Core-Level Spectroscopy to Probe the Oxidation State of Single Europium Atoms

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The valence of individual europium atoms confined in carbon nanotubes is successfully measured by using core-level electron energy loss spectroscopy. Changes in the oxidation state at the atomic scale have been observed in Eu atomic chains exposed to oxygen. A transitory behavior has been identified where multiple atoms show a signal consistent with a sum of Eu^{2+} and Eu^{3+}. This indicates that single atoms change their valence state multiple times during the reaction, suggesting that oxidation in confined spaces and with extra energy input (from the electron beam) might not be a simple one step electron transfer event.

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The physical and chemical properties of nanoscale materials can be influenced by the behavior of individual atoms. For this reason, measuring the valence of single atoms and understanding under which conditions it might change is of great interest. However, two major problems hinder such observations. First of all, we are currently able to probe valence in a thick crystal in different materials using electron energy loss spectroscopy (EELS) [1–4]. But in these we effectively measure entire atomic columns and, therefore, discerning the valence of each atom is unfeasible at this time. From another perspective, we can probe atoms individually in thin crystals or supports [5–7]. But, no reports have demonstrated measurements of changes of valence for individual atoms, the difficulty being to find a well-adapted system and limited signal to noise ratio in EELS measurements.

In this Letter we report the observation of changes in the valence of individual atoms in atomic chains inside carbon nanotubes (NT). More importantly, we describe a transitory behavior of europium (Eu) chains during oxidation in the presence of oxygen (O) inside carbon nanotubes under electron irradiation. This behavior is characterized by single atoms alternating between two valence states multiple times, which we call the "mixed state." EELS in an electron microscope is employed to monitor the valence of Eu atoms.

Electron microscopy experiments have been performed in the CREST-JEOL double corrected electron microscope equipped with a cold field emission electron gun operated at 60 kV. Electron energy loss spectra have been acquired with a low-voltage GIF quantum spectrometer. Edge intensities for chemical mapping have been measured using the two-area fitting method [1]. In this method two regions of the preedge spectrum are used to fit a power law curve. This power law is used to extrapolate the background in the region of interest. Eu EELS has been performed using the $M_{4,5}$ edges, located at 1128.5 and 1157.0 eV for metallic Eu^0, and 1131.0 and 1159.5 eV for Eu^{3+}. We should note that the energy position of the $M_{4,5}$ depends fundamentally on the number of electrons in the $4f$ shell. The spectral signature of the metallic europium (Eu^0) and that of the Eu^{2+}, which have 7 electrons in the $4f$ shell, are closely related, as shown in x-ray absorption experiments performed in metallic Eu deposited in vacuum [8]. An energy shift is observed for the Eu^{3+} ions because one electron is removed from the $4f$ shell. The energy scale in the experiments has been calibrated using Eu_2O_3 which shows only Eu^{3+} contributions. In the reported experiments the energy loss range was large enough to allow the acquisition of the O K edge and the Eu $M_{4,5}$ at the same time. This is crucial to support our interpretation for the observed effects.

Atomically resolved scanning transmission electron microscopy (STEM) was used to study the structures of Eu atomic chains confined inside NT [9] [Fig. 1(a) and Supplemental Material [10], Fig. S1]. There are two possible configurations for the thinnest chains (Supplemental Material [10], Fig. S1), both constituted of pairs of Eu atoms. However, in one of them the pairs are perpendicular to each other [the one in Fig. 1(a)], while in the other they are parallel. For this reason, only the peripheral columns in Fig. 1(a) are constituted of single atoms.

