Decoding fluorescence excitation-emission matrices of carbon dots aqueous solutions with convolutional neural networks to create multimodal nanosensor of metal ions

O.E. Sarmanova*[1,2], G.N. Chugreeva[1], K.A. Laptinskiy[2], S.A. Burikov[1,2], S.A. Dolenko[2], T.A. Dolenko[1,2]

[1]Department of Physics, Moscow M.V. Lomonosov State University
[2]Skobeltsyn Institute of Nuclear Physics, Moscow M.V. Lomonosov State University

*oe.sarmanova@physics.msu.ru

Problem statement

The problem of sensing multiple environmental parameters (temperature, pH, ionic content) is extremely urgent. Nanoparticles (NP) with intense stable photoluminescence (PL), depending on environmental parameters, are often used as sensors. Unfortunately, the analysis of their PL spectra is hampered by the lack of analytical models adequately describing the influence of environmental parameters on the spectra of NP. Therefore, it is reasonable to use data-driven approaches to elaborate such sensors.

Research objects

Carbon dots (CD) obtained by hydrothermal synthesis from citric acid and ethylene-diamine.

CD aqueous solution with concentration of 5 mg/L
Size: 17.3±0.4 nm
ζ-potential: -13.3±0.7 mV

To study CD aqueous solutions in the presence of ions, the aqueous solutions of $Cu(NO_3)_2$, $Ni(NO_3)_2$, $Cr(NO_3)_2$ salts were used, concentrations ranging from 0 to 5 mM.

