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LETTER

Fabrication of fluorescent nanodiamond@C core–shell hybrids via mild carbonization of sodium cholate–nanodiamond complexes

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Nanodiamonds (NDs) represent an elegant carbon allotrope that bears some of the glint of the precious gemstone at the nanoscale level (<10 nm) [1–3]. Besides esthetics, NDs additionally display a set of unique structural, physical, and chemical properties that have drawn the attention of materials' scientists and engineers [4–11]. Though covered in a veil of secrecy for decades, the large-scale commercialization of synthetic nanopowders at reasonable prices has now made this material widely available for research and development, triggering a rapid expansion of the field. High-grade ND powders available in the market today are prepared using the detonation method, i.e., detonation NDs [12]. The prime nanoparticles in these powders are spherical, crystalline, and monodisperse with an average size of ca. 4–5 nm. Moreover, they appear sintered to each other forming coarse, yet tight agglutinates [13, 14]. The agglutinates are few nanoparticles thick and several hundred nanometers long, displaying fractal morphologies. This robust matrix of clustered NDs provides an ideal engineering platform for numerous applications pertinent to polishing, lubricants, reinforcing fillers, field emission, optical materials, coolants, chromatography, metal ion hybrids, catalyst supports, and biomedicine, where particle aggregation and surface chemistry are of great importance [15–22].

In general, detonation NDs displays poor surface functionality. Hence, chemical modification is necessary to endow NDs with new or even improved properties that could make them appealing substrates for implementations as above [15–22]. This has been achieved by the incorporation of surface functional groups through fluorination, hydrogenation, oxidation, silanization, or amidation reactions [5, 7, 8, 10, 23]. In this article, we present an alternative modification pathway based on the carbonization of impregnated organic salts. Such route leads to ND/nanocarbon hybrids where the carbonaceous shell strongly adheres on the underlying ND core through interfacial carbon–carbon covalent bonds. As the new material combines both carbon phases, modification is expected to alter the hybrid's physical properties. In addition, the high reactivity of the carbonaceous shell relative to NDs may facilitate an effective organic functionalization under mild conditions.

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As a case example, we demonstrate in this study the fabrication of a core–shell hybrid obtained by the wet-impregnation of NDs with sodium cholate and subsequent mild pyrolysis in air. In this case, the impregnated organic salt serves as the precursor for the formation of the carbonaceous shell around the ND core. Such modification confers the hybrid new optical properties, e.g., the hybrid displays blue fluorescence upon UV excitation. The synthesis, characterization, and optical properties of the functional solid are described and discussed below.

The modified ND sample (or NDM) was produced as follows: 100 mg ND gray powder (>97% Aldrich, <10 nm) were wet-impregnated with 1 mL aqueous solution containing dissolved 200 mg sodium cholate hydrate (99% Alfa Aesar). The slurry was ground using an agate mortar and pestle by spreading the admixture as much as possible to the inner side walls of the mortar. The wet paste was dried in an oven at 80 °C for 2 h. The dry solid was scratched from the mortar's surface using a spatula and then crushed into a fine powder with a pestle. No phase separation between the mixed ingredients was observed after impregnation and drying, suggesting that the organic salt disperses uniformly on the ND surface. The ND–sodium cholate complex was loaded on alumina crucible and heated in air at 300 °C for 2 h at a heating rate of 10 °C min^{-1}, using a programmed Carbolite chamber furnace. The calcined sample was successively washed five times with 25 mL water to remove water-soluble byproducts and two times with 25 mL acetone. Each washing treatment was followed by centrifugation at 4000 rpm for 10 min. The brown NDM powder was dried in an oven at 80°C for 1 h.

NDM hybrid was prepared in two steps: (i) wet-impregnation of ND agglutinates with sodium cholate hydrate, and (ii) solid-state pyrolysis of the resulting complex at 300 °C in air (Fig. 1). For the first step, it seems that there is a strong affinity of the organic salt toward ND surface. For instance, detonation NDs contain hydrophilic functional groups on the outer surface (carboxyl, hydroxyl, etc.), as well as, distinct hydrophobic graphene fragments located near the boundaries [24]. The hydrophilic groups can be clearly seen by IR spectroscopy. On the other hand, the sp^2 domains give a gray color to NDs and can be directly identified by Raman spectroscopy complementary to sp^3 carbon. Since sodium cholate is an amphiphile containing an ionic group attached to a non-polar steroid skeleton, this organic salt may interact both ways with the ND surface. In particular, the polar group of sodium cholate should have affinity for the hydrophilic part of the ND surface, whereas the steroid part should stick to the outer graphene layer [25]. This surface matching between NDs and sodium cholate eventually favors a

