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Letter to the editor

Conformal nanocarbon coating of alumina nanocrystals for biosensing and bioimaging

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A B S T R A C T

A conformal coating technique with nanocarbon was developed to enhance the surface properties of alumina nanoparticles for bio-applications. The ultra-thin carbon layer induces new surface properties such as water dispersion, cytocompatibility and tuneable surface chemistry, while maintaining the optical properties of the core particle. The possibility of using these particles as agents for DNA sensing was demonstrated in a competitive assay. Additionally, the inherent fluorescence of the core alumina particles provided a unique platform for localization and monitoring of living organisms, allowing simultaneous cell monitoring and intra-cellular sensing. Nanoparticles were able to carry genes to the cells and release them in an environment where specific biomarkers were present.

Carbon nanomaterials are emerging as promising material platform in nano-medicine and nano-biotechnology [1]. Nanocarbon materials appear in different forms and dimensions such as quantum dots, nanocrystals, nanotubes, 2D graphene layers, nanoporous membranes and other 3D nanoarchitectures [2]. The broad diversity in chemical and physical properties of carbon is unique compared to any other element on the periodic table, opening a wide range of opportunities for applications such as electrocatalytic intracellular sensors, neural electrodes, bionic devices and drug/gene delivery agents [3]. However, for some practical applications, carbon needs to be implemented with other materials to provide multifunctional properties [2]. Hybrid composite nanocarbon structures can potentially offer more diverse properties which cannot be obtained with carbon alone. Therefore, development of hybrid nanocarbon composites can promise new possibilities for advanced applications, such as magnetic resonance imaging, photothermal/radio-frequency therapy, multimodal cellular imaging and gene delivery [4].

Over the last decade, fluorescent nanoparticles have become key component of many important biological applications such as biosensing, bioimaging, drug delivery and drug discovery [5]. An appropriate nanoparticle-system as an agent for bioapplications should exhibit multifunctionalities such as tunable surface and optical properties, chemical stability and biocompatibility [6]. Many different types of nanoparticle systems are being introduced to resolve some of the current issues in cell-based studies [7]. Alumina nanoparticles with their natural abundancy and also strong photoluminescence in the near-infrared (NIR) region (~690–710 nm within the tissue transparency window) have some potentials for being implemented in biological assays [8]. However, direct application of alumina nanoparticles in biosystems is hindered due to surface properties (limited water dispersibility, chemical stability and biocompatibility). Carbon coating of alumina nanoparticles could potentially resolve many of those limitations while maintaining the optical properties. However, the conformal coating of the particles faces several considerable technical challenges due to limitations in chemical and physical properties [9].

Here we introduce a fabrication method which allows conformal coating of alumina nanoparticles with an ultra-thin carbon layer using a plasma-assisted technique. We investigate the properties of these materials and the formation mechanism by transmission electron microscopy (TEM), Raman spectroscopy and X-ray photoemission spectroscopy (XPS). A proof-of-principle study was carried out to show that the fabricated core-shell particles can be used as a promising platform for *in vitro* biosensing and bioimaging. In particular, the particles were able to quench the fluorescence of molecular dyes and were successfully implemented in a competitive assay for DNA sensing. Also, the internalization of the particles into the cells was investigated allowing live cell imaging and intra-cellular sensing. The results show that the fabricated core–shell nanoparticles can be used as selective and sensitive signalling platform for observation and eventually engineering biological processes at the subcellular level.

The coating method is based on the exposure of alumina particles to hydrogen/methane plasmas, in which a layer of amorphous carbon was grown on the surface of the particles (supporting information for methods and growth mechanism). Fig. 1 summarizes the approach to fabricate carbon coated alumina particles. The approach is universal for alumina particles with different shapes and sizes (from nm to mm size). Microscope images show that the originally white alumina particles turned to black colour after the plasma induced reaction. TEM images from the cross-sections of larger particles reveal the atomic structure of core-shell material and its comparison to the non-coated particles. The results show the ultra-thin conformal carbon layer with a thickness of 2–5 nm around the particles. It also suggests that the crystalline structure

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of the core alumina (α-alumina) remains unchanged after the plasma treatment.

