Mendeleev Communications

Mendeleev Commun., 2025, **35**, 553–554

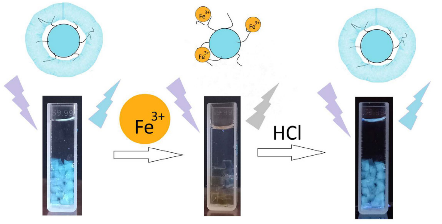
Photoluminescent hydrogel/carbon quantum dots nanocomposite for Fe^{3+} ions sensing: selectivity and recovery

Anastasia M. Borodina, Sergei V. Kostromin and Sergei V. Bronnikov*

Institute of Macromolecular Compounds, Branch of B. P. Konstantinov Petersburg Nuclear Physics Institute
of National Research Centre ‘Kurchatov Institute’, 199004 St. Petersburg, Russian Federation.
E-mail: sergebronnikov@gmail.com

DOI: 10.71267/mencom.7756

Polyacrylamide-based hydrogel filled with carbon quantum dots (PAA@CQDs) exhibiting intensive photoluminescence (PL) under UV irradiation was prepared. The exceptional capability of the Fe^{3+} ions to quench PAA@CQDs PL in aqueous solution was found. The PL recovery after repeated quenching was detected when hydrochloric acid was used as a regenerant, thus ensuring the PAA@CQDs reusability as a chemosensor for the Fe^{3+} ions detection in aqueous media.



Keywords: carbon quantum dots, fluorescent hydrogel, photoluminescence quenching, iron(III) sensing, photoluminescence recovery.

The Fe^{3+} ions are known to control many physiological processes, including oxygen transport and cellular metabolism. Meanwhile, a surplus of the Fe^{3+} ions may be harmful for human organism because of their gradual accumulation in tissues and organs.[1] According to the World Health Organization recommendations, the Fe^{3+} ions concentration in drinking water should not exceed 0.3 mg dm^{-3}. Therefore, regular monitoring the Fe^{3+} ions concentration in water sources is necessary. Among analytical methods, fluorescence spectrometry appears to be an attractive technique for metal ions sensing because of its high sensitivity, diverse selectivity and easy operation.[2]

Carbon quantum dots (CQDs) represent a novel class of the carbon nanoparticles family possessing attractive features. They exhibit intensive tunable photoluminescence, excellent photo- and chemostability, biocompatibility and non-toxicity. These properties enable effective application of CQDs in different areas including optical and optoelectronic devices, biomedicine, biosensors and drug delivery systems.[3–5] In addition, water-soluble CQDs can be used as chemosensors for detection of heavy metal ions and organic compounds.[6] The disadvantages of CQDs include their predisposition to aggregation in aqueous media, which results in the reduction of their PL. The way to solve this problem is the CQDs embedding into a polymer matrix, that should retain PL properties of CQDs and be permeable to detectable ions. In this aspect, polymeric hydrogels (HGs) seem to be suitable matrices for CQDs. The HG@CQDs nanocomposites were reported to be successfully used for detecting metal ions in water solutions.[7–9]

Recently, we have reported on the CQDs synthesis *via* citric acid pyrolysis.[10] The synthesized CQDs[†] were afterwards dispersed into a polyacrylamide (PAA)-based HG. As a cross-linker, *N*,*N*′-methylenebis(acrylamide) was used. We have revealed that PL of the PAA@CQDs nanocomposite was quenched in aqueous $FeCl_3$ solutions because of the non-PL PAA@CQDs + Fe^{3+} complex formation. Therefore, we concluded that the PAA@CQDs nanocomposite is an appropriate material for the Fe^{3+} ions detection in aqueous media.[11] The limit of the Fe^{3+} ions detection was found to be 0.124 μM (for details, see Online Supplementary Materials) ensuring a good detection capability of PAA@CQDs as compared with the available literature data (for details, see Table S1 in Online Supplementary Materials). We found that PL intensity of PAA@CQDs depends on the acidity of the aqueous solution. Therefore, we measured PL of the PAA@CQDs samples in solutions with pH varying from 2 to 11. The maximum PL intensity was observed at pH 7.

We characterized PAA@CQDs *via* various techniques but some valuable aspects of its performance as a chemosensor, *viz.*, selectivity and recovery, still have not been investigated. Here, we fill this gap.