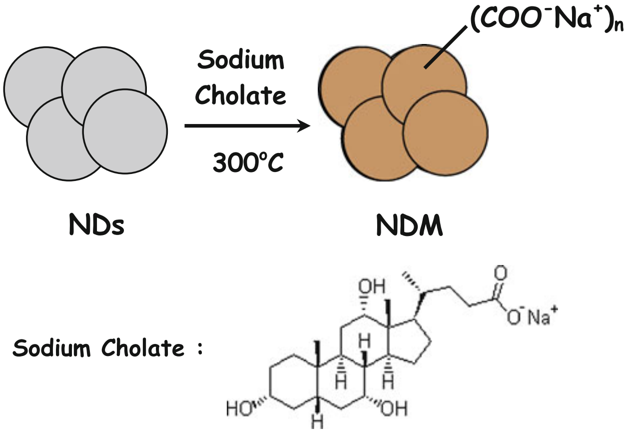


Fig. 1 Wet-impregnation of clustered NDs (*gray powder*) with sodium cholate and subsequent mild pyrolysis in air result in surface modified nanodiamond agglutinates (NDM, *brown powder*). Residual carboxylate groups are also depicted in the scheme (6.5 μmol g^{-1}) (Color figure online)

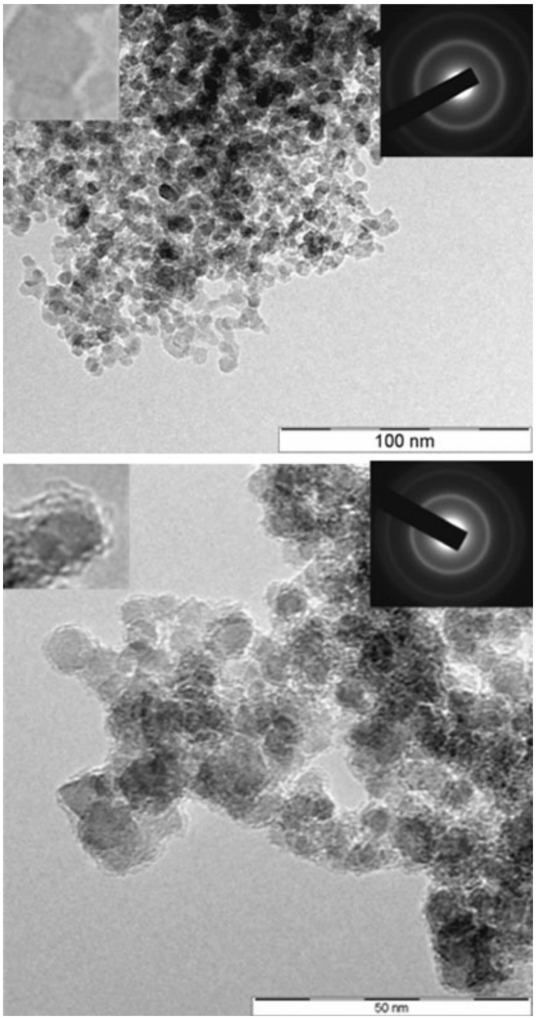
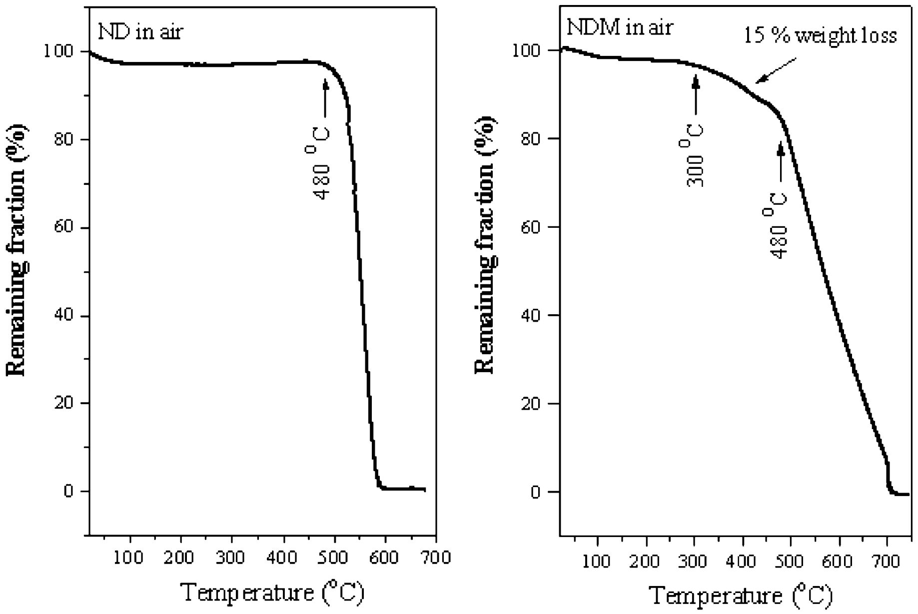


