Charge injection into the Ni-phylosilicate nanoscrolls with reduced Ni nanoparticles using Kelvin force probe microscopy

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Abstract: The evolution of the electrical charge injected into Ni-doped phyllosilicate nanoscrolls composites deposited on a conductive substrate was studied by Kelvin probe force microscopy. The nanoscrolls were synthesized by hydrothermal method and then annealed in H₂/Ar flow at 400-900°C in order to reduce Ni up to metal. A typical agglomerate of the Ni₅Si₃O₉(OH)₈ nanoscrolls accumulated the charge on one nanoscroll followed by a subsequent partial destruction of the agglomerate. For the Ni₅MgSi₃O₉(OH)₈ nanoscrolls, the whole agglomerate could be charged, and the injected charge was retained for hours. The shortest charge relaxation time was revealed for the nanoscrolls annealed at the highest temperature, when Ni was completely reduced.

1. Introduction
Currently, 1:1 phyllosilicates and clays with tubular morphology gained increased attention due to a number of peculiar properties [1,2]. Size mismatch together with difference in chemical composition between the two sheets [3] endue the phyllosilicate layer with ability of spontaneous curling. Resulting nanotubes and nanoscrolls possess a high specific surface area (from one to several hundreds of m²/g [4-6]), aspect ratio and completely different outer and inner surfaces. Tubular hydrosilicates like halloysite, chrysotile, pectolite, and related compounds can be found in mineral form [1,7,8] or synthesized involving hydrothermal process [3,5,9,10]. One of the frequently mentioned nanoscrolls application related with their natural abundance and specific morphology is adsorption and encapsulation. Tubular particles can serve for wastewater remediation [4,11-13] or for controlled release of drugs and corrosion inhibitors [1].

Doping of hydrosilicate structure by d-elements like Fe, Co, and Ni opens up additional perspectives in the fields of magnetic materials [14-16] and catalysts [6,17-20]. A remarkable feature is that those dopants can be reduced by hydrogen up to metal nanoparticles, which are strongly coupled with the residual oxide matrix. Heterogeneous nanostructured metal catalysts possess great interest for application in a wide range of chemical process [21,22]. To create many active sites, it is necessary not only to form catalytically active nanoparticles, but also to find a way to separate and isolate them from each other. Traditional methods assume depositing metal nanoparticles upon initially prepared support using laser-assisted techniques [23-25] or various chemical methods [26-28]. Here, we study Ni-doped phyllosilicate nanoscrolls [11,29] with partially or completely reduced metallic nickel. A little has been
known about the properties of such composite nanoscrolls and their ability to accumulate and retain the injected charge. One of the most suitable methods for studying the kinetics of charge accumulation and relaxation in nanoparticles is Kelvin probe force microscopy (KPFM) [30-32].

2. Experimental
The nanoscrolls were prepared by hydrothermal treatment (350 °C, 20 MPa, 12 hours, 0.25 M NaOH water solution) of Mg and Ni hydroxides coprecipitated in the presence of amorphous SiO₂ (hydrothermal synthesis is described in details elsewhere [29]). Phyllosilicates of two compositions were synthesized: nickel, Ni₃Si₂O₅(OH)₄, and nickel-magnesium, Ni₂MgSi₂O₅(OH)₄, ones.

In order to form metal nanoparticles inside the nanoscroll matrix, the samples were annealed in argon-hydrogen flow at various temperatures for 1 hour. For the nickel phyllosilicate samples, the annealing temperatures were 540, 670, and 900°C, whereas for the nickel-magnesium phyllosilicate ones – 400, 600, and 900°C.

Powder X-ray diffraction (PXRD) patterns of synthesized Ni-doped phyllosilicate nanoscrolls and the products of the reduction reaction were acquired using Rigaku Smartlab SE powder diffractometer (CuKα radiation λ=0.15406 nm). A PDF-2 database was used for peak indexing.

Scanning transmission electron microscopy (TEM/STEM) was performed on JEOL ARM 200 F Cold FEG electron microscope operating at 200 kV and equipped with a spherical aberration (Cs) probe corrector (point resolution 0.19 nm in TEM mode and 0.078 nm in STEM mode).

Atomic force microscopy (AFM), KPFM, and scanning spreading resistance microscopy (SSRM) [33] measurements were performed on NTegra Aura system (NT-MDT SI, Russia). Conductive HA_C/W2C+ cantilevers (NT-MDT SI, Russia) with a probe tip radius <35 nm, a resonant frequency of about 37 KHz, and a stiffness coefficient of about 0.65 N/m were used. For the measurements, the nanoscrolls were deposited from isopropanol suspension on Si substrate (n-type conductivity, doping level 10¹⁶ cm⁻³) covered by the 100-nm-thick nickel layer. All experiments were conducted in air at the room temperature and a relative humidity of about 30%.