First, we studied the capability of the PAA@CQDs nanocomposite to sorb the ions of different metals (Co^{2+}, Cr^{6+}, Pb^{2+}, Ba^{2+}, Ag^{1+}, Hg^{2+}, Sr^{2+}, Cd^{2+}, Ca^{2+}, Fe^{2+}, Fe^{3+}, Ni^{2+}, Mg^{2+} and Cu^{2+}) in aqueous solutions. We have separately prepared the solutions containing one type of the ions listed above at the concentration of 600 μM. The PAA@CQDs samples were cut into cubic pieces (edge size was *ca.* 3 mm), placed in the solutions and kept there for 1 h. Afterwards, the PL peak intensity of the immersed samples was measured under UV irradiation (λ_{ex} = 340 nm). As Figure 1 illustrates, only the Fe^{3+} ions have completely quenched PL of PAA@CQDs, whereas the other ions have poorly decreased the initial PL intensity. These results indicate the high selectivity of PAA@CQDs for Fe^{3+} ions sensing which makes it possible to use PAA@CQDs as an effective chemosensor for the Fe^{3+} ions detection in aqueous media.

[†] A portion of citric acid monohydrate was subjected to pyrolysis in a muffle furnace at 200 °C for 4 h. After synthesis and cooling to room temperature, the pyrolysis products were neutralized with 1M NaOH solution. To separate CQDs from by-products, the neutralized solution was dialyzed for 48 h. After dialysis, the CQDs solution was freeze-dried. The PL spectra were recorded using a RF-6000 spectrofluorimeter (Shimadzu, Japan). The measurements were performed between 300 and 700 nm at the 340 nm excitation wavelength.

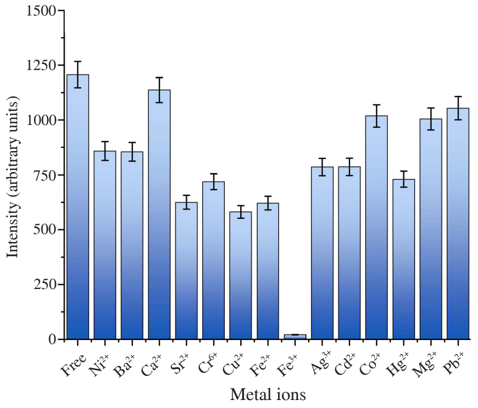


Figure 1 PL peak intensity of PAA@CQDs immersed in water solutions containing different metal ions.

Figure 2 illustrates PL quenching in the course of the Fe^{3+} ions sorption. Figure 2(*a*) shows transformation of the PL spectrum (λ_{ex} = 340 nm) of PAA@CQDs immersed in the $FeCl_3$ aqueous solution ([Fe^{3+}] = 250 μM) over time, whereas Figure 2(*b*) depicts the maximum PL intensity depending on the sorption time. Obviously, PL is quenched very rapidly (within 1 min) because of the strong interactions between the Fe^{3+} ions and functional groups of CQDs, resulting in the non-PL PAA@CQDs + Fe^{3+} complex formation.[11] This demonstrates high sensitivity and fast response of PAA@CQDs for the Fe^{3+} ions detection.

To evaluate the reusability of the PAA@CQDs + Fe^{3+} complex as a chemosensor, efforts have been made to restore its PL intensity after the Fe^{3+} ions sorption. Our attempts to use ascorbic acid[2,12] and sodium thiosulfate as reducing agents revealed that only 50% and 25% of the initial PL intensity, respectively, was achieved after reduction. Meanwhile, following the data reported by Budtova,[13] we have been more successful when using 0.1 M hydrochloric acid as a regenerant. Thus, the original PL intensity of PAA@CQDs + Fe^{3+} placed in the acid solution was restored to 86% in 90 min [Figure 3(*a*),(*b*)]. The use of the strong acid as a regenerant provokes the PAA@CQDs + Fe^{3+} complex dissociation and removal of Fe^{3+} ions from PAA@CQDs + Fe^{3+}. Following this way of restoring, we detected the PL recovery after repeated quenching in the $FeCl_3$ solution. Figure 3(*c*) demonstrates that PL intensity is considerably recovered (80%) after triple repeated PL quenching. This suggests the PAA@CQDs reusability for the Fe^{3+} ions detection, at least three times.

In summary, based on our results, we believe that the PAA@CQDs nanocomposite can be successfully used as a reusable selective fluorescent chemosensor for the Fe^{3+} ions detection in aqueous media.