Fig. 2 TEM images for the ND (*top*) and NDM (*bottom*) agglutinates. Unlike NDs, NDM exhibits a core–shell structure of an intact ND core and a round carbonaceous shell (*left side insets*). The crystallinity of NDs is preserved after modification (*inset* SAED patterns)

Fig. 3 TGA traces under air of the ND and NDM samples



homogeneous surface coverage of NDs by the impregnated salt. Regarding the second step, the pyrolyzation temperature is well below the thermal decomposition of NDs (ca. 500 °C) but sufficient for the mild thermal oxidation of the organic precursor. The thus-formed carbonaceous shell is amorphous and roughly contains 50% C, 3% H, and oxygen. Some sodic carboxylate groups present in the organic salt remain intact in the shell after pyrolysis; however, potentiometric titrations showed that their concentration is very low (6.5 μmol g^{-1}).

TEM studies revealed a core–shell structure for the modified ND agglutinates (Fig. 2). Unlike NDs, NDM clearly exhibits thin carbonaceous shells around intact ND cores. As a result, NDM displays slightly lower BET surface area than the pristine NDs, i.e., 270 versus 300 $m^2\ g^{-1}$. In addition, the ND particles retain their crystallinity after modification, based on SAED patterns. According to TGA measurements in air, the carbonaceous shell content for NDM nears 15% (Fig. 3). In brief, the thermal decomposition of the unmodified NDs commences at 480 °C and completes in a single step with no other phases being present. On the other hand, NDM shows two discrete decomposition steps thanks to a core–shell structure: one at 300 °C assigned to the removal of the amorphous carbonaceous shell and another at 480 °C assigned to the ND core combustion. Note that the decomposition temperature of NDs remains the same before and after modification, signaling minor structural changes for NDs during thermal treatment in air at 300 °C (<480 °C).

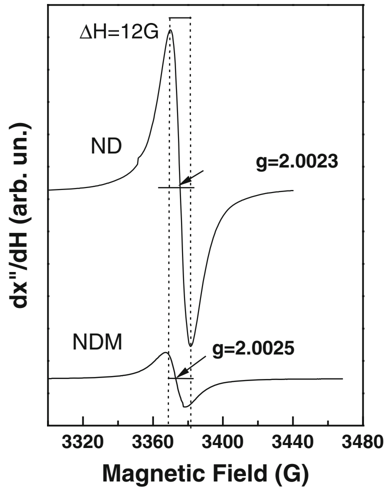


Fig. 4 Continuous wave EPR spectra of the ND and NDM powders at 77 K. *Experimental conditions*: Microwave frequency 9.5104 GHz, modulation amplitude 4.00 G_{pp}, modulation frequency 100 kHz, and microwave power 6 mW

The solid-state EPR spectra of the ND and NDM powders showed the presence of stable, free radicals (Fig. 4). DPPH was included as a *g*-marker and spin standard for detailed qualitative and quantitative studies. The EPR features of the ND samples are summarized in Table 1. With respect to qualitative analysis, the spectrum of ND recorded at 77 K is characterized by a single Gaussian derivative with peak-to-peak linewidth $\Delta H_{pp} = 12$ G and $g = 2.0023 \pm 0.001$. This signal is often designated to dangling bonds at the diamond cluster surface as well to unpaired electrons located in the bulk of a ND particle

Table 1 EPR features of nanodiamond samples

Sample	*g*	ΔH_{pp} (G)	Spin conc. (μmol g^{-1})
ND	2.0023	12	1.13
NDM	2.0025	12	0.55