The hybridization state of the carbon layer can be controlled during the growth by changing the plasma power. Different growth temperature (650–1300 °C) was achieved by varying the input power from 1250 W to 3000 W in the plasma discharge. The Raman spectrum of the samples grown at different temperatures are shown in Fig. 2. Raman studies suggest that the influence of the temperature on the hybridization state of the grown nanocarbon layer was significant. The spectrum of the carbon coated particles contains two significant modes at 1347 cm^{-1} (D peak) and 1607 cm^{-1} (G peak), which are associated with the modes of amorphous carbon (a-C) films [10]. Pristine alumina particles did not show any detectable resonance in this region of Raman spectrum. The intensity ratio between D and G peaks (*I(D)/I(G)*) varied with temperature (Fig. 2(b and c)). A higher ratio was obtained for the films that were grown at lower temperatures (650–800 °C). Also, as confirmed by XPS (high-resolution C 1s spectra), sp^3 content of the films decreased with temperature (Fig. 3(a)). The grown film became considerably graphitic-like at 900–1100 °C (major sp^2 content with disordered structure). At temperatures higher than 1100 °C, coatings exhibited more ordered sp^2 bonding, as was

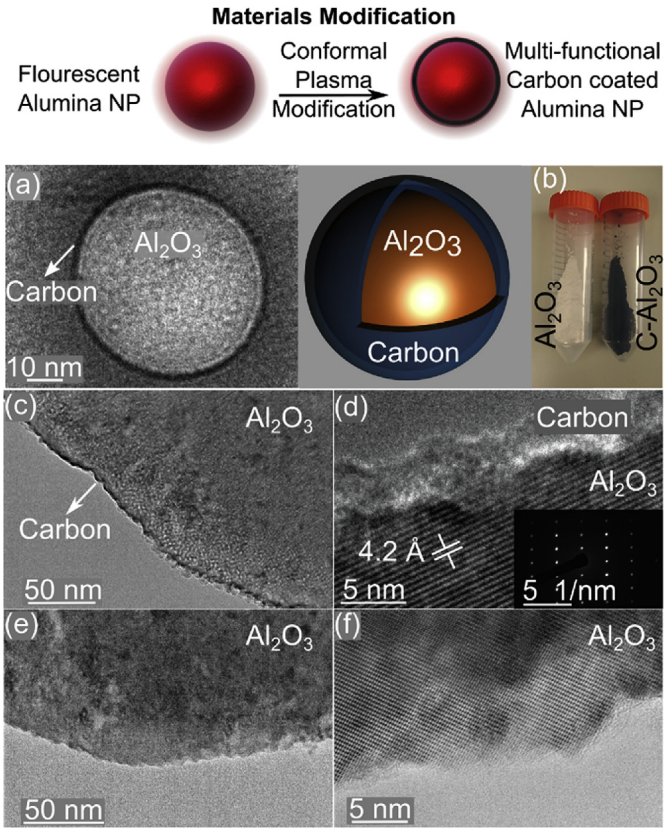

Fig. 1. Conformal carbon coating of alumina particles with plasma. (a) TEM image and schematic of a carbon coated alumina nanoparticle. (b) A photograph of alumina particles before and after carbon coating (~35 g in weight). Carbon coating of the particles also transforms the color of the alumina particles from white to black (c) TEM image from focused-ion-beam milling cross-sectioned carbon coated particle (see SI). The dark line around the edges of the particle is the thin carbon layer. (d) High resolution TEM image from the interface of the core alumina and carbon layer. The inset shows the selected area (electron) diffraction (SEAD) of the core alumina with its crystal structure. The lattice spacing is measured to be 4.2 Å which corresponds to the D spacing of (1120) planes in α-Al_2O_3. (e,f) TEM images of uncoated alumina particles. In comparison to the coated particles, the thin amorphous carbon layer is not present in these images. (A colour version of this figure can be viewed online.)

