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Pulsed Laser Syntheses of Layer-Structured WS_2 Nanomaterials in Water

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We used water as an environmental friendly medium for the synthesis of hexagonal WS_2 nanoparticles by the pulsed laser method. The materials collected on substrates were oriented with the 2H-WS_2 basal planes parallel to the surface. The use of water, UV lasers, and large WS_2 targets prevented the nanoparticles from restructuring into inorganic fullerenes, which were observed in research using hydrocarbon solvents, longer wavelength lasers, and dispersed powder targets. Fairly good dispersion of nanoparticles suggests that large surface areas are available for chemical reactivity.

Transition metal dichalcogenides, that is, MX_2, where M is Mo or W and X is S or Se, are well-known lubricants and catalysts. Their properties are determined by anisotropic layer structures (strong covalent bonding between Mo/W−S/Se but weak van der Waals attraction between lattice layers). Small-size particles of these materials have a high surface area and may form unique microstructures that can improve material properties. For example, the inorganic fullerene-like (IF) nanoparticles of MoS_2 and WS_2 were synthesized by solid−gas reactions and used effectively as solid lubricant additives for oil.[1,2] Near-monodisperse nanofibers and nanotubules of MoS_2 were prepared by template synthesis and considered for use as hydrodesulfurization catalysts or as battery cathodes.[3] Open-ended MoS_2 nanotubes produced by a solid−gas reaction were used for catalytic conversion of CO + H_2 to CH_4 + H_2O.[4] Polycrystalline MoS_2 nanoribbon arrays produced by electrochemical/chemical synthesis were studied for electronic properties.[5] The cost of making nanomaterials is relatively high because of the use of vacuum chambers and gas handling systems. To obtain high surface areas, highly dispersed MoS_2 materials had been synthesized by using reactions of $(NH_4)_2MoS_4$ in aqueous solution in the presence of an organic surfactant.[6] High-surface-area nanostructured MoS_2 was also produced via the decomposition of $(NH_4)_2Mo_3S_{13}\cdot xH_2O$ in solvothermal toluene.[7] Recently, powerful lasers have been employed to ablate materials and to prepare, at a low yield, IF-Hf_2S from HfS_3 powders in an organic solvent of *tert*-butyl disulfide.[8] Nanotubes and nano-onions have been produced by similar methods using GaS and GaSe powders in di-*tert*-butyl disulfide/toluene/*n*-octylamine,[9] and IF-TaS_2 was made from a pure TaS_2 pellet in liquid CS_2.[10] From the large-scale manufacturing perspective, water is a preferred medium because it is environmentally friendly. Nanostructured carbons and metal colloids have been synthesized by laser ablation in water, and IF-MoS_2 nanoparticles were produced in water using an electric arc discharge.[11−13] In this study, new layer structures and nanoparticles of hexagonal WS_2 were produced using pulsed laser ablation in water.

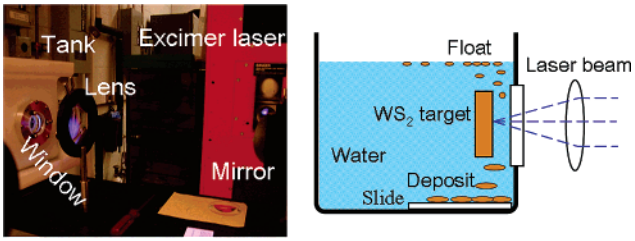

Figure 1. Experimental devices and schematic diagram of using a pulsed laser to produce WS_2 nanomaterials in water.