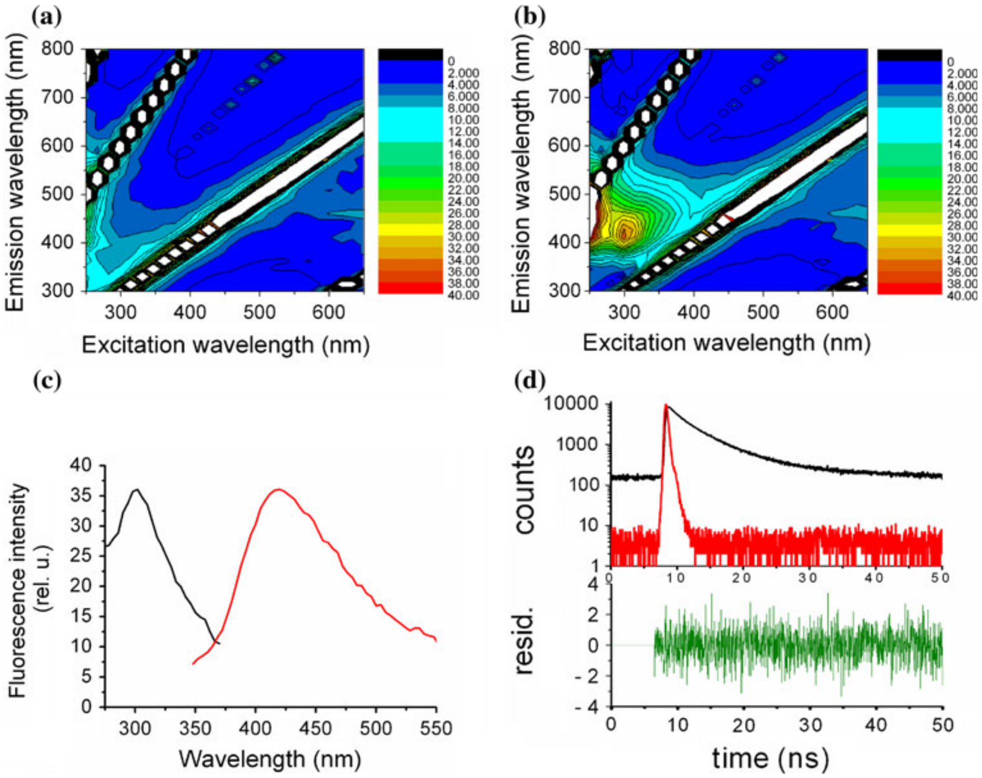


Fig. 5 Optical properties of NDs and NDM (0.1 mg mL^{-1} aqueous suspensions). **a** 3D spectrum (excitation–emission matrix) for NDs. **b** 3D spectrum (excitation–emission matrix) for NDM. **c** Excitation spectrum for emission at 420 nm (*black*) and emission spectrum for excitation at 302 nm (*red*) for NDM. **d** Kinetic of the fluorescence decay of NDM (*black*), instrument response function obtained with scatterer (*red*), and the first residuals for the best fit (*green*) (Color figure online)

[26–28]. After modification, the signal's shape remains largely unchanged with only a small up-shift to the average g-value, $g = 2.0025 \pm 0.001$. The up-shifted g-value in NDM can be attributed to C-based radicals localized at the carbonaceous shell. Regarding quantitative analysis, spin-counting showed that the radical concentration was 1.13 μmol g^{-1} for NDs and 0.55 μmol g^{-1} for NDM. This implies that surface modification results in disappearance of half of the radicals. This decrement could be attributed to partial saturation of the surface dangling bonds by the carbonaceous shell through the formation of interfacial carbon–carbon covalent bonds.

The present surface modification brings dramatic changes in the optical properties of the material, e.g., the hybrid becomes blue fluorescent upon UV excitation. Similar changes in the optical properties after surface modification or surface oxidation are common in carbon nanoparticles, including NDs [10, 29, 30]. More specifically, we found no observable fluorescence for the pristine NDs throughout the studied UV–Vis range of the spectrum (Fig. 5a). However, a novel fluorescence peak appeared for the NDM sample. It has maxima in the excitation and emission spectra located at 302 and 420 nm, respectively (Fig. 5b, c). The large Stokes-shift allows very efficient spectral separation of the incident light, thus enabling the emission detection with very high signal-to-noise ratio. Kinetic of the fluorescence decay is another fundamental characteristic of the fluorophore (Fig. 5d). The fluorescence decay of NDM is rather complex with an intensity-weighted mean fluorescence lifetime of 4.92 ns. This value is rather similar to common polyaromatic fluorophores. Such polyaromatics might exist within the carbonaceous shell after mild pyrolysis [31]. For instance, sodium cholate already has a closed ring structure. Furthermore, it is expected to easily lose its hydroxyl groups upon heating to form polyaromatic domains. On account of these optical properties, the hybrid could be used as a fluorescent label in biomedical fields (e.g., cellular biomarkers) [32].

In summary, a novel core–shell hybrid composed of a ND core and a surface-bonded carbonaceous shell was synthesized by the solid-state pyrolysis of a ND–sodium cholate complex in air at mild temperature. The functional solid displays blue fluorescence upon UV excitation as a result of modification. The material was characterized using several techniques, like TEM, TGA, EPR, and fluorescence spectroscopy. The method provides an alternative pathway toward surface modified NDs with interesting properties and could be generalized to versatile organic precursors.

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