple charge transfer and successive deexcitation processes [4, 5]. Besides the near-surface potential energy deposition, an expected increased pre-equilibrium kinetic energy loss (stopping force) [6] is confined to the first few nm below the surface.
In experiments with bulk materials, HCIs reach charge equilibration after penetrating only a few nanometers of the solid and thus the dependence of the energy loss on the projectile charge state is experimentally not accessible. For a target film in the sub-10-nm range, the interaction time is no longer sufficient for a complete relaxation of the projectiles. Studying energy loss and charge state distributions of slow highly charged ions after passing ultrathin layers enables the investigation of non-equilibrium stopping phenomena.

Recently it could be shown that slow HCIs create nanopores in 1 nm thick carbon nano membranes, where the pore diameters can be tuned by the potential energy of the incident ions [7]. Carrying this idea further by irradiating stacks of these thin membranes and inspecting each layer of the stack independently opens another possibility to study the charge state distribution of the ions after passing a membrane. The results obtained from these measurements are in good agreement with the observations from the direct transmission measurements by means of an electrostatic analyzer.

2. Experimental setup

For the transmission measurements, freestanding 1 nm thick carbon nano membranes and freestanding single layer graphene sheets were irradiated with highly charged ions at various kinetic energies. The measurements have been performed at the Ion Beam Center of the Helmholtz-Zentrum Dresden-Rossendorf (HZDR) and at TU Wien.

At the HZDR, highly charged Xe$q^+$ ions with $q=10-35$ were produced in a room-temperature electron beam ion trap (EBIT) [8]. The kinetic energy is adjusted by means of an electrostatic deceleration system in the range between 40-135 keV. A separate rotation stage holds a cylindrical electrostatic analyzer equipped with a HAMAMATSU PHOTONICS channeltron for ion counting inside the experimental chamber. The analyzer has an energy resolution of $\Delta E=1.5*10^{-3}E$ and an acceptance angle of 1.6°. At TU Wien, medium charged Ar$q^+$ ions with $q=2-9$ were produced in an electron cyclotron resonance ion source (ECRIS) [9] at kinetic energies between 4.5 and 6 keV. In the experimental chamber, a 170° concentric spherical electrostatic analyzer (COMSTOCK AC-903B) is assembled on a separate manipulation stage and ions are counted by a microchannel plate detector. The resolution of the spherical sector analyzer is given by the fraction $\Delta E/E\sim 6*10^{-3}$ where $\Delta E$ is the energy full width at one-half maximum signal and $E$ is the pass energy through the analyzer. In both experimental setups the base pressure in the beam line and the experimental chamber is kept below $5*10^{-9}$mbar to prevent charge exchange processes by residual gas.

In the experiments the free standing carbon nano membranes from CNM TECHNOLOGIES Bielefeld (Germany), that were used were produced by low energy electron irradiation of a self-assembled monolayer of 1,1’-biphenyl-4-thiol (H-(C$_6$H$_4$)$_2$-SH) and transferred onto a TEM grid with an underlying holey- or lacey carbon support film [3, 10]. The thickness of the membrane was determined to be 1 nm. From Auger electron spectroscopy analysis the presence of heavy elements above a concentration of 1at% can be excluded and therefore neglected in the following discussion. Thus, the CNMs is treated as a pure amorphous carbon material. For the measurement of stacked CNMs, three carbon nano membranes, mounted on individual transmission electron microscopy grids without any support film, have been squeezed together in one scanning electron microscopy holder and then suspended inside the target chamber.

After irradiation at the HZDR, every single layer of the stacks were inspected with high resolution imaging techniques like TEM (transmission electron microscopy) and HIM (helium ion microscopy). The samples were analyzed with an aberration corrected FEI TITAN 80-300 TEM operated at 300 keV and a ZEISS Orion Nanofab helium ion microscope at the Ion Beam Center Dresden-Rossendorf. Some samples were sent to the University of Bielefeld and investigated with a ZEISS OrionPlus HIM and others to TU Wien and imaged with a FEI TECNAI F20 TEM at 200 keV at USTEM TU Wien.

By analyzing the samples at different facilities, it was assured that the results did not depend on the type of machine used for the evaluation.
3. Results and Discussion

3.1. Transmission spectra

Two independent methods were used to determine the amount of potential energy deposition per ion. The analysis of transmission spectra, obtained by the electrostatic analyzer, provides direct access to the charge state and energy loss of the ions after the passage through thin membranes. For highly charged Xe ions on CNMs two distinct exit charge state distributions can be observed. One part of the ions passes the membrane with almost no charge loss, whereas the other part loses most of its charge [11]. The bimodal exit charge state distribution is assumed to reflect two different impact parameter regimes which are also connected to different energy losses. Ions with large impact parameter have trajectories far away of any C atom in the membrane, capture only few electrons and are practically not stopped. In contrast, ions with trajectories close to a C atom undergo close collisions exhibiting high stopping force.