Oxygen entry in the NT (schematized in Fig. 1) can be triggered by puncturing the NT wall using the electron beam (pristine chains are free of oxygen and show only the initial state Eu spectrum, Supplemental Material [10] Fig. S2). Because the vacuum level of a TEM column is around 10^{-5} Pa, the partial pressure of residual oxygen or water vapor will contribute to oxygen entry. As O K edge signal can be isolated from the noise level in an EEL spectrum acquired within 200 ms exposure time, chemical mapping of oxygen by means of the spectrum imaging [1,11] is feasible (Supplemental Material [10], Fig. S3). O atoms cannot be observed in the simultaneously recorded annular dark field (ADF) image because the contrast of the oxygen atom is extremely weak compared to the brighter Eu atoms and hindered by the NT walls (four walls in

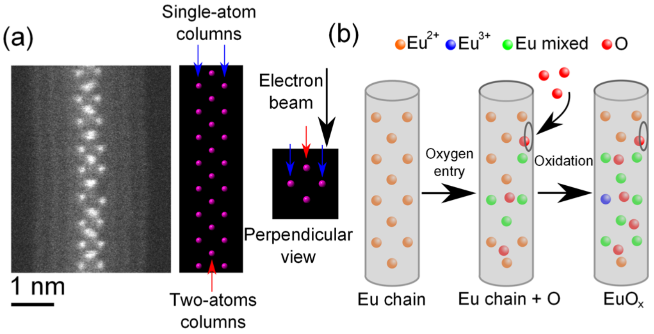

FIG. 1 (color online). (a) Example of a typical Eu atomic chain encapsulated in a NT. In this viewing direction the chain is formed by columns of single (periphery) and double atoms (center), as pointed by the blue and red arrows, respectively. The single atomic spectra shown in the manuscript have been measured in the peripheral atoms. The ADF intensity of both types of columns is consistent with 1 and 2 atoms (Fig. S1 in the Supplemental Material [10]). (b) NTs contain pristine Eu chains free of oxygen (O, Supplemental Material [10], Fig. S2). Because of the creation of defects at the nanotube wall by the electron beam, O atoms enter the NT from the local environment. By monitoring the peak position of Eu M_5 edge, the oxidation state of all the Eu atoms can be tracked as the reaction proceeds. As the oxidation takes place, Eu^i (Eu^0 or Eu^{2+}) atoms in the initial state sequentially change to the oxidation state Eu^{3+} and the number of the Eu atoms in the mixed state increases (see text).

projection). The oxygen map thus obtained represents the positions where oxygen atoms are located, after entering in the NT. The signal to noise ratio of the O K edge does not allow fine structure measurement as shown in Fig. S3 and S12 of the Supplemental Material [10]. We note that the initial valence state of the Eu atoms should be between Eu^0 and Eu^{2+}, as charge transfer from the Eu atoms to the carbon nanotube is known to occur [12]. Because of this and the impossibility to distinguish Eu^0 and Eu^{2+} using the $M_{4,5}$ edge, we will refer to the initial state of the atoms in the chain as Eu^i. We will refer to the spectral signature of Eu^0 or Eu^{2+} as Eu^{2+}.

To probe the electronic structure of each Eu atom, the peak positions of Eu $M_{4,5}$ edge of individual atoms were monitored by EELS [1] during the reaction. The prominent peak at the M_5 edge of Eu^{2+} and Eu^{3+} appears at 1128.5 and 1131.0 eV in bulk metallic Eu^0 and $\mathrm{Eu_2O_3}$, respectively, as observed by x-ray absorption spectroscopy studies [8,12–15]. With a change in valence state from Eu^{2+} to Eu^{3+}, an energy shift of 2.5 eV in the M_5 peak is expected for EELS fine structure analysis (Supplemental Material [10], Figs. S4 and S5). In our experiments three different spectral signatures have been observed (Fig. 2). Note that they are all recorded from single Eu atoms in a typical specimen described above, as shown in the images to the right of Fig 2. Two of them represent the expected EELS spectra for Eu^{2+} and Eu^{3+} (orange and blue curves, respectively). The third, indicated by a green line, is a sum

