Detecting nitrite in water using a Metal Organic Framework paper-based analytical device

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1. Importance of detecting nutrients in coastal waters.

- Measuring the concentration of nutrients in coastal waters is essential for safeguarding against harmful algal blooms.
- However, transporting a water sample to a laboratory is limited by cost and availability of transport.[1]
- Microfluidic paper-based analytical devices (μPADs) provide accurate and sensitive data, are simple to fabricate and are made of inexpensive materials compared to other in-situ sensors.[1]
- Metal organic frameworks (MOFs) will be used as the detection material, as they can be rationally designed to target specific molecules such as nitrite (NO_2^-).

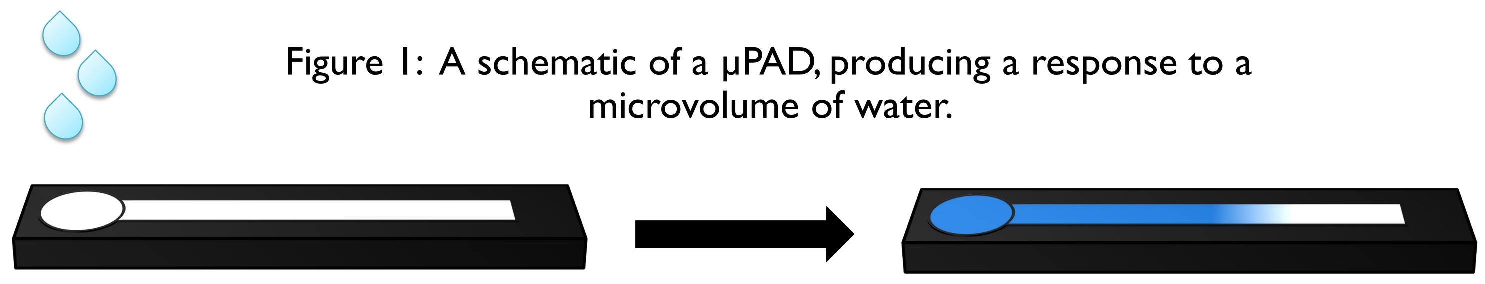

Figure 1: A schematic of a μPAD, producing a response to a microvolume of water.

2. Rh6G@UiO-66-NH_2 as a sensor for NO_2^-

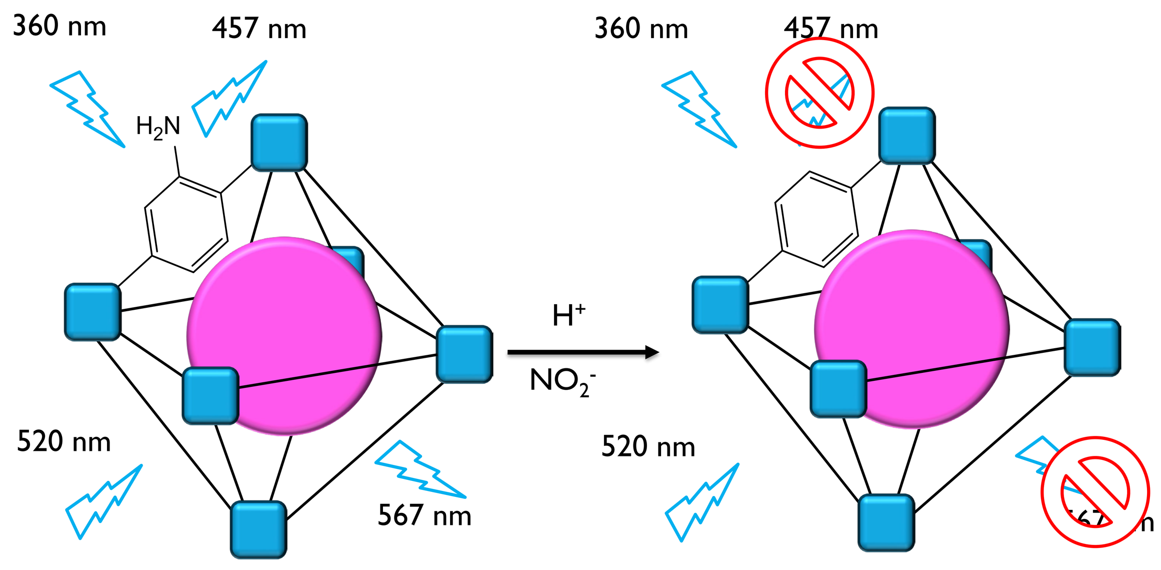

Figure 2: A schematic of the sensing mechanism of Rh6G@UiO-66-NH_2 towards NO_2^-.

