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La_2O_3-carbon composite with core–shell structure and features of its gas-phase oxidation

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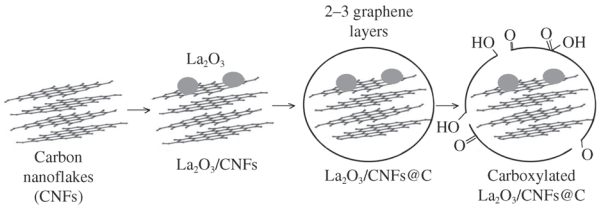
The synthesis of new carbon nanoflake (CNF)-supported composites with a La_2O_3/CNFs@C core–shell structure is described. The carbon surface is functionalized by oxidation with nitric acid vapor for 1, 3, or 6 h. The evolutions of the structure and composition are investigated by transmission electron microscopy and X-ray photoelectron spectroscopy.



Keywords: carbon nanoflakes, graphitization, gas-phase oxidation, core–shell structure, surface functionalization.

Nanoparticles with a core–shell structure are highly functional materials. Their properties can be quite different and depend on the composition, size, and core/shell mass ratio.[1] Graphite and graphite-like shells are reported for different M@C nanoparticles, where M is a transitional metal, such as Fe,[2,3] Co,[4–6] Ni,[5] NiAl,[7] Au,[5] and M_2O_n@C nanoparticles (*e.g.*, M = Al[8]). These particles are used as catalysts,[9] targeted drug carriers, contrasts agents in roentgenology and magnetic resonance imaging techniques,[10] and components of materials for electronic and magnetic devices.[5]

Graphite shells are synthesized by laser ablation, pulsed laser action, laser-induced pyrolysis, arc discharge, detonation, methane conversion on supported metal particles, or conjugated thermolysis of metal-containing monomers.[5–11] Carbon surfaces are normally chemically inert to a wide range of reagents. However, the graphite shell can be covalently or non-covalently functionalized.[12,13] Carbon surfaces are often oxidized with acid solutions resulting in hydroxyl and carboxyl surface groups. However, the liquid oxidation could dissolve the core, and so alternative methods for synthesis of the oxidized shells are needed.

In the present work we propose (i) the synthesis of La_2O_3 particles 2–3 nm in size stabilized in the carbon nanoflake matrix (La_2O_3/CNFs) (such nanoparticles are used for multiple purposes, for example, as a contrast agent for photon-counting computed tomography);[14] (ii) their encapsulation with a few graphene layers (La_2O_3/CNFs@C); and (iii) gas-phase oxidation of the resulting La_2O_3/CNFs@C_*x* (*x* = 1, 3, and 6 h) nanoparticles with nitric acid vapor.

CNFs were synthesized by templated pyrolytic decomposition of hexane.† According to the TEM data,‡ the morphology of CNFs replicated the shape of MgO template particles.[14,15] The thickness of CNF particles was 7–15 graphene layers. CNFs were then refluxed for 1.5 h in HNO_3 solution to obtain a carboxylated carbon surface. The CNF-supported La_2O_3/CNF composite was obtained by impregnation of the oxidized CNFs with ethanolic solution of $La(NO_3)_3{\cdot}6H_2O$ with subsequent annealing under N_2 atmosphere at 400 °C.§ The size of La_2O_3 particles was 2–3 nm, with the uniform distribution of the particles driven by carboxylic and hydroxyl groups of the oxidized CNFs. Graphitization of La_2O_3/CNFs was performed *via* methane decomposition at 400 °C for 10–15 min. According to the TEM data, graphitization encapsulated La_2O_3/CNFs particles with 2–3 graphene layers (Figure 1).