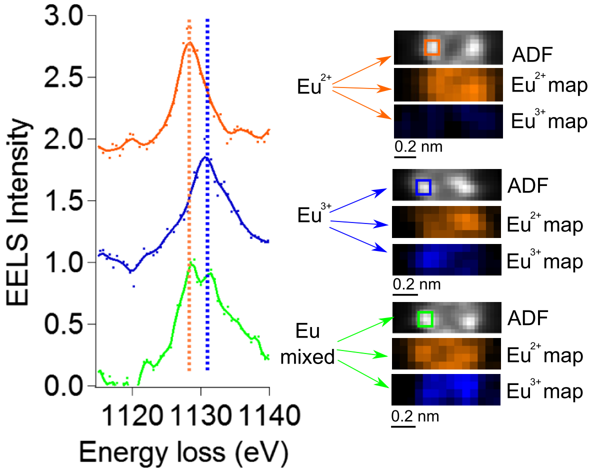

FIG. 2 (color online). Three different spectral signatures observed in our oxidation experiments: Eu^{2+} (1128.5 eV), Eu^{3+} (1131.0 eV), and mixed Eu (two peaks). Dots are the experimental data and curves are the smooth data. Each spectrum has been measured in individual atoms.

of the first two signatures and can be interpreted as a temporal average of an atom suffering transitions between the initial and the 3+ states (at any given time it is in either of the two). We see this as a transitory behavior between the initial state chain and a fully oxidized one, which is always $\mathrm{Eu_2O_3}$ in our experiments. We call this a mixed state. This state repeatedly appears during the experiment which lasts more than a few minutes. For this reason, it cannot be simply interpreted by the occurrence of single valence change during the acquisition time of single spectrum.

In order to investigate precisely the oxidation process a number of sequential EELS fine structure maps on the same Eu atomic chains were recorded. Maps of Eu^{2+} and Eu^{3+} derived from the distinct peak intensities of M_5 edge as well as the oxygen K-edge intensity are useful to identify atomic positions of these species, as shown in Figs. 3(b)–3(c) and 3(e). To identify Eu atoms in the mixed state the spectral signature at each atomic position was inspected (See Supplemental Material [10]). With this procedure we have successfully labeled the valence of each Eu atom [Fig. 3(d)]. Our signal to noise ratio does not allow the determination of the position of individual oxygen atoms [the red circles in Fig. 3(f) mark the maxima in Fig. 3(e)]. We have calculated the total number of oxygen atoms in each chemical map using $\mathrm{Eu_2O_3}$ as a reference for the O-K to Eu-M ratio (avoiding the necessity of calculated cross sections). We observed (Fig. S6 in the Supplemental Material [10]) that the total number of oxygen atoms increased from 16 ± 6 to 25 ± 8 from the first to the third maps. Moreover, as seen in the oxygen maps in Figs. S6–S9 the oxygen atoms converge to the position where the higher valence Eu are located.

Charge balance might give us hints if the initial state of Eu is 0 or closer to 2+. First of all, in the first chemical map

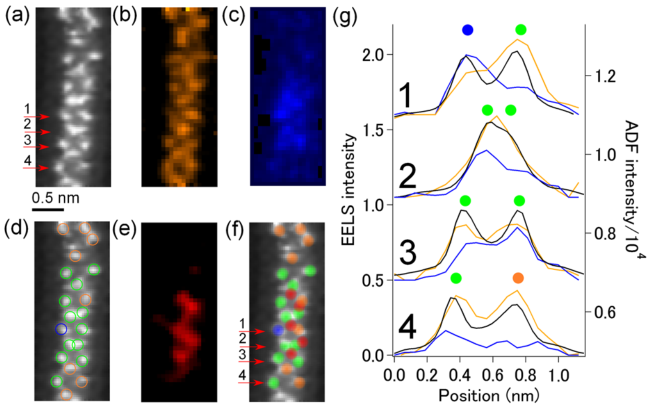

FIG. 3 (color online). (a) ADF image showing Eu atomic chains acquired during chemical mapping. The contrast of NT is suppressed and barely seen. (b), (c) Maps for Eu^{2+} and oxide Eu^{3+}, respectively. (d) Labeling of Eu valence states (color code as in Fig. 2, orange: initial state, blue: oxidized and green: mixed states) built from the fine structure analysis of Eu M_5 peak. (e) Oxygen chemical map. (f) A full chemical map of Eu atoms in different states with the regions where oxygen is present (the red circles mark maxima in the oxygen map, not atomic positions). (g) ADF (black curves), Eu^{2+} (orange curves) and Eu^{3+} (blue curves) profiles across regions marked by arrows and numbers in (a) and (f). In this chemical map the pixel size was 0.6 Å and the exposure time was 100 ms per pixel.