Charge injection into the nanoscrolls and the investigation of the injected charge retention were carried out as follows. First, the topography and surface potential data of a sample area with an agglomerate of the nanoscrolls were collected in the tapping AFM and noncontact KPFM modes. Then, the probe touched the agglomerate in the AFM contact mode with the force of about 15-20 nN, and a charge was injected into the nanoscrolls by applying a rectangular positive pulse (τ = 1.5 min, amplitude + 10 V) between the grounded probe and the sample. After that, multiple scans of the surface potential of the sample region were performed, and the changes occurred were recorded. Then, the surface potential of the agglomerate relative to the surrounded substrate was analysed as a function of time.

Figure 1. PXRD patterns of Ni-doped phyllosilicate nanoscrolls and their annealing products.
3. Results and discussion

Figure 1 shows changes in the crystal structure of Ni-doped phyllosilicate nanoscrolls after the annealing in the argon-hydrogen atmosphere. Temperature increase leads to a gradual degradation of the tubular phyllosilicate structure with simultaneous formation of the crystalline nickel phase. At 900°C, all Ni cations are supposed to be reduced to metal. Residual matrix phase composition depends on the nanoscrolls initial chemical composition. If there are magnesium cations in the system, then they form Mg$_2$SiO$_4$ crystal phase, otherwise SiO$_2$ stays in amorphous form at 900°C.

Figure 2 reflects morphological changes that occur with phyllosilicate nanoscrolls annealed at various temperatures. For the Ni$_2$MgSi$_2$O$_5$(OH)$_4$ nanoscrolls, the annealing at the lowest temperature, 400°C, was inefficient: it is difficult to say whether the metal has been reduced in this case (Fig. 2d). At the highest annealing temperature, 900°C, separate crystalline metallic particles embedded in the oxide matrix are visible for both samples (Fig. 2c,f). Typical sizes of the nanoparticles reduced out from Ni$_3$Si$_2$O$_5$(OH)$_4$ are 10-30 nm, and around 25-75 nm for the Ni$_2$MgSi$_2$O$_5$(OH)$_4$ case. The annealing at intermediate temperatures resulted in the Ni reduction in the nanoscrolls of both compositions. However, the resulted nanoparticles are smaller and not so clearly shaped.

**Figure 2.** TEM/STEM micrographs of nanoscrolls after annealing: (a-c) Ni$_3$Si$_2$O$_5$(OH)$_4$, (d-f) Ni$_2$MgSi$_2$O$_5$(OH)$_4$. Annealing temperatures: (a-c) 540, 670, 900°C, respectively; (d-f) 400, 600, 900°C, respectively.
First, the local conductivity measurements of the samples were made. Using the SSRM mode, the local current-voltage characteristics of nanoscrolls were recorded: the probe was pressed against the nanoscroll, a bias voltage was applied, and the current was recorded. The substrate surface areas free of the nanoscrolls were conductive; the conductivity of the nanoscrolls was not detected for all the samples studied (for probe-sample biases in the range of +/- 10 V and the current noise level of about 10 pA).

After the verification described above, the KPFM studies of the nanoscrolls were carried out. The difference in the properties of the nanoscrolls of various compositions was already observed at the charge injection stage. Independently on the annealing temperature, the Ni$_2$Si$_2$O$_5$(OH)$_4$ samples could be easily modified by this process: at the place of the voltage pulse application, changes in the topography were observed. As an example, Figure 3 shows results detected before, (a), and after the charge injection, (b) and (c), for the same agglomerate consisting of the Ni$_2$Si$_2$O$_5$(OH)$_4$ nanoscrolls annealed at 900 °C. The charge injection increased the surface potential locally by 120 mV (an insert in Figure 3b) and the one nanoscroll turned around across its initial orientation in the agglomerate. This nanoscroll was loosely coupled with the rest ones. It received the main injected charge and turned around due to the electrostatic repulsion from the neighbouring nanoscrolls, which was detected in the topography data. The observed weak nanoscroll-nanoscroll binding inside the agglomerates, as well as the low nanoscroll-substrate adhesion, facilitated the easy capture of some nanoscrolls onto the probe, even if the AFM worked in the tapping mode. In the charge injection experiments on the Ni$_2$Si$_2$O$_5$(OH)$_4$ samples, such arbitrary probe modifications made the time dependences of the KPFM data unreliable.