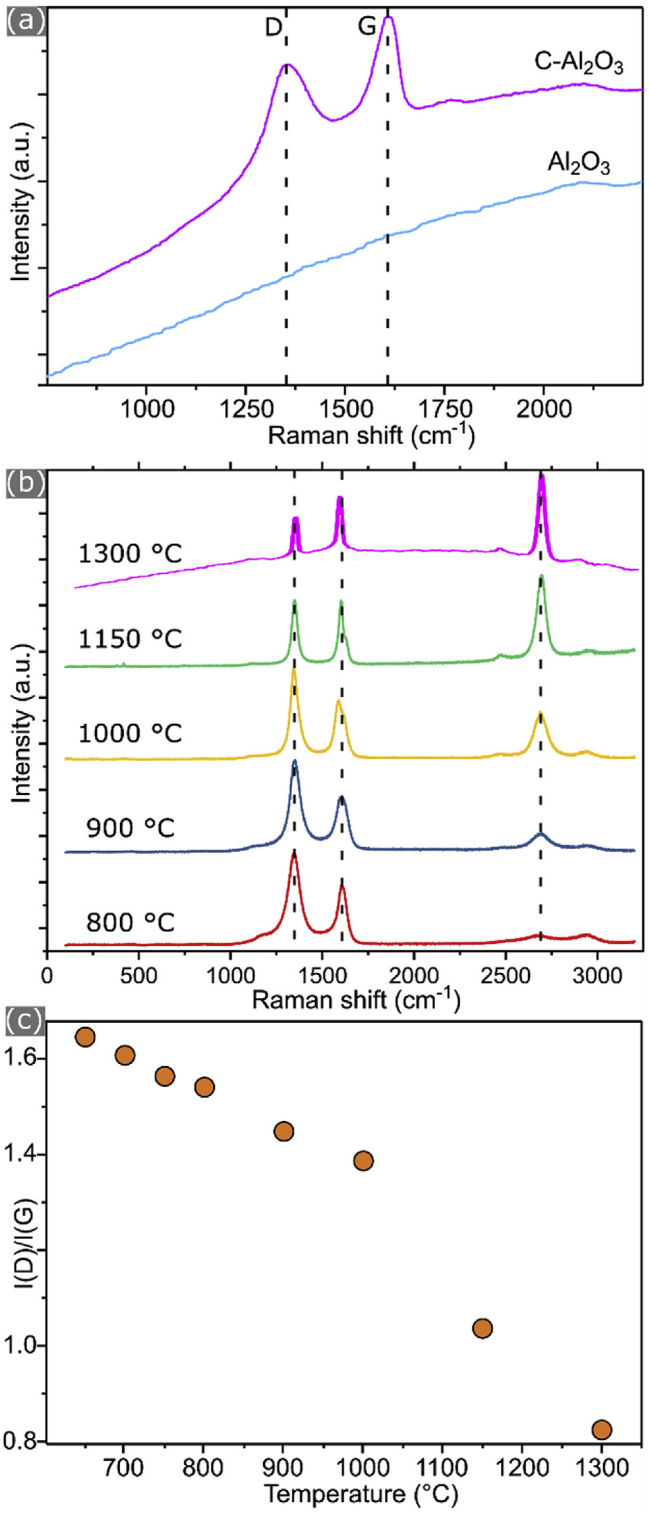

Fig. 2. (a) Typical Raman spectra of uncoated/coated alumina nanoparticles. The Raman spectrum shows that there exists a significant amount of carbon on the surface of the nanoparticles after plasma treatment (D and G peaks are at 1347 cm^{-1} and 1607 cm^{-1}, respectively). Pristine alumina particles did not show any detectable Raman resonance in this region. (b) The influence of the temperature on the chemistry of the grown layer. The amorphous carbon starts to graphitize at higher temperatures and forms ordered sp^2 structure. The intensity of the Raman peak at 2691 cm^{-1} (second order resonance of the sp^2 network) increases with temperature. (c) The intensity ratio between D and G peaks (I(D)/I(G)) with temperature. The ratio decreases steadily with temperature, suggesting that the chemistry of the grown film is temperature dependent. At higher temperatures the coating contains more ordered sp^2 bonded carbon. (A colour version of this figure can be viewed online.)