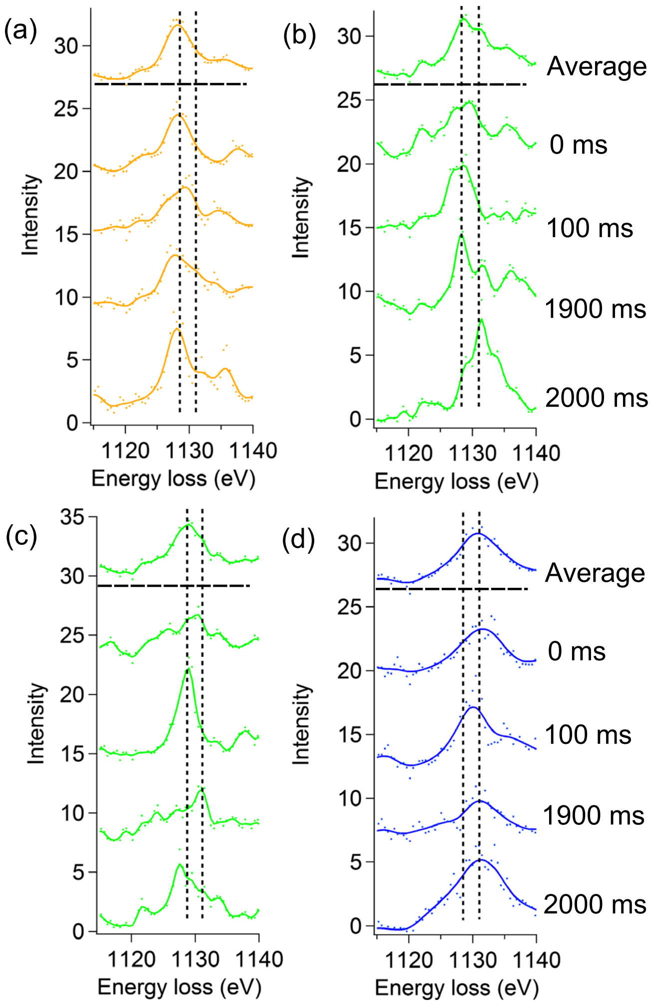

FIG. 4 (color online). (a)–(d) Temporal sequences of spectra for Eu^{2+} (a), mixed (b), (c) and Eu^{3+} (d) atoms. For each sequence, the spectrum on the top is the temporal average of the four spectra below. From top to bottom the relative starting time of the acquisition are 0, 100, 200, 1900, and 2000 ms. Time delays have been fixed by the exposure time and the sampling of the two dimensional maps. Two dotted vertical lines indicate the references for Eu^{2+} and Eu^{3+} M_5 peak positions.

20 Eu are seen, 17 with the Eu^{2+} signature and 3 in the mixed state, along with 16 oxygen atoms (32 electrons). The number of atoms in the mixed state does not seem to be consistent with the available electrons. However, if we consider that the other atoms have also received some of the charges (going from 0 to 2+), balance can be retrieved. Supposing that in the mixed state the atom stays half the time in each valence, 36 electrons would be necessary to explain our observations (closer to the value available).

Moreover, in the last map [Fig. 3, 25 oxygen are observed (50 in total)]. In this image 11 atoms with the Eu^{2+} signature, 13 atoms in the mixed state and 1 in the 3+ state are seen. Considering that the initial state is 2+, only 20 electrons are necessary to arrive in the final configuration. However, if the initial valence state is 0, 57 electrons are necessary, closer to the value available. These two points indicate that the initial state of the Eu atoms is closer to Eu^0 than to Eu^{2+}, even though it is likely to be higher than 0.