The charge injection tests of the Ni$_2$MgSi$_2$O$_5$(OH)$_4$ samples produced different and more informative results. First, the charge injection was not local: the voltage pulse charged either the entire conglomerate or most of its parts. Figure 4 represents the results of the charge injection into the Ni$_2$MgSi$_2$O$_5$(OH)$_4$ nanoscrolls annealed at various temperatures: topography (insert), surface potential before (a-d) and after the voltage pulse application (e-h).

To explore the charge leakage from the nanoscrolls, we analysed $\Delta \phi(t)$, the potential of the nanoscrolls relative to the uncharged substrate. To determine a $\Delta \phi(t)$ value, we used the profile data taken along the lines shown in Figure 4 and subtracted the background signal on the uncharged substrate from the signal averaged over the nanoscroll. Then, a nanoscroll normalized potential was determined as $\Delta \phi(t)/\Delta \phi(0)$; the $\Delta \phi(0)$ values corresponded to the KPFM data obtained immediately (a few minutes) after the charge injection. Figure 5 shows the evolution of the nanoscroll normalized potential for four different samples.

**Figure 3.** Ni$_2$Si$_2$O$_5$(OH)$_4$ nanoscrolls annealed at 900°C. AFM topography images of the same agglomerate (a) before and (c) after the charge injection. (b) KPFM surface potential image of the agglomerate. (insert) surface potential profile along the dashed line in the image. Frame size is 2.5x2.5 μm$^2$, profile length 1 μm. Scanning parameters: (a,c) free/set point oscillation amplitude 8 nm/5 nm; (b) probe-sample distance 10 nm, the probe is grounded.

**Figure 4.** Images (a-d) show nanoscroll topography data. (b) The surface potential profile along the dashed line in the image. Frame size is 2.5x2.5 μm$^2$, profile length 1 μm. Scanning parameters: 8 nm/5 nm, the probe is grounded.
Figure 4. KPFM surface potential images of Ni$_2$MgSi$_2$O$_5$(OH)$_4$ nanoscrolls annealed at different temperatures: before (a-c) and after (d-f) the charge injection. Corresponding topography images are on the inserts. The dashed lines show the sections, along which the profiles were taken to prepare the data presented in Figure 5. Scanning parameters are close to Figure 3.
Figure 5. Injected charge relaxation for the Ni$_2$MgSi$_2$O$_5$(OH)$_4$ nanoscrolls annealed at different temperatures.

Using the data of Figure 5, we estimated the characteristic relaxation times (the time at the half value of the signal was used): for the sample without annealing – 100 min, for the sample annealed at 400°C – 45 min, 600°C – 45 min, and 900°C – 35 min. Hence, one can conclude that the metal reduction leads to a decrease in the characteristic relaxation time.

4. Conclusion
We used scanning probe microscopy to perform the electrical charge injection experiments on the nanostructured samples of complex composition. The accumulation and retention of the injected charge for Ni-doped phyllosilicate nanoscrolls with reduced metal nanoparticles were investigated.

The charge injection processes for the Ni$_3$Si$_2$O$_5$(OH)$_4$ and the Ni$_2$MgSi$_2$O$_5$(OH)$_4$ samples were significantly different: in the first case, only separate nanoscrolls were charged; in the second case, the charge was distributed over the nanoscroll agglomerate. This result clearly shows the significant difference between the levels of adhesive interaction of nanoscroll-nanoscroll and nanoscroll-substrate for the two studied compositions.

Unlike the Ni$_3$Si$_2$O$_5$(OH)$_4$ sample, the charge injected into the agglomerates of Ni$_2$MgSi$_2$O$_5$(OH)$_4$ nanoscrolls spread over the whole agglomerate (or most of it), and the agglomerate morphology did not change. The stability of the Ni$_3$MgSi$_2$O$_5$(OH)$_4$ samples morphology upon charge injection was used to study the charge relaxation time. It was found that this time decreases with increase in annealing temperature growth. It could be directly related with the efficiency of Ni reduction in the nanoscrolls at different temperatures.

We believe that these results could be in demand when characterizing metal inclusions distributed inside the dielectric nanostructures.

