Design of Carbon-Silicon hybrid nanostructures

Lisnyak V.V.[1,2], Mussabek G.K.[2,3], Zhylkybayeva N.Zh.[3], Baktygerey S.Z.[2,3], Orishko A.Yu.[1], Zaderko A.N.[1]

[1] Taras Shevchenko National University of Kyiv, Volodymyrs'ka Street, 64/13, Kyiv 01601, Ukraine. E-mail: lisnyak@chem.univ.kiev.ua
[2] Institute of Information and Computational Technologies, 125, Pushkin Str., 050000 Almaty, Kazakhstan
[3] Al-Farabi Kazakh National University, 71, Al-Farabi Ave., 050040 Almaty, Kazakhstan

INTRO: Silicon nanoparticles (Si NPs) are the objects of increased scientific interest to be used as new electronic probes. Here, we focused on preparing Si@C hybrids; they will be based on structured Si NPs of 7–20 nm. The desired result, the decorated Si NPs with small carbon NPs, attracts attention. The nanohybrids when carbon NPs formed at the interface and edge dislocations of nanosilicon are unique. They have great potential for creating sensor-type devices. To prepare silicon hybrid nanostructures to be used as a probe, we elaborated a special synthesis method.

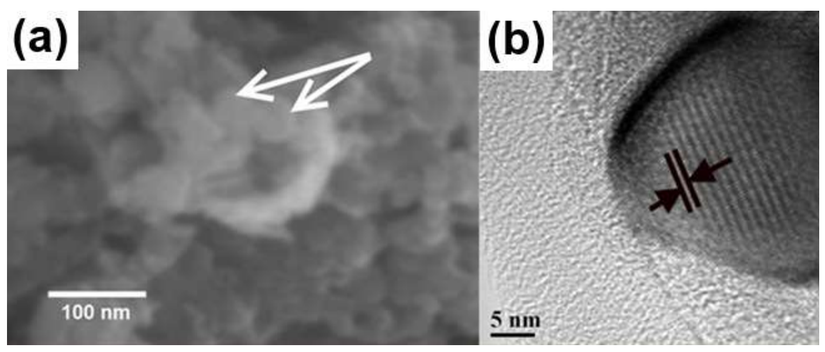

Fig. 1 SEM (a) and TEM (b) micrographs: Si@C hybrids.

Silicon nanopowder (Si NPD) was prepared from (80%Al–20% Si) alloy by acid etching. After the etching, the resulting silicon NPD was filtered and dried at 120 °C. To create the Si@C interface, the prepared Si NPs weighing 100 mg were treated with polyvinylpyrrolidone solution (1 g) in EtOH (100 ml) under sono-mechanical activation. The prepared powder was dried at 75 °C for 12 hours. To obtain Si NPD, the samples were placed in a fluidized bed furnace and calcined at 400 °C and 500 °C in an Ar for 4 h. An unstructured C of 0.5 to 2-nm thick covers the prepared Si NPs. It keeps the crystallinity and integrity of the Si grains (Fig. 1b). With the surfactant, large micelles were formed from the pseudospherical silicon NPs (d ≤ 50 nm). The colloids were centrifuged at 5000 rpm, and the sediments were dried for 12 h at 120 °C. Further, the claimed carbonization led to the thermal decomposition of the ethoxylate shell forming the Si@C hybrids of 5 to 100 nm in size, SEM showed 100-nm aggregates (Fig. 1a). They are composed of Si NPs of 20-50 nm. A layer of unstructured C forming a stable layer on the surface of Si crystalline grains; the layer thickness ranges from 0.5 to 2 nm. The C layer on Si keeps the crystallinity and integrity of the original Si grains (Fig. 1b). For the structured Si NPs, the interplanar distances (Fig. 1b) are 0.31 nm; they are attributed to the Si(111) plane forced to the NP surface. Fig. 1b shows C layers of a low degree of crystallinity. The 3D structuring of thin C layers for the Si/m-C interface is probably impossible. From the TEM data, the formation of a Si-C interface occurs, but, for the obtained pseudo-spherical NPs (20 nm in diameter), it is impossible to assert that the formation of multilayers is based on a 2D carbon nanostructure is realized. AFM shows that the NPs diameter is from 20 to 40 nm. PXRD patterns of the agglomerated nanohybrids (Fig. 2) showed a halo with a maximum at 25° attributed to amorphous C. For all patterns, both structured and unstructured components are presented. After carbonization, the peaks of crystallographic reflections for the elementary Si lattice are seen. The broadening of diffraction peaks indicates an ultra-dispersed state of nanohybrids. Fig. 4 shows the formation of 2D carbon nanostructures. The rapid pyrolysis at 500 °C allows small clusters to grow larger with subsequent growth of large 2D ellipsoids (Fig. 3). A STEM-HAADF micrograph (Fig. 3(insert)) shows the adhesion of Si NPs by a Si-C-Si interface. Here Si NPs are decorated with a homogeneous set of nanostructured C particles of about 5 nm. They are semi-amorphous; the thickness of their interface layer is below 1 nm and performs an auxiliary function, regulating the size of NPs, preventing aggregation. A surface interface performs a passivation function, preventing deep amorphization during oxidation of carbon NPs, and plays the role of a spacer between amorphous C and structured Si NPs, forming the nanohybrids. A large curvature of the surface of Si@C hybrids changes the surface bond topology that will lead to a change in chemical potentials, so the ability of hybrids to adsorb different gases should increase. Upon NH_3 exposure, the interaction between gas and the hybrid results in the change of the sensor resistance, so we evaluate the selectivity of the Si@C hybrids sensors (Fig. 4). The sensing responses to 1,000 ppm of methanol and ethanol were measured at RT and compared with that for from 1 to 10 ppm NH_3. The sensors are more sensitive upon exposure to 10 ppm NH_3 than to alcohol gases. Our data reveal that the prepared hybrids as sensor materials have high selectivity towards NH_3 in the alcohol/ammonia binary mixed gases. The hybrids show a linear response in the range of 1-20 ppm NH_3, from 5 to 40 r.u.

