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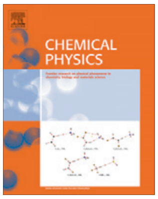

Light induced selective heating of nanostructured pyrolitic graphite surfaces investigated by Raman scattering

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ABSTRACT

Nanostructured surfaces of highly oriented pyrolytic graphite (HOPG) were characterized by Raman spectroscopy. The disc-shape nanostructures ~110 nm high and with two different diameters ~147 and 217 nm are prepared on HOPG using hole–mask colloidal lithography and oxygen reactive ion etching. Significant roughening of the HOPG surface is introduced by the nano-fabrication process, but the nano-disc structures preserves their crystalline structure. Resonant light absorption results in selective heating of nanostructures, although the surrounding medium remains relatively unaffected. Temperature differences of up to 350 K were measured under irradiation with ~11 mW/μm^2. Further increase of the light intensity leads to combustion of structures.

1. Introduction

Because of the importance and abundance of carbon materials, considerable efforts have been spent to characterize their physical properties and to correlate these with the microscopic structure of the material [1–4]. Most physical properties are correlated to the electronic configuration of the specific material, which in turn depend on the inter-atomic bond type. Therefore, structural properties of the material can be conveniently characterized via the atomic vibrations in the material, which is directly dependent on the strength of the bonds between the constituent atoms. A widely used technique for detailed characterization of bond strengths, via the lattice vibrations in a solid material, is Raman spectroscopy.

Some of the properties of carbon materials that have been successfully investigated using Raman spectroscopy are; the phase and purity of the material (amorphous, graphitic, diamond, intercalated, hydrogenated), the stacking properties of graphitic materials and the number of layers in thin graphene stacks as well as nanocrystal size [5–9]. Studies of nanosized carbons have been conducted on fullerenes, metallic and semiconducting carbon nanotubes (CNT's), soot and lithographically prepared nanostructured carbon surfaces. From such studies, subtle details regarding e.g. size, spatial distribution, electric and thermal conductivity of various carbon nanostructures have been mapped [3,5,10,11].

A convenient approach to systematic investigations of physical properties of nanosized objects is that of lithographic preparation of model system [12–15]. Previously, others and we have shown that lithographically prepared, highly oriented pyrolytic graphite (HOPG) nanostructures resonantly absorb light at visible wavelengths and that the resonance conditions and the absorption efficiency depend on the nanostructure sizes [12,14,16]. Motivated by these results, we decided to perform a Raman study of such nanostructures to answer the following questions; (i) How does the fabrication process influence the intrinsic properties of the carbon material and (ii) does the resonant optical absorption influence the Raman scattering.

2. Experimental

The nanostructured samples are prepared using hole–mask colloidal lithography in combination with oxygen reactive ion etching (RIE) [14,17]. The technique utilizes self-assembly of colloidal spheres to produce uniform arrays of well-separated nanostructures with random position. The gold disc arrays are subsequently used as etch masks in an oxygen RIE process, which in a controlled way removes carbon atoms from the HOPG sample (*grade ZYB, GE Advanced ceramics*) surface not protected by gold discs. Hence, the gold disc pattern is transferred into the HOPG, resulting in slightly tapered HOPG discs etched out of the bulk carbon material. Finally, the gold discs are removed in a wet-etch process using a potassium–iodine solution (*Gold etch 22196, Sunchem electrograde products*) and cleaned in acetone and de-ionized water. In addition to the nanostructured samples we also investigate two references; pristine HOPG and a HOPG sample, subject to an equivalent oxygen RIE process as the nanostructured samples. The nanostructured samples will be referred to as HOPG147 and HOPG217 and the pristine and roughened crystals will be referred to as HOPGp and HOPGr, respectively.

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The size and distribution of the nanostructures on the HOPG-surfaces are characterized using scanning electron microscopy, SEM, (*SEM JEOL-JSM630 1F*) and tapping mode atomic force microscopy, AFM, (*DI-dimension 3000 SPM*). Structure diameters, heights and surface coverage's are then evaluated from the SEM and AFM images using ImageJ and the scanning probe image processor (*SPIP*, *version 4.5.7*, *Image Metrology Inc., Denmark*) software, respectively. Optical reflectance of the nanostructured samples and a pristine reference sample is measured using a spectro-photometer (*Varian Cary 500 Spectrophotometer*) equipped with an integrating sphere detector. From these measurements we determine the spectrally resolved decrease in reflectance (specular as well as diffuse) associated with the nanostructures. Since bulk HOPG does not transmit light at the wavelengths investigated here, the only cause of light attenuation is through absorption and hence a measurement of the reflectance also provides a measurement of the absorption. We present the absorption of the four samples as 100Reflectance%. For the wavelengths used in the Raman experiments, we also calculate the ratio of the intensity of absorbed light for each of the samples to that of the pristine sample. This gives values of the enhancement of optical absorption stemming from the nanofabrication process.