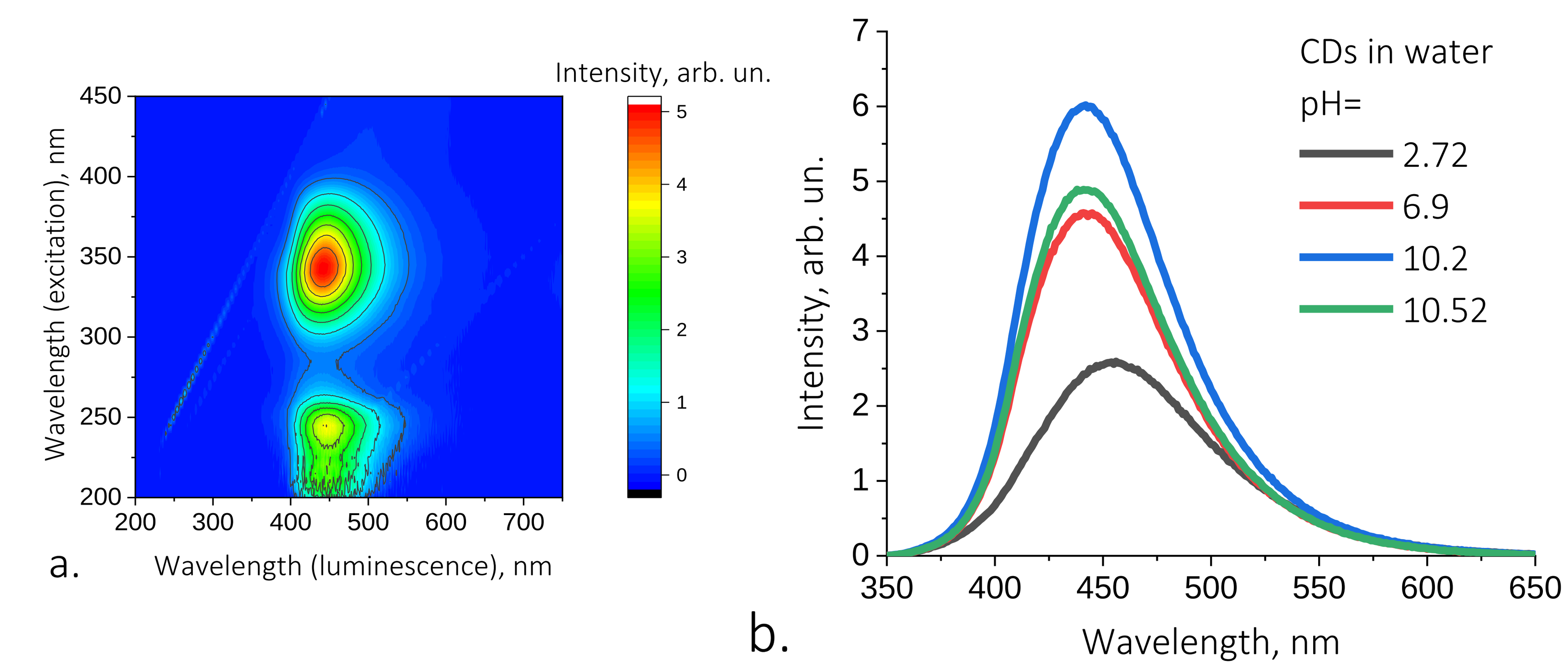

Fig.1. a) PL excitation-emission matrix (EEM) of the CD aqueous solution with concentration of 5 mg/L. b) PL spectra of CD aqueous solution at different pH.

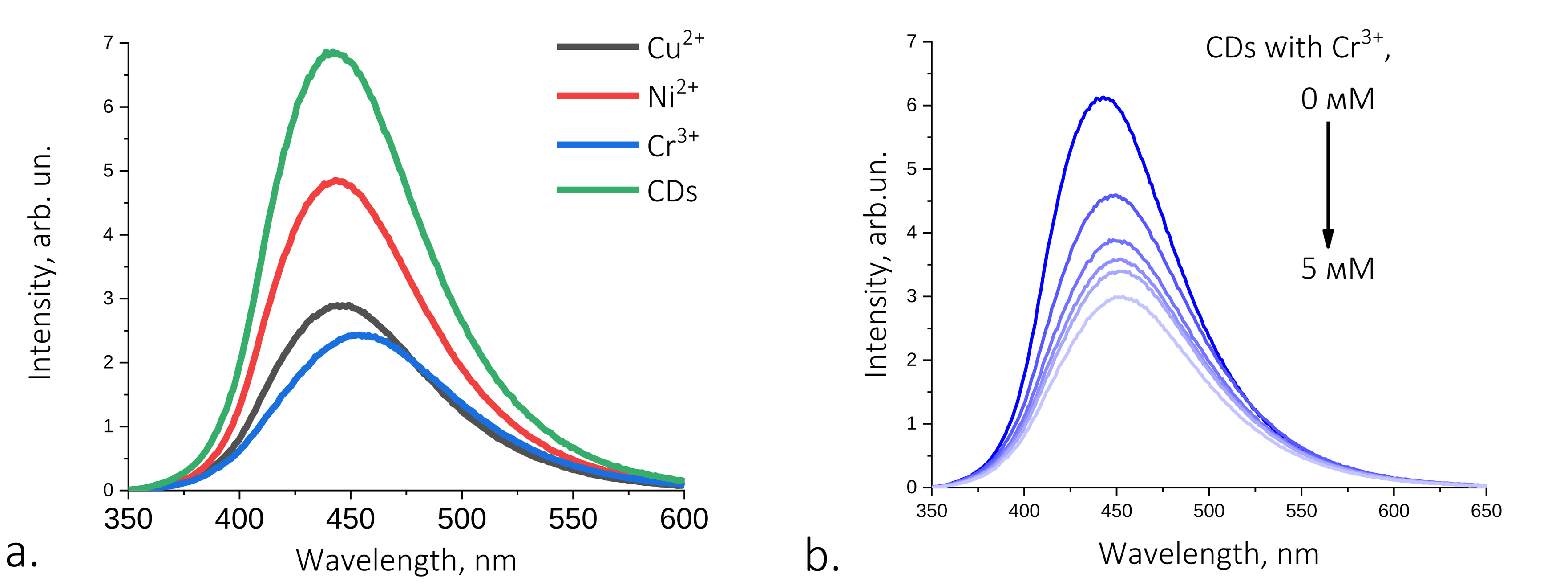

Fig.2. PL spectra of the CD aqueous solutions: a) with $Cu(NO_3)_2$, $Ni(NO_3)_2$, $Cr(NO_3)_2$ (concentrations of CD and cations are 5 mg/L and 5 mM, respectively); b) with $Cr(NO_3)_2$ salt (CD concentration is 5 mg/L, Cr^{3+} concentration varied from 0 to 5 mM). Excitation at 350 nm.