A compact disk (1 in. diameter by $^1/_4$ in. thickness) of pure WS_2 was set in distilled water. The pulsed beam from a Lambda Physik COMPex 205 KrF excimer laser (248 nm wavelength, 20 ns duration, 1−50 Hz rate, and 200−600 mJ energy) was focused and directed through a window in front of the water tank, where the distance of the WS_2 target is about 5 mm behind the window. The syntheses occurred with 50 Hz pulses of about 400 mJ for 10−20 min. The left image in Figure 1 shows the devices used in the experiments. A schematic diagram on the right-hand side of Figure 1 shows the synthesis process, where most products of laser ablation sink in the water while some nanoparticles float on the surface because they are small and hydrophobic. The yield rate is approximately 10 mg/min. A glass slide was put on the bottom of the tank to deposit films for X-ray diffraction (XRD) measurements. Crystallographic data were collected using a Rigaku XRD system with a monochromator in front of the Cu Kα X-ray source, which was operated in Θ-2Θ mode. Standard powder XRD patterns of hexagonal WS_2 (PDF Card# 08-0237 JCPDS) were used for data interpretation. Some films floated on water, while the remainder of the laser ablated materials sunk to the bottom. The floating and sunk materials were kept separate and were collected on holey carbon grids for electron diffraction and transmission electron microscopy (TEM) analyses. High-resolution microstructures were observed using a Philips CM200-FEG transmission electron microscope operated at 200 keV, which had a field

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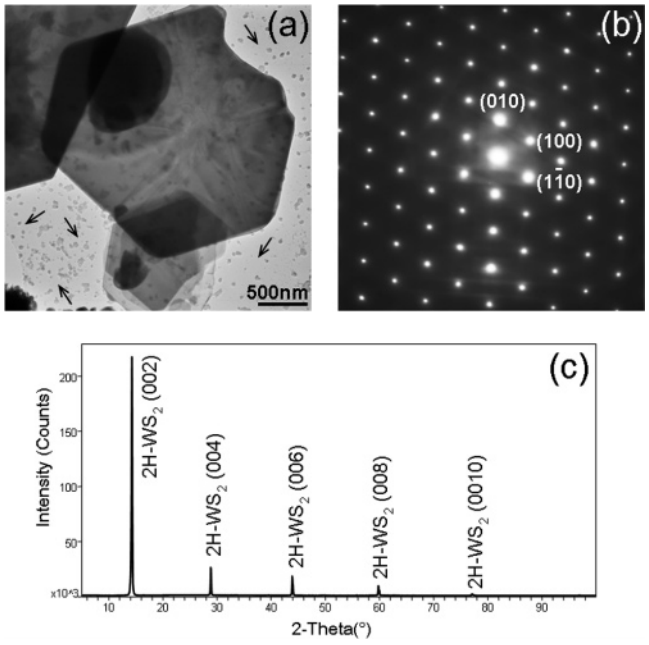

Figure 2. (a) TEM image showing WS_2 thin films and nanoparticles. (b) Selected area electron diffraction pattern of WS_2 thin films in the *c*-axis orientation. (c) XRD spectrum of the films deposited on a slide in water, which was produced by parallel basal planes of 2H-WS_2.

emission gun to provide a complete coherent electron source and nanometer-sized probe for nanostructure analyses.

The TEM observations showed that micron-sized thin films/flakes of WS_2 were produced along with a number of nanoparticles, as indicated by arrows in Figure 2a. Selected area electron diffraction patterns were indexed according to 2H-WS_2 phases with *c*-axis orientation, as shown in Figure 2b. Therefore, the normal direction of the films is parallel to the *c*-axis. The thickness of the films was measured to be less than dozens of nanometers via TEM. Considering film microstructure and thickness, it appears that pulsed laser irradiation results in the delamination and fracture of WS_2 targets at a nanometer level. Figure 2c presents the XRD spectrum of the films deposited on substrates under water, which is also indexed to 2H-WS_2. Only the (00*l*) peaks appear in the pattern because the 2H-WS_2 (002) basal planes were stacked parallel to the substrate surfaces.

The films that floated consisted of WS_2 nanoparticles, as shown in Figure 3a. They were quite evenly dispersed and exhibited little agglomeration. The nanoparticle diameters were measured to be around 10 nm, and the thickness was approximately 10 nm or less. Figure 3b and c shows the high-resolution TEM images taken from the nanoparticles, where the {100} lattices of 2H-WS_2 are directly visible. Therefore, WS_2 nanoparticles and thin films with the normal direction in the *c*-axis can be produced by pulsed laser irradiation of WS_2 targets in water. They were deposited on substrates with the basal planes lying parallel to the surface.

