BORONIC ACID MODIFIED SILVER NANOPARTICLES FOR SACCHARIDE RECOGNITION

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Determination of saccharides is important in many respects. Glucose plays a pivotal role in various metabolic processes. The boronic acid moiety represents a widely used recognition element for the determination of saccharides. Boronic acids have been known for over 100 years, but the interaction between boronic acids and diols has not been recognized until the 1950s (ref. 1).

This work deals with preparation of silver nanoparticles modified by 4-mercaptophenylboronic acids (Fig.1) and their interactions with selected saccharides (D(+)-glucose, D(+)-saccharose, D(+)-fructose, D(+)-lactose) (Fig.2). Metal nanoparticles have attracted considerable attention both fundamentally and technologically because of their unique physical and chemical properties One of the most fascinating aspects is the manner how they interact with light.

Nanoparticles were prepared by reduction of $AgNO_3$ by EDTA (ref. 2) and they were characterized by variety of techniques including electron microscopy, absorption spectroscopy and surface enhanced Raman spectroscopy (SERS). The latter method is based on collective plasmon oscillation of ametal surface electrons that causes enormous amplification of Raman scattered light intensity.

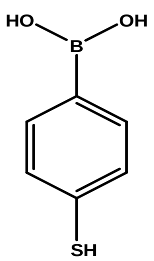

Fig. 1: Structure of 4-mercaptophenylboronic acid

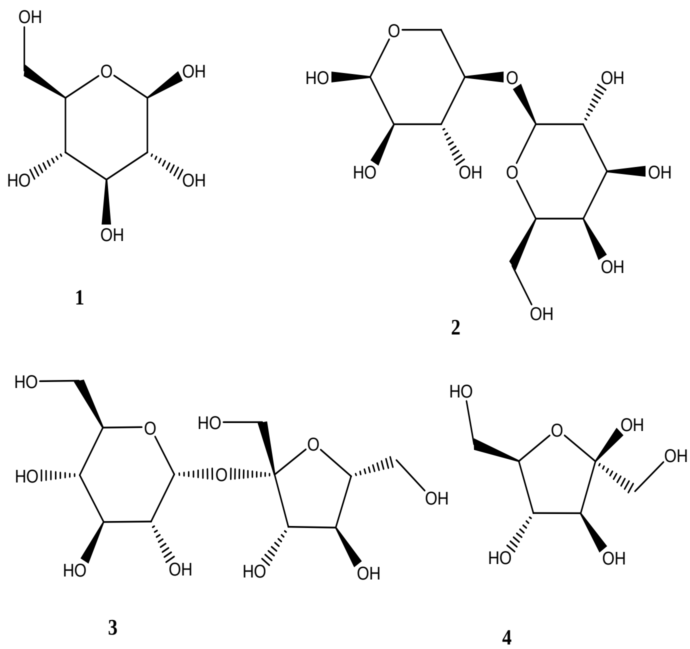

Fig. 2: Structure of used saccharides.

An influence of increasing ionic strength (ref. 3) of the silver nanoparticles solution on SERS intensity was studied. Partial aggregation of nanoparticles led to increasing absorbance at about 785 nm and consequently to increasing of SERS intensity (measured using laser excitation at 785 nm). Ionic strength was increased by 1 $mol \cdot L^{-1}$ calcium chloride and UV/Vis absorption spectra and SERS spectra of 3-mercaptopropanoic acid immobilized on the silver surface were recorded and evaluated.

Direct immobilization of 4-mercaptophenylboronic acid was confirmed by SERS spectroscopy after aggregation of silver solution nanoparticles as mentioned above. Signals of 4-mercaptofenylboronic acid SERS spectrum were assigned by *ab initio* calculation and wavelengths of B-OH vibrations were confirmed by experiment with deuterated water. Optimal pH for interaction of modified nanoparticles was tested. Interactions of modified nanoparticles with saccharides were monitored by Raman spectroscopy. Signal of γ (C-B) vibration at 635 cm^{-1} disappeared with increasing molar ratio of glucose (Fig. 3).

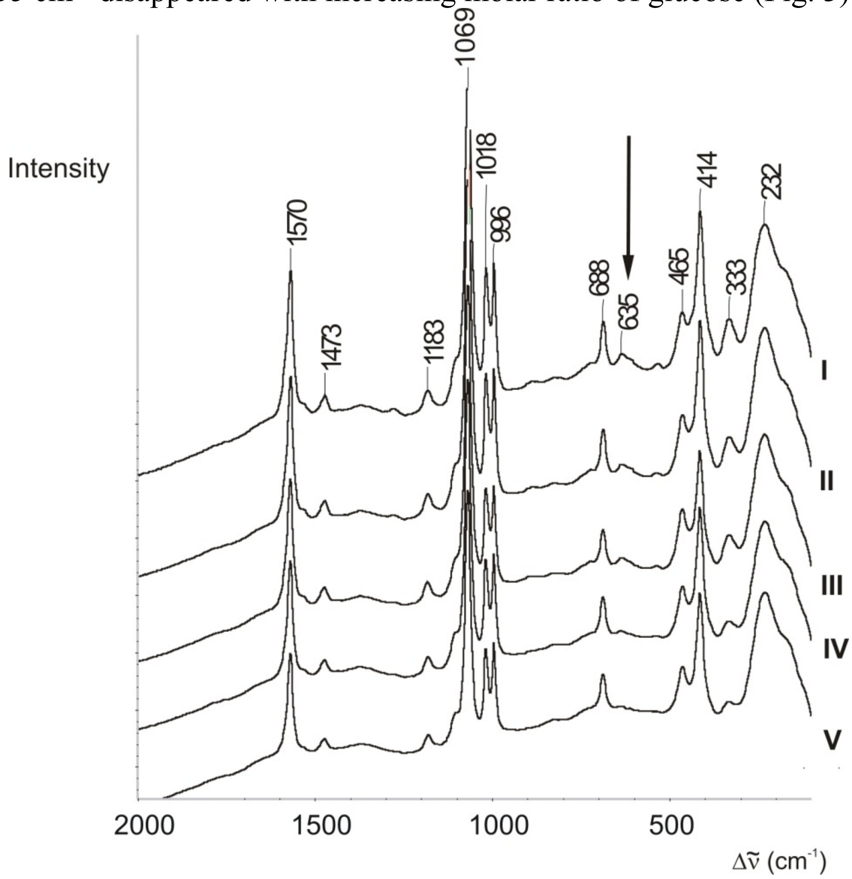

Fig. 3: SERS spectra modified nanoparticles with D(+)-glucose. Molar ratio of the 4-mercaptophenyl boronic acid towards glucose was 0 (spectrum **I**), 50 (spectrum **II**), 100 (spectrum **III**), 250 (spectrum **IV**), and 500 (spectrum **V**).

Spectra showed no selectivity of saccharides interaction with modified nanoparticles. In the next step, we would like to focus on better reproducibility this complicated measurements and use to obtain data for estimating stability constants for complex modified silver nanoparticles and saccharides.

References:

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