Advantages of the dye@MOF according to the literature:[2]

- water stable framework across pH 1-10,
- dual fluorescence emission of MOF and dye,
- both components interact with NO_2^-,
- low limit of detection,
- good selectivity for NO_2^-.

5. UiO-66-NH_2 as a sensor for NO_2^-

- UiO-66-NH_2 can be used to detect NO_2^- through fluorescence quenching.[3]
- Immersing the paper in solutions of metal ions and ligand may be a better of growing the MOF.[4]
- However, this method is not viable for the dye@MOF due to its synthesis method.

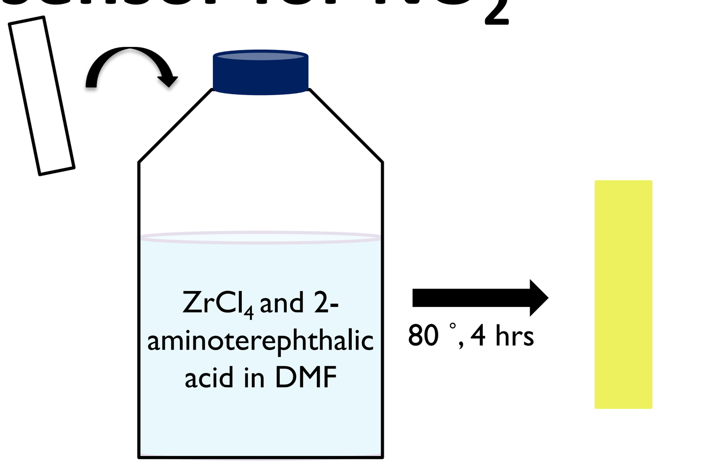

Figure 6: A schematic of the process of growing UiO-66-NH_2 on the functionalised filter paper.

