New AuNPs-Si@C probes for analysis applications

Lisnyak V.V.[1,2], Mussabek G.K.[2,3], Zhylkybayeva N.Zh.[3], Baktygerey S.Z.[2,3], Lavska V.O.[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 promising candidates for a diverse range of applications, in part because of their tunable photoluminescence, bio-compatibility, and low toxicity. We can adapt them to changes in the surroundings and are the objects of increased scientific interest to new probes. Here, we focused on preparing AuNPs-Si@C hybrids; they will be based on structured Si NPs of 7–20 nm. The AuNPs decorated Si NPs attracts much attention. The probes with AuNPs are unique for SERS applications since they have considerable potential to be used for creating a new sensor probe. To prepare AuNPs-Si@C hybrids, we elaborated a reasonable approach.

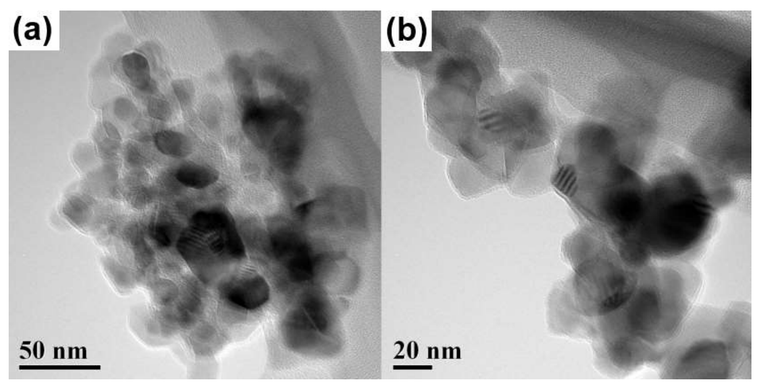

Fig. 1 (a, b) TEM micrographs: Si@C hybrids.

Preparation and characterization: Silicon nanopowder (Si NPD) was prepared by acid etching of (80%Al–20% Si) alloy. The Si@C interface were prepared with polyvinylpyrrolidone solution calcined at 400 °C in an inert medium. Organic 2-nm-thin carbon layer covers the Si NPs, keeping the surface of the Si grains in shell (Fig. 1b). The carbonization is caused the formation of the Si@C hybrids of 5 to 25 nm in size, SEM showed their aggregation (Fig. 1b). 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 protect the surface of Si shells (Fig. 1b). The interplanar distances (Fig. 2) are about 0.3 nm; they are attributed to the Si(111) plane. Fig. 2 shows C layers of a low degree of crystallinity. The formation of a Si-C interface occurs, which is based on a 2D carbon nanostructure. A STEM-HAADF (Fig. 2, insert) shows a Si-C-Si interface. The thickness of their interface layer is below 1 nm and it regulates the size of NPs, preventing aggregation 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 molecules and ions should increase. AFM shows the 50 to 150-nm Au NPs prepared by phytosynthesis [1] and modified the hybrid. Au NPs, as a substrate, activate PR and usually increase the intensity of the SERS by several orders of magnitude from 10^3 to 10^6. However, the signal sensitivity in the case of spherical gold nanoparticles is still insufficient to detect trace amounts of biomolecules and/or interactions between biomolecules. Testing the potential of the created nanohybrids was performed by determining the presence of avidin molecules in real time.

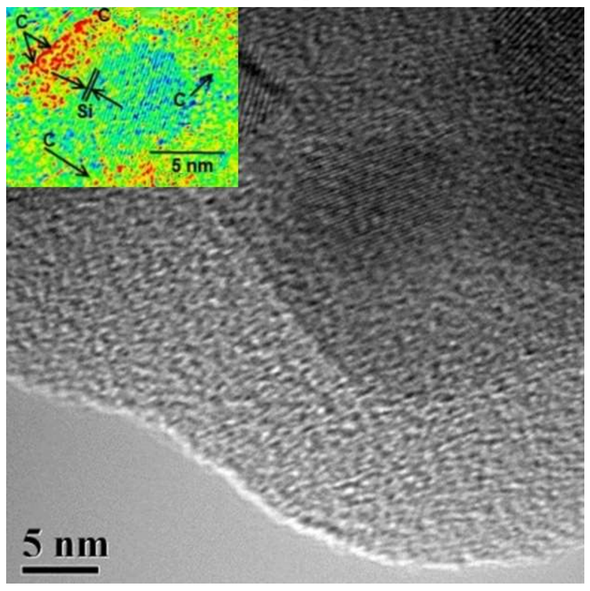

Fig. 2 TEM micrograph of nanohybrids and STEM-HAADF insert.