The mechanism of making these nanomaterials may involve two processes. The first process is laser-induced thermal shock. Stresses produced by thermal shock were not relieved by melting and would finally lead to cracking and flake detachment. This process has been termed "exfoliation" by Kelly et al.[14] It is highly likely that laser exfoliation caused the delamination of nanosized layer-structured WS_2 materials. The second process follows delamination where the ejected WS_2 thin flakes and fragments were hit by shock waves produced during subsequent pulses, causing further diminution of particles. In addition, the energy of two 248 nm photons (~10 eV) is significantly higher

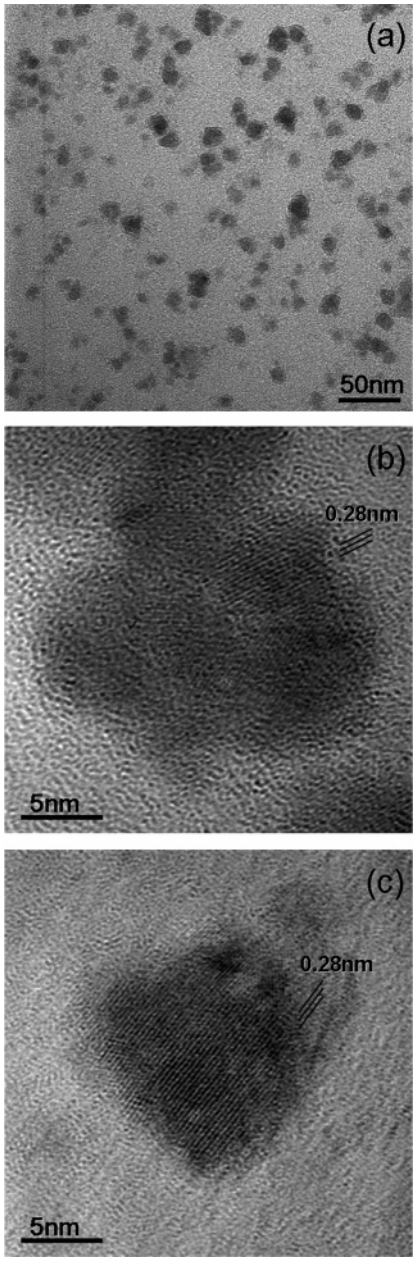

Figure 3. (a) Dispersed nanoparticles as observed by TEM. (b and c) High-resolution TEM images of nanoparticles showing the {100} lattices of 2H-WS_2.

than the dissociation and ionization thresholds of water molecules (~6.5 eV).[15] Therefore, the two-photon excitation of H_2O under UV radiation leads to the generation of reactive water radicals, such as OH_{aq} and H_{aq} radicals, hydrated electrons (e_{aq}^-), and H_3O^+ ions.[16] Those photodissociation products can act as intercalants of 2H-WS_2 materials and help the exfoliation of WS_2 in water.

Fullerene or fullerene-like structures were not detected in the present study. Their absence is likely related to the short duration of heating during the ablation/quench cycle. There were several differences compared to the previous studies: (1) Water was used as the liquid medium in place of organic/sulfide solvents, and hence, water acted as a cooling and retarding medium rather than a precursor for reaction. (2) A compact WS_2 disk was used as the laser target in place of sulfide powders/suspensions, facilitating heat dissipation in the larger solid. (3) A KrF excimer laser (248 nm) was used in place of a Nd:YAG laser (532 nm wavelength), and shorter wavelength lasers generated less

heating on the target impact. These factors acted together to preserve layered nanosized fragments instead of producing fullerene-like structures.

In conclusion, water was used as an environmental friendly medium for the synthesis of hexagonal WS_2 nanoparticles by the pulsed laser method. The use of water, UV lasers, and large WS_2 targets prevented the nanoparticles from restructuring into inorganic fullerenes, which were observed in research using hydrocarbon solvents, longer wavelength lasers, and dispersed powder targets. Fairly good dispersion of nanoparticles was observed, which suggests large surface areas are available for chemical reactivity. The materials collected on glass substrates were oriented with the 2H-WS_2 basal planes parallel to the substrate surface.

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