Angle resolved transmission measurements confirmed this assumption. The distribution of high charge states vanishes with increasing tilting angle of the analyzer, while low charge states are transmitted up to 4° (maximum deflection angle of 5.2° for one elastic scattering between a Xe and C atom). Furthermore, a clear increase of the energy loss with an increase of the deflection angle can be observed. The fact that the high charge state distribution is only observable in forward direction and that the energy loss increases with deflection angle, points to small impact parameters for the ions of the high charge state distribution and large impact parameters for the ions of the low charge state distribution.

Figure 1 summarizes these results. A CNM on a lacey carbon support film was irradiated with Xe\textsuperscript{30+} at 40 keV and the transmitted ions were detected by the electrostatic analyzer at HZDR in forward direction. From the transmission spectra [11], the charge loss and energy loss were evaluated. The observed charge state dependent energy loss is depicted in fig. 1 and the corresponding intensities are visualized by the area of the circles. Fig. 1 displays a clear separation of the two impact parameter regimes: ions with low charge loss and almost no energy loss and ions with high charge loss and a charge state dependent energy loss.

![Figure 1](image)

**Figure 1:** Energy and charge loss of 40 keV Xe\textsuperscript{30+} ions after the passage through a 1 nm thick CNM on a lacey carbon support film. The area of the dots represents the relative abundance. Two well separated regimes are visible: ions with low charge loss and almost no energy loss and ions with high charge loss and a charge dependent energy loss.
Further transmission measurements with ions at lower incident charge states and energies have been performed at TU Wien. Figure 2 shows a transmission spectrum of Ar$^{4+}$ ions at a kinetic energy of 5.76 keV after the passage through a CNM. Thereby the Ar$^{4+}$ peak represents the ions passing through cracks in the membrane. The inset in Fig. 2 shows the energy distribution of a certain exit charge state reflecting a large energy straggling.

Looking at the energy loss in more detail (see Fig. 3a), the charge state dependent energy loss can be reproduced, as has been seen before for higher incident charge states (see Fig. 1) and reported earlier by Schenkel et al. [12, 13]. Fig. 3b shows a quadratic dependency of the energy loss on the incident charges state for ions with $q_{\text{exit}}=1$, as recently reported in [11] for Xe ions with $q$ between 10 and 30.

**Figure 2:** Charge state and energy spectrum of 5.76 keV Ar$^{4+}$ ions after transmission through a 1 nm thick carbon nano membrane. For ions with higher charge loss an increase of the energy straggling can be observed.

**Figure 3:** (a) Energy loss of 5.76 keV Ar$^{4+}$ and 4.48 keV Ar$^{7+}$ ions as a function of the charge loss. The dashed lines are drawn to guide the eye.
(b) The energy loss is shown for ions with exit charge state $q_{\text{exit}}=1$. The dashed curve is a polynomial fit of second order to the obtained data.
3.2. Irradiation of stacks of CNMs

The second method to determine the amount of deposited potential energy per ion was to irradiate a stack of CNMs and inspect each layer afterwards. From earlier experiments it is known that HCIs above a potential energy threshold of about 10-12 keV (Q~28) can lead to the creation of nanopores in CNMs [7]. Taking this into account, the irradiation of stacks of three CNMs and TEM and HIM inspection of the 3 membranes afterwards gives an indirect access to the exit charge state distribution of each layer.

Surprisingly, pores could be detected in the first, second and even in the third layer. Figure 4 shows three HIM images of the three CNM layers, stacked together before irradiation and inspected separately afterwards. The stack was irradiated with 12 keV Xe$^{35+}$ ions. Figure 5 shows the pore size distribution for each layer. A mean pore size of 10 nm was found in the first layer. With increasing layer, the size of the pores and the pore density decreases. Each data set was obtained from a different number of images.

![Figure 4: Evolution of pore diameters induced by incident Xe$^{35+}$ at 12 keV ions in a stack of CNMs from first to second to third layer, imaged with HIM.](image)

To evaluate the pore creation efficiency the pore density was compared with the measured incident ion electrical charge. The pore density was determined by dividing the total number of counted pores of each layer by the total area of all images of this layer. The uncertainties of this method are determined by inaccuracies in the ion electrical current measurement on the target in the range of only a few 100 fA and a limited number of high resolution images of each layer. Taking this into account it was evaluated that at least 50% of the incident ions produce a pore upon impact (for $E_{\text{kin}} = 10-40$ keV) [14]. While the inspection of the layers makes also highly deflected ions visible (maximum deflection angle of 5.2°), the electrostatic analyzer measures only ions that are scattered in a small solid angle in forward direction (1.6°). Ions scattered out of the acceptance angle are ignored. To determine the total pore formation efficiency from the transmission measurements would require to perform angle resolved measurements and to integrate over all of the data.