The gas-phase oxidation of different carbon nanostructures was earlier reported for carbon nanotubes (CNTs),[16] CNTs and CNFs consolidated by spark plasma sintering,[17,18] and carbon

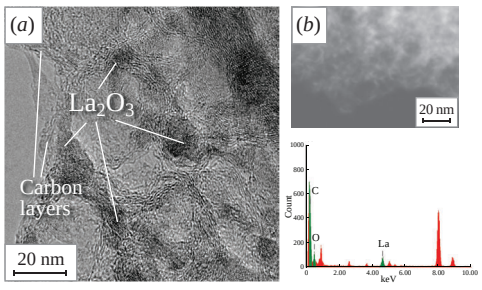


Figure 1 (*a*) HRTEM and (*b*) HAADF-STEM images with EELS spectra of La_2O_3/CNFs@C.

† CNFs were synthesized in a quartz tube reactor in a nitrogen flow (1000 ml min^{-1}) at 900 °C for 30 min over the MgO template. The template was removed from the sample by treatment with boiling HCl solution. Then CNFs were washed with distilled water and dried at 120 °C for 24 h.

‡ Transmission electron microscopy (TEM) images were recorded using a JEOL 2100F/Cs microscope (Jeol, Japan) operated at 200 kV and equipped with an UHR pole tip, a spherical aberration corrector (CEOS, Germany), and an EEL spectrometer (Gatan, Germany).

§ The La_2O_3/CNFs composite was prepared by impregnation of CNFs with a 2 M ethanolic solution of $La(NO_3)_3{\cdot}6H_2O$ (99%, China Northern Rare Earth group High-Tech Co. Ltd., Baotou, China). The La content in the final product was 15 wt% according to XPS data. The solvent was evaporated at 60 °C under sonication within 4 h. Then the sample was placed in a quartz flow bed reactor and heated in N_2 flow (200 ml min^{-1}) at 400 °C for 1.5 h, resulting in decomposition of nitrate.

Table 1 XPS surface compositions of La_2O_3/CNFs and La_2O_3/CNFs@C_*x* (*x* = 1, 3, 6).

Sample	La content (wt%)	N content (wt%)	C content (wt%)			O content (wt%)		
			sp^2	sp^3	C−O, −COOH	O^{2-}	OH^-	O−C, O=C
La_2O_3/CNFs	15.42	0.00	67.16	0.33	6.32	0.00	2.00	8.76
La_2O_3/CNFs@C	13.78	0.00	70.59	0.00	5.78	0.00	1.47	8.38
La_2O_3/CNFs@C_1	9.96	0.00	48.77	10.32	11.44	0.00	1.95	17.55
La_2O_3/CNFs@C_3	11.66	0.00	42.36	13.51	10.65	0.11	3.69	18.01
La_2O_3/CNFs@C_6	9.89	1.09	38.38	17.48	11.00	0.11	4.43	17.62

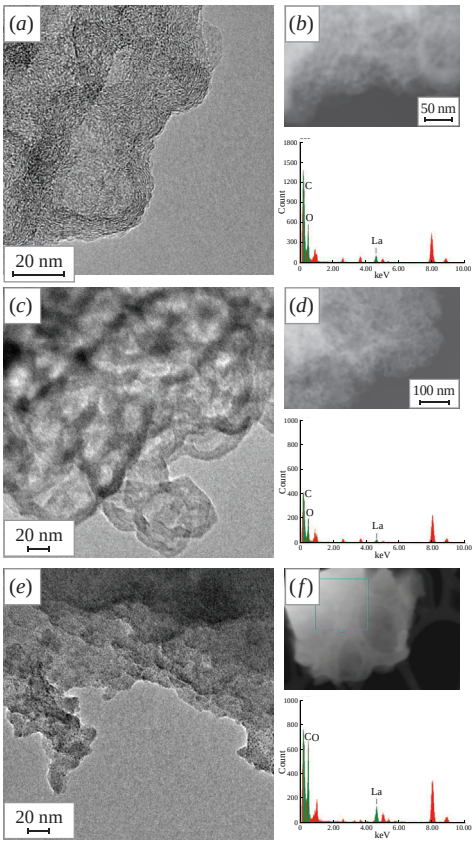


Figure 2 (*a*) HRTEM and (*b*) HAADF-STEM images with EELS spectra of La_2O_3/CNFs@C_1; (*c*) HRTEM and (*d*) HAADF-STEM images with EELS spectra of La_2O_3/CNFs@C_3; (*e*) HRTEM and (*f*) HAADF-STEM images with EELS spectra of La_2O_3/CNFs@C_6.