Surprisingly, Eu atoms in the mixed state can be continuously found in the sequentially recorded chemical maps (Supplemental Material [10], Fig. S6). The observation of the mixed state in sequential two-dimensional maps with 100 ms exposure per pixel gives hints about their behavior. Figure 4 shows examples of this transitory behavior by chronospectroscopy derived from individual atoms (at a time scale far too long compared to atomic processes). The relative start time for spectra in Fig. 4 are 0, 100, 1900, and 2000 ms. While the Eu^{2+} and Eu^{3+} atoms show static valence states [Figs. 4(a) and 4(d)], the mixed Eu atom seems to switch between two states [Figs. 4(b) and 4(c)]. It is important to note that at each time all atoms have a well-defined valence and that two peaks are observed because of our "long" exposure time. The mixed state is represented by the continuous change between valence states. Thus the oxidation process observed here does not appear to be a simple one step process, but a multistep electron transfer one.

The temporal evolution towards the final state (stoichiometric Eu_2O_3) is possibly regulated by the availability of oxygen. Eu atoms are highly reactive and readily oxidize in the presence of oxygen. However, in a situation where the quantity of oxygen atoms is insufficient to form a stable oxide, a group of Eu atoms may compete for the available atoms leading to a sequence of transitions between the Eu^{2+} and the Eu^{3+} states.

The same mixed behavior can be observed in small, nanometer-wide Eu clusters (Supplemental Material [10], Fig. S11). In this case, a sequence of EELS spectra shows the evolution from a mixed state to a fully oxidized one, most probably because the sufficient oxygen can be provided from ambient surroundings (where the nanotube does not limit the O content available). Interestingly, once the full oxide is reached the mixed state is no longer observed, even under the influence of the electron beam.

The energy deposited by the electron beam might accelerate the oxidation reaction and play a role in the switching between oxidation states. However, the presence of the beam alone cannot drive it. Pristine chains show the Eu^i signal unless oxygen is present (Supplemental Material [10], Fig. S12). Also, the electron beam cannot be the main driving force for the formation of the mixed state (by Eu-O bond breakage, for example). Finally, dangling bonds in the carbon nanotube caused by electron beam damage may also induce changes in the Eu atoms (by formation of europium carbide). But again, no valence change has been observed unless O atoms were present.

Eu atoms are lanthanides with a $4f^7$ half-filled shell. For this reason, its most favorable valence state is $2+$, contrary to other lanthanides which favor the $3+$ state (ytterbium, Yb, is another exception, with $4f^{14}$ configuration). Contrary to transition metals with a partially filled $3d$ shell, the electronic structure of the $4f$ levels is much less sensitive to the local crystal structure effects [16]. Essentially, the $4f$ orbitals are shielded by the more spread out $5s$ and $5p$ orbitals. For this reason, crystal field effects, which are related to local symmetry, should be of the order of 10 meV [16]. Therefore, the M_5 peak shifts observed should not be explained by crystal field variation. Even for chains containing a defect and broken chain tips, the Eu atoms show the Eu^{2+} feature and no large variation in the M_5 edge can be detected (Supplemental Material [10], Figs. S4 and S5).

Our results indicate that oxidation in confined spaces with energy input from an electron beam takes place in multistep events through a mixed valence state for a surprisingly long time scale. Also, the reaction seems to be limited to regions of the order of 1 or 2 nm in the vicinity of oxygen atoms. Finally, a quantification of the total number of oxygen observed and the local valence indicates that the initial state of the Eu atoms is closer to the neutral one, Eu^0. In this picture, after oxygen enter the nanotube Eu^i atoms are oxidized to Eu^{2+} and then to Eu^{3+}. The transitory state probably occurs due to $Eu^{2+} \Leftrightarrow Eu^{3+}$ transitions. However, we cannot rule out a participation of the Eu^i state.

The reported experiments demonstrate fundamentally important advances in understanding the electronic structures of atoms during oxidation in confined spaces. First of all, the observation of a transitory behavior at long time scales indicates that, under our conditions, oxidation is not a simple one step electron transfer event between atoms.

