Green-Extraction of Graphene from Natural Mineral Shungite

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Abstract: With the increasing demand for graphene, the need for a simple, fast, efficient, low-stage and environmentally safe method of its production also increases. In our work, we used physical ultrasound treatment without the addition of surfactants to extract graphene films from a mineral of shungite. From our study of the structures of the resulting graphene, we see that they have the form of films with a surface length of 200 nm with a graphene structure with a hexagonal center and a lattice pitch of 0.335 nm.

We investigated two regions of shungite, as illustrated in Figure 1a,d, and conducted EDS analysis on each region. Our results indicate that the completely dark areas in region 1 (Fig. 1b) and 21 (Fig. 1e) are composed entirely of carbon. Conversely, region 2 (Fig. 1c) and 21 (Fig. 1f) is composed of carbon containing impurities, including low concentrations of oxygen, silicon, aluminum, nickel, iron, and vanadium.

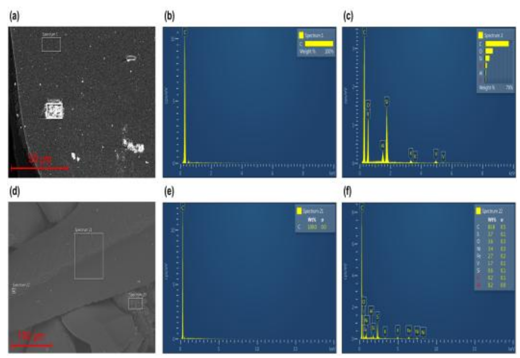

Figure 1. Scanning electron microscopy with EDS image of shungite particles: (a) first-selected sample study areas, chemical composition of area spectrum (b) 1, (c) 2, (d) second-selected sample study areas, chemical composition of area spectrum (e) 20 and (f)21.

Next, we characterized the surfaces of samples processed from shungite with a carbon concentration of 100%.

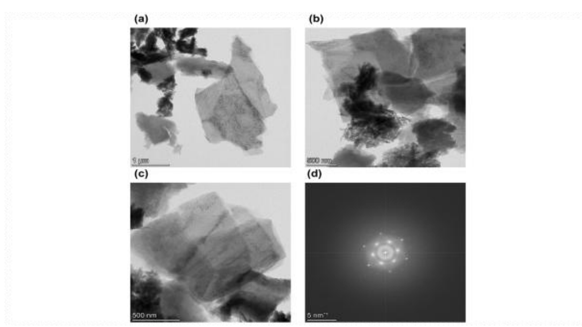

Figure 2. TEM images of sonicated shungite sample at magnifications of (a) x13,500, (b) x35,000 and (c) x22,000. (d) Fast Fourier transform pattern of sonicated shungite sample.

Transmission electron microscopy (TEM) images of a sonicated shungite sample (Fig. 2a-c) reveal the formation of thin films with a high specific surface area. For a sample with a carbon concentration of 98%, the particles have collapsed into thin monolayers. The fast Fourier transform pattern [1, 2] of the resulting films exhibits a symmetrical hexagonal pattern characteristic of primary graphene (Fig. 2d).

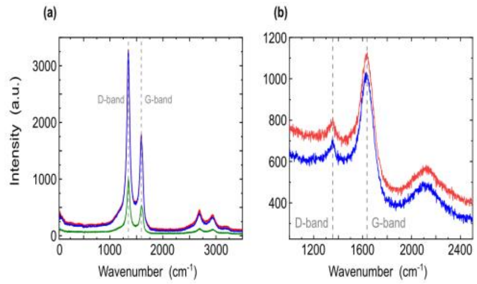

Figure 3. Raman spectra of natural shungite (a) before and (b) after sonication

Raman spectra of natural shungite from the different regions investigated (Fig. 3a) reveal the presence of a G-band at 1600 cm^{-1}, indicating the tangential stretching vibrations of sp2-bonded carbon atoms in the hexagonal graphene planes[3,4]. A D-band at 1330 cm^{-1}, indicating diamond-like sp3 bonds, corresponds to the amorphous structural state of carbon (graphite), indicating that the main allotrope of carbon in natural shungite rock is graphite. However, in Raman spectra of sonicated shungite samples (Fig. 3b), the graphene-related G-band shows increased intensity, with a corresponding decrease in the graphite-related D-band. No obvious second-order peaks appear in the spectra.

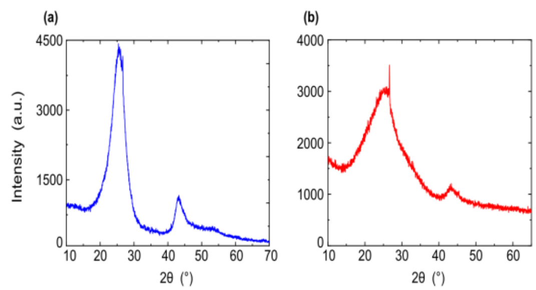

Figure 4. X-ray spectra of shungite sample (a) before, and (b) after sonication.

Figure 4 shows the X-ray spectra of shungite before and after ultrasound treatment. For the sample before sonication (Fig. 4a), wide spectra at 26.5° refer to graphite-like carbon, as well as a secondary peak at 42°, 44°, corresponding to the hexagonal structure. Here 26.5° is the angle of the base plane of centered graphene and the lattice pitch of 0.335 nm. Figure 4b shows X-ray spectra after ultrasound treatment. The positions of the peaks are located at 26.5°, 42° and 44°. The vertex is 26.5°, increased compared to the peak before processing, which means that the carbon peak can be interpreted as a decrease in the size of the coherent scattering region along the c axis in stacked graphene layers. The peak is 44° is more intense than that of shungite before ultrasound treatment, which means that the size of the hexagonal structure has been increased. Our results show that graphene films were obtained from shungite using green-extraction methods.

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References

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