Analysis Methods: For this purpose, a complex between hybrids and biotins for the determination of avidin was prepared according to the following procedure: (i) purified tin-indium oxide (TIO) glass was placed in a nanocolloid, removed after 24, purged with argon, and dried. The functionalized surface of the AuNPs-Si@C-TIO was reacted with 0.1 mg/ml of 3-sulfo-N-hydroxysuccinimide biotin in 0.1 M phosphate buffer, washed and dried by the same procedure. Next, a drop (50 µl) containing 1000, 100, 10 and 1 µg/ml of avidin solutions was pipetted onto pre-prepared dried hybrids and detected immediately (after 2 min). To record the spectra, the laser (785 nm) was focused (20 ×) using a 0.4 NS lens (Fig. 4). The laser intensity was about 1.2 mW/cm, and the size of the focal spot was 5 µm, the spectral resolution was 1 cm^{-1}, and the integration time did not exceed 600 s. The studies were performed using a confocal Raman microscope (Renishaw, RM 2000). Biotin has a very high affinity for binding to avidin, a known protein in egg white. The bond between biotin and avidin opens up new possibilities for the detection of avidin and the detection of different concentrations of avidin in real-time by the band at ~648 cm^{-1} that belongs to the biotin-avidin complex. All recorded SER spectra can be reproduced on different parts of the substrate of the created chip with a standard deviation <5%. As the avidin concentration decreases from 1 mg/ml to 1 µg/ml, the signal intensity corresponding to the complex with the biotin and avidin ligand progressively decreases (Fig. 4). The signal obtained using 1 µg / ml avidin is difficult to recognize, but it can be clearly identified using a longer integration time. These results indicate that nanohybrids containing gold nanoparticles can efficiently and real-time detect avidin molecules up to 0.01 mg/ ml using its highly sensitive biotin-responsive activity and SERS.

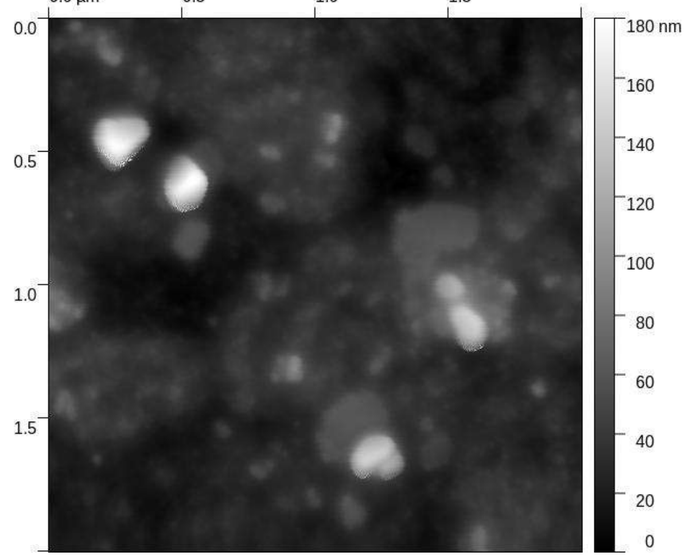

Fig. 3 AFM images of AuNPs Si@C nanohybrids

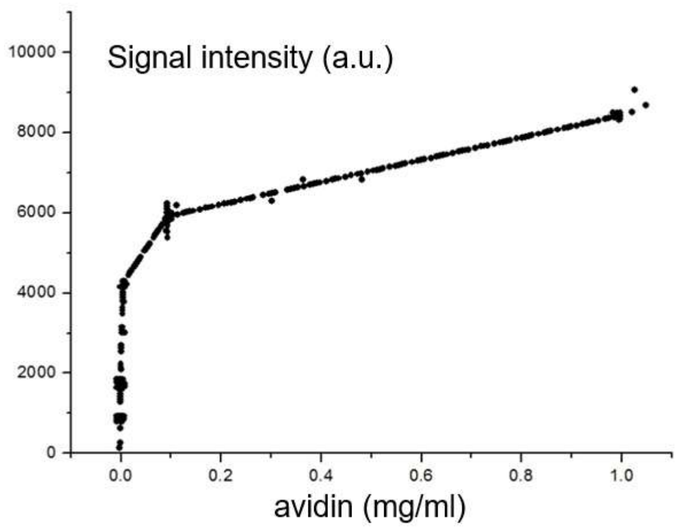

Fig. 4 SER intensity ~648 cm^{-1} versus avidin concentration.

Conclusions: Specific synthetic methods have been developed, which provide for the production of effective hybrid materials for biocompatible chips for rapid diagnostics of biomolecules. For the first time, a chip that is based on hybrid nanomaterials containing phytosynthesized Au NPs was developed. The studies of hybrid materials have shown their high response rates for biomolecules. Effective determination of avidin using responses in surface-enhanced Raman spectra for a chip prepared with Au NPs is shown. The practical value of the results is in the creation of qualitatively new hybrid nanomaterials to be used for the quantitative analysis of biomolecules.

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