Monitoring the deeper M edge is essential to achieve the atomic resolution in this experiment. The delocalization of M edge is quite small and 0.1 nm spatial resolution is achieved. On the other hand, the use of N edge suffers a non-negligible delocalization [17,18] and absorption of individual atoms with atomic resolution cannot be assessed.

To conclude, we have shown how EELS experiments with a few atoms in a confined space allow the detection of mixed atomic states. The possibility of following EEL spectral changes as a function of time is a step further towards understanding various nanoscale physics phenomena such as chemical reactions or phase transitions with a limited number of atoms.

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[1] R. Egerton, *Electron Energy-Loss Spectroscopy in the Electron Microscope* (Springer, New York, 2011).

[2] A. Ohtomo, D. A. Muller, J. L. Grazul, and H. Y. Hwang, Nature (London) **419**, 378 (2002).

[3] J. A. Mundy, D. Hodash, A. Melville, R. Held, T. Mairoser, D. A. Muller, L. F. Kourkoutis, A. Schmehl, and D. G. Schlom, Appl. Phys. Lett. **104**, 091601 (2014).

[4] F. Pailloux, D. Imhoff, T. Sikora, A. Barthélémy, J.-L. Maurice, J.-P. Contour, C. Colliex, and A. Fert, Phys. Rev. B **66**, 014417 (2002).

[5] K. Suenaga, M. Tencé, C. Mory, C. Colliex, H. Kato, T. Okazaki, H. Shinohara, K. HIrahara, S. Bandow, and S. Iijima, Science **290**, 2280 (2000).

[6] M. Varela *et al.*, Phys. Rev. Lett. **92**, 095502 (2004).

[7] S.-Y. Chen, R.-J. Chen, W. Lee, C.-L. Dong, and A. Gloter, Phys. Chem. Chem. Phys. **16**, 3274 (2014).

[8] J. H. Richter *et al.*, Phys. Rev. B **84**, 235120 (2011).

[9] R. Kitaura, R. Nakanishi, T. Saito, H. Yoshikawa, K. Awaga, and H. Shinohara, Angew. Chem., Int. Ed. **48**, 8298 (2009).

[10] See Supplemental Material at http://link.aps.org/supplemental/10.1103/PhysRevLett.114.197602 for experimental and data analysis procedures. Additional spectroscopic results are included to corroborate findings described in the main text.

[11] C. Jeanguillaume and C. Colliex, Ultramicroscopy **28**, 252 (1989).

[12] R. Nakanishi, R. Kitaura, P. Ayala, H. Shiozawa, K. de Blauwe, P. Hoffmann, D. Choi, Y. Miyata, T. Pichler, and H. Shinohara, Phys. Rev. B **86**, 115445 (2012).

[13] B. T. Thole, G. van der Laan, J. C. Fuggle, G. A. Sawatzky, R. C. Karnatak, and J.-M. Esteva, Phys. Rev. B **32**, 5107 (1985).

[14] R. P. Panguluri, T. S. Santos, E. Negusse, J. Dvorak, Y. Idzerda, J. S. Moodera, and B. Nadgorny, Phys. Rev. B **78**, 125307 (2008).

[15] D. F. Forster, J. Klinkhammer, C. Busse, S. G. Altendorf, T. Michely, Z. Hu, Y.-Y. Chin, L. H. Tjeng, J. Coraux, and D. Bourgault, Phys. Rev. B **83**, 045424 (2011).

[16] B. Fromme, V. Bocatius, and E. Kisker, Phys. Rev. B **64**, 125114 (2001).

[17] K. Suenaga, Y. Iizumi, and T. Okazaki, Eur. Phys. J. Appl. Phys. **54**, 33508 (2011).

[18] K. Suenaga, Y. Sato, Z. Liu, H. Kataura, T. Okazaki, K. Kimoto, H. Sawada, K. Omoto, T. Tomita, T. Kaneyama, and Y. Kondo, Nat. Chem. **1**, 415 (2009).