Database

The PL excitation-emission matrices (Fig.1a) of the aqueous mixtures-solutions containing CD, metal cations Ni^{2+}, Cu^{2+}, Cr^{3+} and NO_3^- anions.

Signal excitation: from 250 to 450 nm with 5 nm increment.
Signal registration: from 250 to 750 nm with increment of 1 nm.
Shimadzu RF-6000 spectrofluorimeter

Total: 1000 patterns

- 27 single-component solutions (containing one type of cation)
- 240 two-component solutions (two types of cations)
- 732 three-component solutions (three types of cations)

CD concentration: fixed 5 mg/L
Ni^{2+}, Cu^{2+}, Cr^{3+} concentration: from 0 to 5 mM, 0.55 mM increment
NO_3^- concentration: from 0 to 34.65 mM depending on the concentration of cations

Convolutional neural networks (CNN)

- For model's parameters see Fig.3.
- Train/validation/test split: 7/2/1;
- 5-fold cross-validation;
- 3 initializations of CNN weights;
- Stopping criterion: mean squared error on the validation set did not decrease for 100 epochs.

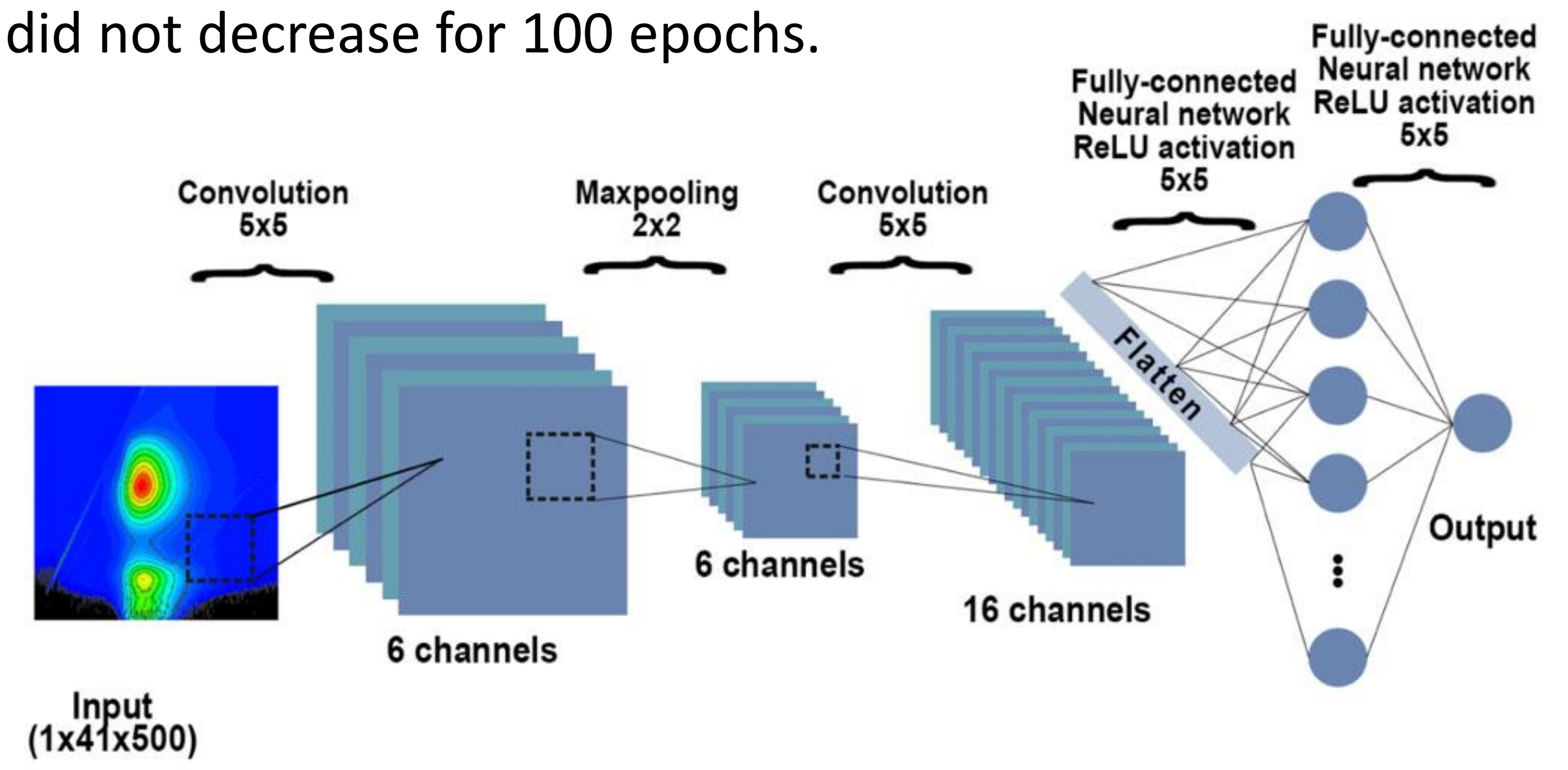

Fig. 3. 2D-CNN architecture.

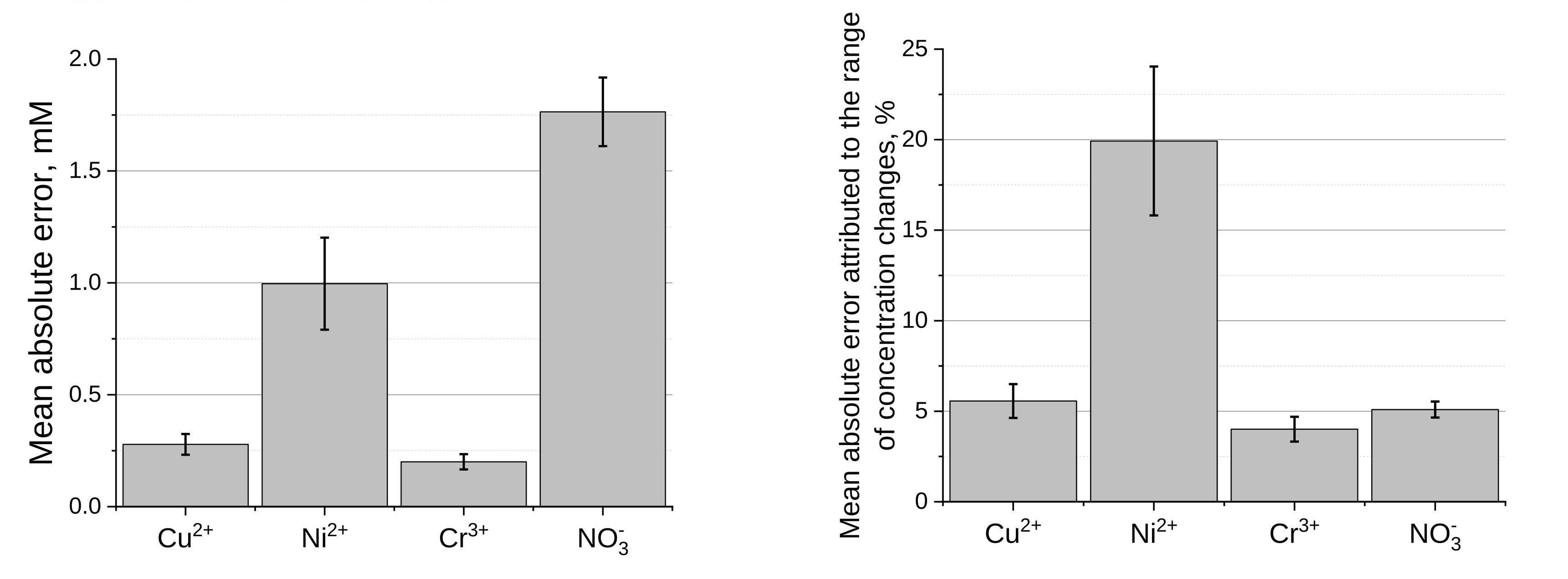

Fig.4. The mean absolute error (MAE) of determination of the concentration of ions (left) and MAE divided by the range of concentration changes (right).

Conclusion

Using 2D CNN allows to determine the concentrations of heavy metal cations Cu^{2+}, Ni^{2+}, Cr^{3+}, NO_3^- anions and pH value of aqueous solutions with MAE of 0.29 mM, 0.96 mM, 0.22 mM, 1.82 mM and 0.05, respectively. The resulting errors satisfy the needs of monitoring the composition of technological and industrial waters.

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