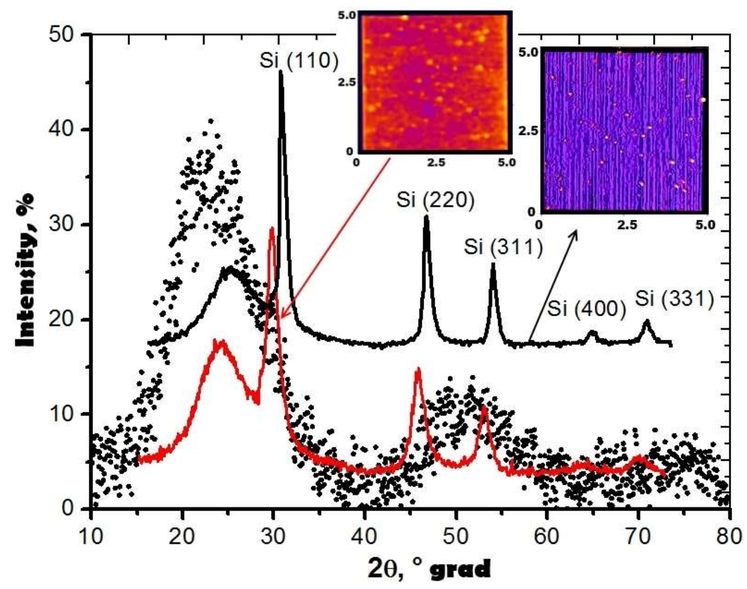

Fig. 2 PXRD patterns: Si NPs (black line) and nanohybrids (red line); points: before carbonization. Inserts: AFM images of Si NPs and C-Si nanohybrids, scale in mkm.

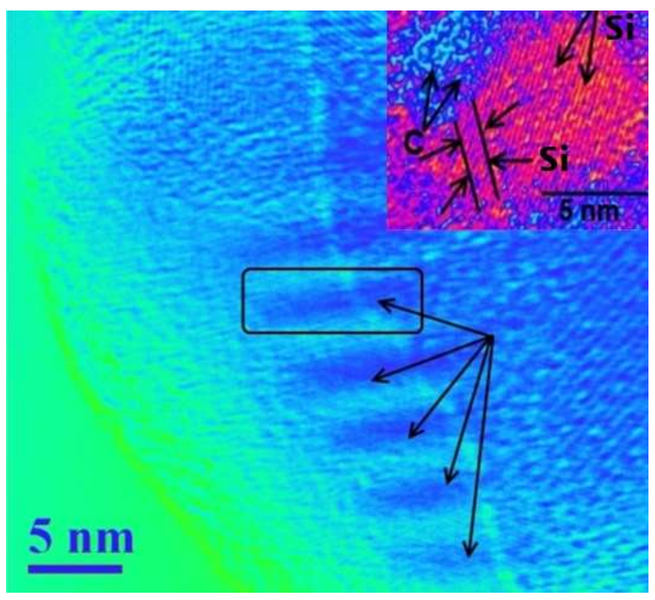

Fig. 3 TEM micrograph of nanohybrids and STEM-HAADF insert.

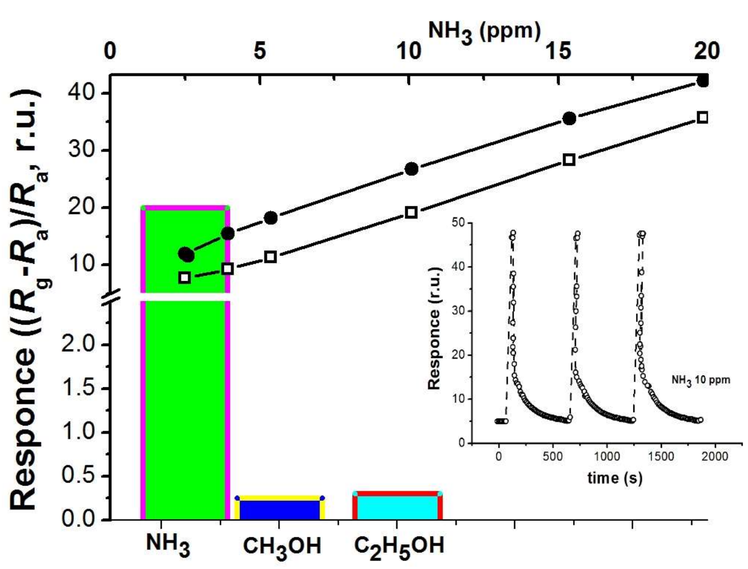

Fig. 4 Response towards NH_3, response comparison, and the response of hybrid sensors in alcohol/ammonia binary mixed gases.

Conclusions: Here we showed the possibility of synthesizing nanopowders of Si@C hybrids based on structured silicon with a particle size of 7–20 nm by the chemical-thermal method using inexpensive and available silicon NPDs. Hybrids are obtained from a polyvinyl pyrrolidone precursor. The obtained hybrids are formed by crystalline pseudo-spherical silicon NPs, which are decorated with carbon NPs, mainly unstructured, 2D, and also amorphous. It is shown that by the proposed method it is possible to achieve the desired result – decorating Si NPs with small carbon NPs. The structural features of nanohybrids and the shown special character of the formation of carbon nanoparticles at the interface and edge dislocations of nanosilicon are unique. The proposed method has great potential for creating sensor-type devices with silicon in hybrid nanostructures as a probe.

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