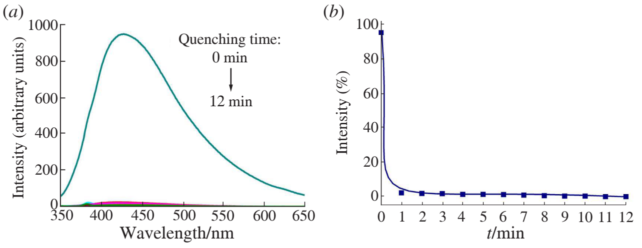


Figure 2 (*a*) PL spectra of PAA@CQDs immersed in $FeCl_3$ water solution at different Fe^{3+} sorption times; (*b*) PL maximum intensity as a function of Fe^{3+} sorption time.

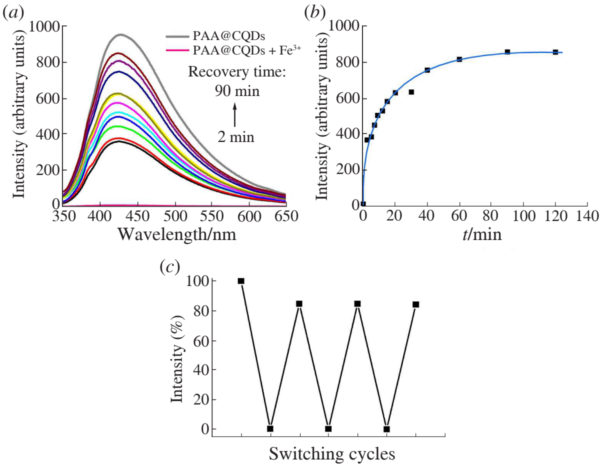


Figure 3 (*a*) PL spectra of PAA@CQDs + Fe^{3+} in the course of PL restoring; (*b*) PL maximum intensity *vs.* restoring time; (*c*) PL restoring after triple repeated quenching.

The work was carried out within the state assignment of NRC ‘Kurchatov Institute’ (project no. 124013000728-0).

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.71267/mencom.7756.

References

1 A. A. Belaidi and A. I. Bush, *J. Neurochem.*, 2016, **139**, 179; https://doi.org/10.1111/jnc.13425.

2 L. Guo, Y. Liu, R. Kong, G. Chen, Z. Liu, F. Qu, L. Xia and W. Tan, *Anal. Chem.*, 2019, **19**, 12453; https://doi.org/10.1021/acs.analchem.9b03143.

3 C. Ji, W. Xu, Q. Han, T. Zhao, J. Deng and Z. Peng, *Nano Energy*, 2023, **114**, 108623; https://doi.org/10.1016/j.nanoen.2023.108623.

4 B. Wang and S. Lu, *Matter*, 2022, **5**, 110; https://doi.org/10.1016/j.matt.2021.10.016.

5 S. Sharma, R. Kumar, K. Kumar and N. Thakur, *Mater. Sci. Eng., B*, 2024, **305**, 117414; https://doi.org/10.1016/j.mseb.2024.117414.

6 A. Hebbar, R. Selvaraj, R. Vinayagam, T. Varadavenkatesan, P. S. Kumar, P. A. Duc and G. Rangasamy, *Chemosphere*, 2023, **313**, 137308; https://doi.org/10.1016/j.chemosphere.2022.137308.

7 B. Sui, Y. Li and B. Yang, *Chin. Chem. Lett.*, 2020, **31**, 1443; https://doi.org/10.1016/j.cclet.2019.08.023.

8 Y. Wang, T. Lv, K. Yin, N. Feng, X. Sun, J. Zhou and H. Li, *Small*, 2023, **19**, 2207048; https://doi.org/10.1002/smll.202207048.

9 D. K. Kar, V. Praveenkumar, S. Si, H. Panigrahi and S. Mishra, *ACS Omega*, 2024, **9**, 11050; https://doi.org/10.1021/acsomega.3c07612.

10 S. Kostromin, A. Borodina, A. Podshivalov, D. Pankin, O. Zhigalina and S. Bronnikov, *Fullerenes, Nanotubes Carbon Nanostruct.*, 2023, **31**, 931; https://doi.org/10.1080/1536383X.2023.2224467.

11 A. Borodina, S. Kostromin, D. Pankin, A. Povolotskiy, E. Ushakova and S. Bronnikov, *Int. J. Environ. Anal. Chem.*, 2024; https://doi.org/10.1080/03067319.2024.2395485.

12 J. Zhao, Y. Zhang, M. Chen, Y. Ding, B. Liu, G. Yue, L. Guan, C. Wang, B. Liang and X. Li, *Opt. Express*, 2024, **32**, 12394; https://doi.org/10.1364/OE.519541.

13 T. Budtova, *J. Controlled Release*, 1998, **54**, 305; https://doi.org/10.1016/S0168-3659(98)00011-X.

Received: 3rd March 2025; Com. 25/7756