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References
[1] Lvov Y, Wang W, Zhang L and Fakhrullin R 2016 Adv. Mater. 28 1227-50
[2] Smith R J, Holder K M, Ruiz S, Hahn W, Song Y, Lvov Y M and Grunlan J C 2017 Adv. Funct. Mater. 28 1703289
[3] Krasilin A A, Nevedomsky V N and Gusarov V V 2017 J. Phys. Chem. C 121 12495-502
[4] Belkassa K, Bessaha F, Marouf-Khelifa K, Batonneau-Gener I, Comparot J-D and Khelifa A 2013 *Colloids & Surfaces A: Physicochem. Eng. Asp.* 421 26-33
[5] White R D, Bavykin D V and Walsh F C 2012 *J. Phys. Chem. C* 116 8824-33
[6] Ashok J, Bian Z, Wang Z and Kawi S 2018 *Catal. Sci. Technol.* 8 1730-42
[7] Dödony I and Buseck P R 2004 *Int. Geol. Rev.* 46 507-27
[8] Villanova-de-Benavent C, Nieto F, Viti C, Proenza J A, Gali S andRoqué-Rosell J 2016 *Am. Mineral.* 101 1460-73
[9] Korytkova E N, Semyashkina M P, Maslenikova T P, Pivоварова L N, Al’myashev V I and Ugolkov V L 2013 *Glas. Phys. Chem.* 39 294-300
[10] Lafay R, Fernandez-Martinez A, Montes-Hernandez G, Auzende A L and Poulain A 2016 *Am. Mineral.* 101 2666-76
[11] Krasilin A A, Danilovich D P, Yudina E B, Bruyere S, Ghanbaja J and Ivanov V K 2019 *Appl. Clay. Sci.* 173 1-11
[12] Cataldo S, Lazzara G, Massaro M, Muratore N, Pettignano A and Riela S 2018 *Appl. Clay. Sci.* 156 87-95
[13] Maslenikova T P and Korytkova E N 2010 *Glas. Phys. Chem.* 36 345-50
[14] Krasilin A A, Semenova A S, Kellerman D G, Nevedomsky V N and Gusarov V V 2016 *EPL* 113 47006
[15] Borghi E, Occhiuzzi M, Foresti E, Lesci I G and Roveri N 2010 *Phys. Chem. Chem. Phys.* 12 227-38
[16] Yang Y, Liang Q, Li J, Zhuang Y, He Y, Bai B and Wang X 2011 *Nano. Res.* 4 882-90
[17] Sarvaramini A and Larachi Mössbauer F 2011 *J. Phys. Chem. C* 115 6841-8
[18] Zhang C, Zhu W, Li S, Wu G, Ma X, Wang X and Gong J 2013 *Chem. Commun.* 49 9383-5
[19] Bian Z, Suryawinatna I Y and Kawi S 2016 *Appl. Catal. B: Environ.* 195 1-8
[20] Bian Z and Kawi S 2017 *J. CO2 Util.* 18 345-52
[21] Bulut A, Yurderi M, Ertas İ E, Celebi M, Kaya M and Zehmakiran M 2016 *Appl. Catal. B: Environ.* 180 121-9
[22] Bukhtiyarov V I and Slin'ko M G 2001 *Russ. Chem. Rev.* 70 147-59
[23] Golubina E V, Loktева E S, Maslakov K I, Rostovshchikova T N, Shilina M I, Gurevich S A, Kozhevni V M and Yavsin D A 2017 *Nanotechnologies in Russia* 12 19
[24] Zhang J, Chaker M and Ma D 2017 *J. Colloid Interface Sci.* 489 138-49
[25] Marzun G, Leviš A, Mackert V, Kallio T, Barcikowski S and Wagoner Ph 2017 *J. Colloid Interface Sci.* 489 57-67
[26] Venta K, Wanunu M and Drndic M 2013 *Nano Lett.* 13 423-29
[27] Yashutulov N A, Lebedeva M V and Flid V R 2015 *Russ. Chem. Bull.* 64 1837-41
[28] He L, Weniger F, Neumann H and Beller M 2016 *Angew. Chem. Int. Ed.* 55 12582-94
[29] Krasilin A A, Khrapova E K, Nominí A, Ghanbaja J, Belmonte T and Gusarov V V 2019 *Chem. Phys. Chem.* 20 719-26
[30] Escasain E, Lopes-Elvira E, Baro A M, Colchero J and Palacios-Lidon E 2011 *Nanotechnol.* 22 37504
[31] Dunaesvkiy M S, Alekseev P A, Girard P, Lahderanta E, Lashkul A and Titkov A N 2011 *J. Appl. Phys.* 110 84304
[32] Dement’ev P A, Dunaesvkiii M S, Aleshin A N, Titkov A N and Makarenko I V 2014 *Phys. Solid State* 56 1054-7
[33] De Wolf P, Snauwaert J, Clarysse T, Vandervorst W and Hellemans L 1995 *Appl. Phys. Lett.* 66 1530-2