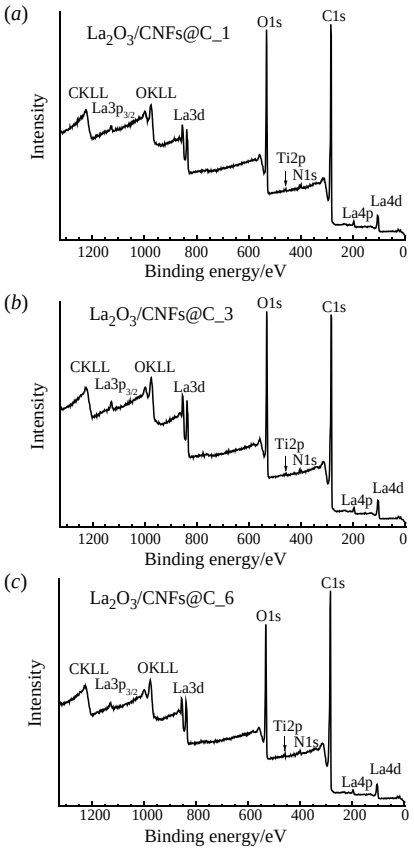


Figure 3 Survey XPS spectra of La_2O_3/CNFs@C_*x* [*x* = (*a*) 1, (*b*) 3, and (*c*) 6].

onion-like structures.[19] This method of surface oxidation is simple because no isolation of the final product is required. In the present work, the prepared composite La_2O_3/CNFs@C was placed in an open box filled with vapor of boiling nitric acid and treated for 1, 3, or 6 h. The obtained composites La_2O_3/CNFs@C_*x* (*x* = 1, 3 and 6) were washed with water and dried at 110 °C for 8 h.

The degree of carbon surface degradation increased as the oxidation time increased (Figure 2). According to the X-ray photoelectron spectroscopy (XPS) data, the oxygen content in La_2O_3/CNFs@C_*x* increased upon oxidation.¶

The survey XPS spectra of La_2O_3/CNFs@C_*x* demonstrate the presence of carbon, oxygen, and La as the main elements in these materials (Figure 3). Fitting of the C1s spectra revealed the components with binding energies of 284.4, 284.9, and 286–289.3 eV that can be attributed to sp^2- and sp^3-hybridized carbon atoms and different oxygen bonded carbon species, respectively. The O1s spectra showed the components at 529.0, 530.8, and 531.0–533.4 eV that can be respectively assigned to lattice oxygen (O^{2-}), metal bonded hydroxyl groups (OH^-), and different oxygen species bonded to carbon atoms. The content of metal bonded hydroxyls on the La_2O_3/CNFs@C_*x* surface increased as the oxidation duration increased (Table 1), while the content of different oxygen species bonded to carbon atoms remained practically unchanged. At the same time, the content of sp^3-hybridized carbon atoms increased because of an increase in the content of terminal carbon atoms.

In summary, we obtained a new La_2O_3/CNF@C core–shell composite and developed a method of its surface functionalization not affecting the La_2O_3 core. The CNF matrix allowed one to stabilize La_2O_3 nanoparticles 2–3 nm in size. We proposed gas-phase oxidation of La_2O_3/CNFs@C with HNO_3 vapor. As the oxidative treatment duration increased from 1 up to 3 and then to 6 h, the oxygen content in the samples increased from 19.50 up to 21.81, and finally to 22.16 wt%.

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¶ XPS spectra were recorded by an Axis Ultra DLD spectrometer (Kratos Analytical, UK) using monochromatic AlKα radiation (1486.7 eV). The pass energies of the analyzer were 160 eV for survey spectra and 40 eV for high resolution scans.

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