The formation of pores of some nanometer in diameter corresponds to a sputter yield of a few 1000 atoms. Regarding binding energies of a few eV, the potential energy of the incident ions is already consumed after one pore formation and hence, an ion cannot produce a nanohole in more than one layer. Since pores could be found in all of the three layers of a stack, this indicates that the transmission through each layer is related to a bimodal exit charge state distribution, which is consistent with the observations obtained from the transmission spectra. Some of the projectiles are transmitted in low charge states after energy deposition upon pore formation, while others still remain in sufficiently high charge states, thus enabling pore formation in the second or in the third layer.
4. Conclusion and Outlook

We could show two different methods to study the charge exchange processes and to determine the potential energy deposition by interaction of highly charged ions with ultrathin carbon membranes. The direct transmission measurements as well as the inspection of each single layer of an irradiated stack of CNMs reveal a bimodal charge state distribution which indicates an impact parameter selection. The spectra clearly show that the projectile ions have by far not reached charge equilibrium within these thin materials and therefore non-equilibrium effects have to be considered. Both, ions with high incident charge states (q=10-35) as well as ions at lower incident charge states (q=2-9) show a strong charge state dependent energy loss (stopping force).

The observed bimodal exit charge state distribution with charge states far away from the equilibrium charge state and an increase of energy loss (stopping force) with charge state implicates that these thin membranes cannot be described in terms of an averaged energy loss per unit length and the HCI-membrane interaction process can be described better in a picture of ion-molecule interaction rather than ion-solid interaction.

For studying ion interaction with a very well defined target, irradiation and transmission measurement with single layer graphene are currently being performed and compared with CNMs which might help to understand the non-equilibrium interaction process of HCIs.

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**Figure 5:** Histograms for pore sizes obtained from different CNM layers in a stack of three, irradiated with Xe$^{35+}$ at 12 keV. The mean pore size of 10 nm was found in the first layer and the size decreases for increasing layer number. Each data set was obtained from a different number of images.
References

[1] Geim, A.K. and Novoselov, K.S. 2007 Nat. Mater. 6 183.
[2] Geim, A.K. 2009 Science 324 1530.
[3] Turchanin, A. and Göhlhäuser 2012 Prog. Surf. Sci. 87 108
[4] Arnau, A., Aumayr, F., Echenique, P.M., Grether, M., Heiland, W., Limburg, J., et al. 1997 Surf. Sci. Rep. 27, 113
[5] Aumayr, F., Facsko, S., El-Said, A.S., Trautmann, C. and Schleberger, M. 2011 J. Phys.-Cond. Mat. 23 393001
[6] Biersack, J. P. 1993 Nucl. Instrum. Meth. B. 80-81 12
[7] Ritter, R., Wilhelm, R.A., Stöger-Pollach, M., Heller, R., Mücklich, A., Werner, U., et al. 2013 Appl. Phys. Lett. 102 063112
[8] Zschornack, G., Kreller, M. Osvyannikov, V.P., Grossamn, F., Kentsch, U., Schmidt, M., Ullmann, F., and Heller R. 2008 Rev. Sci. Instrum. 79 02A703
[9] Galutschek, E., Trassl, R., Salzborn, E., Aumayr, F. and Winter, H. 2007 J. Phys. Conf. Proc. 58 395
[10] Turchanin, A., Beyer, A., Nottbohm, C.T., Zhang, X., Stosch, R., Sologubenko, A.S., et al. 2009 Adv. Mat. 21 1233
[11] Wilhelm, R.A., Gruber, E., Ritter, R., Heller, R., Facsko, S., Aumayr, F. 2014 Phys. Rev. Lett. 112 153201
[12] Schenkel, T., Briere, M.A., Barnes, A.V., Hamza, A.V., Bethge, K., Schmidt-Böcking, H., et al. 1997 Phys. Rev. Lett. 79 2030
[13] Schenkel, T., Hamza, A.V., Barnes, A.V., Schneider, D.H. 1999 Progr. Surf. Sci. 61 23
[14] Wilhelm, R.A., Gruber, E., Ritter, R., Heller, R., Beyer, A., Turchanin, A., Klingner N., Hübner, R., Stöger-Pollach, M., Vieker, H. 2015 2D Mater 2 3