Raman scattering measurements are performed in two series using two commercially available setups (Renishaw In via Raman confocal microscope, Jobin Yvon T64000 Spectrometer). Initial measurements are done using low laser power and high magnification (514 nm, 3 mW, ×100, NA = 0.9, estimated spot size $\sim$1 μm^2) comparing the HOPGp, the HOPGr and the sample HOPG217 samples. These measurements give an overview of sample properties in the wave number regime including both the fundamental and the strongest overtones of graphite (1300–2800 cm^{-1}).

The second measurement series is done with different laser intensities from a larger measurement spot (532 nm, 9.7–46.7 mW, ×50, NA = 0.5, measured spot size $\sim$4 μm^2). These measurements are performed, first in the anti-Stokes wavenumber regime (-1750 to -1250 cm^{-1}) and then, for the same sample location in the Stokes regime (1250–1750 cm^{-1}). Raman scattering in the anti-stokes range is boosted by heat, thus, the anti-Stokes peak (at the same wavenumber as the Stokes peak but with opposite sign, i.e. around -1580 cm^{-1}) has negligible contribution from the substrate and is an unambiguous determination of the wavenumber position of the Raman peak associated with the discs.

Lorentzian functions are fitted to the sample data and peak-positions and intensities are derived from these fits. The integral area of each peak rather than the peak amplitude represents the peak intensities. This evaluation is preferred in order to avoid underestimation of peak intensities due to broadening. For high laser intensities an asymmetric broadening of the fundamental Raman-peak at 1582 cm^{-1} is observed. These spectra are therefore fitted with two Lorentzian functions, referred to as G1 and G2. Please see Supplementary Fig. 1 for more on the fitting procedure of the G-peak. The Raman-peak attributed to disorder in the material (D-peak) at $\sim$1360 cm^{-1} exhibit a bimodal distribution even at low laser intensities and is therefore always fitted with a double Lorentzian function.

3. Results and discussion

3.1. Physical and optical properties of nanostructured graphite

The physical and optical properties of the four samples investigated in this work are presented in Table 1. The height of the structures, as well as the surface coverage, is similar for both samples whereas the diameters and the number densities are distinctly different. Although the vast majority of the produced nanostructures are very similar, there are some statistical variations in the size parameters, as indicated in the table. Occasionally it is also observed that nanostructures have disintegrated into two pieces (see Fig. 1a), reflecting the known weak inter-planar bonds in graphite. In addition to the intentionally fabricated nanostructures with various diameters, the fabrication process introduces a roughening of the surface in between the nanostructures, with a root mean square value of $\sim$6.5 nm.

The optical measurements, displayed in Fig. 1b, reveal increased absorption for the nanostructured samples compared to the pristine graphite. In Table 1, the optical absorption values for the wavelengths used in the Raman measurements (514 and 532 nm) for each of the samples, as well as the absorption enhancement factors relative to the HOPGp sample are presented. In agreement with previous reports it is demonstrated that the nanostructures enhances the optical absorption and that the enhancement is correlated to the size of the nanostructures [12,14,16]. These differences in absorption can be explained by the excitation of geometrical resonances in the carbon nanostructures [16]. The roughened sample also shows some enhanced optical absorption but this enhancement is much smaller and significant mainly in the UV-part of the investigated spectral interval. Notice, that in the wavelength regime for the present Raman measurement ($\sim$500 nm) the absorption increases with decreasing disc diameter in agreement with previous work [16].

3.2. Raman peaks

From the overview Raman measurements (Fig. 2) the main characteristics of the different samples can be determined. A sharp, main peak at $\sim$1582 cm^{-1} and a wider double peak at $\sim$2700 cm^{-1} is observed for all the investigated samples. These peaks are referred to as the G- and G'-peaks and derive from the fundamental stretch mode and the overtone of the breathing mode of the carbon rings in graphite, respectively [7]. The sharp G-peak is characteristic for graphite samples and the double peak structure of the G'-peak is associated with a well-ordered A–B stacking in the material.

Table 1

Physical and optical properties of the four investigated HOPG samples (pristine (HOPGp), rough (HOPGr) and nanostructured (HOPG147, HOPG217)). Absorption (*A*) of the light is given for the wavelengths used in the Raman measurements, 514 and 532 nm both in absolute numbers and in relation to the absorption of pristine graphite (A/AHOPGp). Size and surface coverage are given for the two nanostructured samples.

Sample name	HOPGp	HOPGr	HOPG147	HOPG217
Diameter [nm]	Pristine HOPG	Rough HOPG	147 ± 5	217 ± 7
Height [nm]	–	–	110 ± 4	112 ± 4
Particles/area[1/μm^2]	–	–	10.6	4.98
Surface coverage	–	–	18.0%	18.4%
A, 514 nm	72.4%	74.1%	89.2%	86.2%
A/AHOPGp, 514 nm	1	1.02	1.23	1.19
A, 532 nm	72.3%	73.8%	88.9%	86.5%
A/AHOPGp, 532 nm	1	1.02	1.23	1.20