3. Rh6G@UiO-66-NH_2 in solution responds to NO_2^- but suffers from interference.

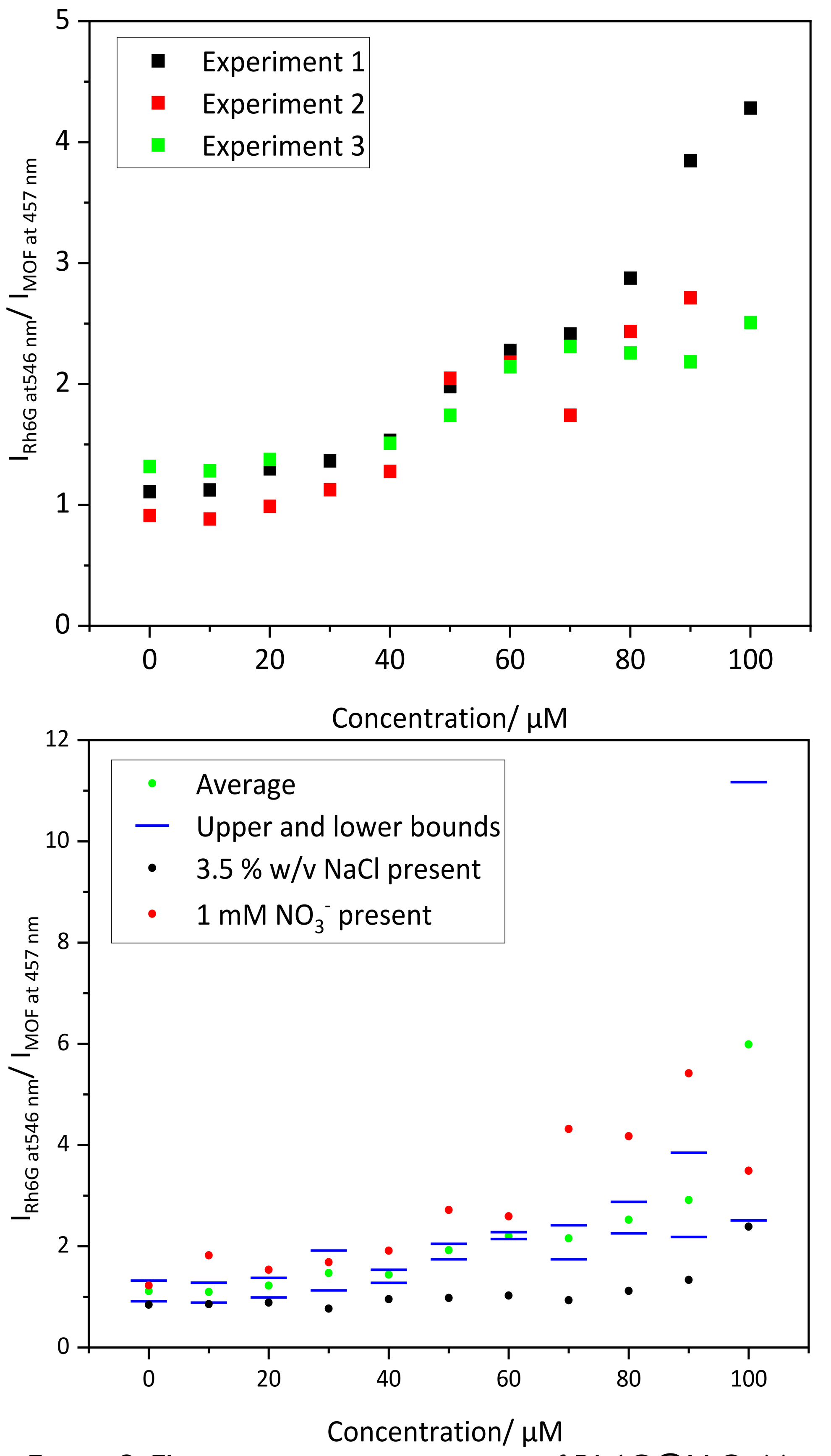

Figure 3: Fluorescence intensity ratio of Rh6G@UiO-66-NH_2 with changing NO_2^- concentration (top) and with interference ions present (bottom).

4. Rh6G@UiO-66-NH_2 grafted on functionalised paper detaches in the presence of NO_2^-.

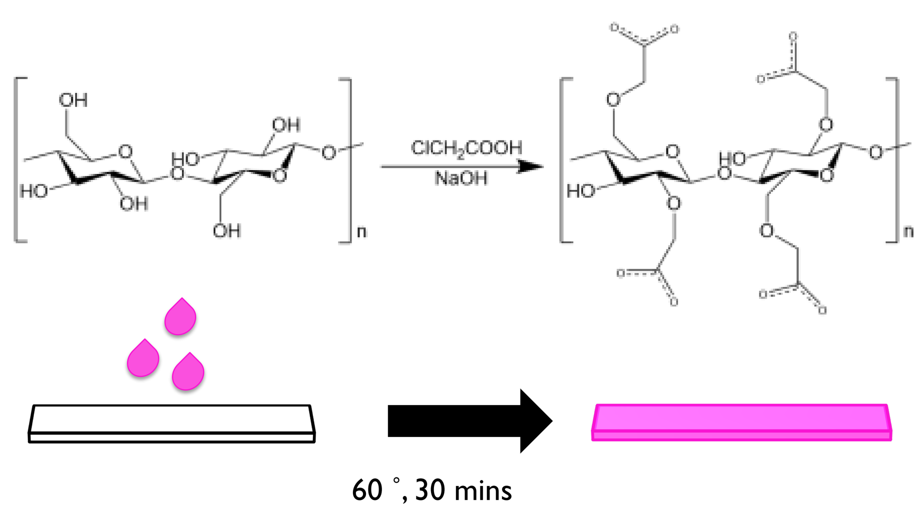

Figure 4: A schematic of the carboxymethylation of filter paper and then the process of grafting Rh6G@UiO-66-NH_2 on the carboxymethylated filter paper.

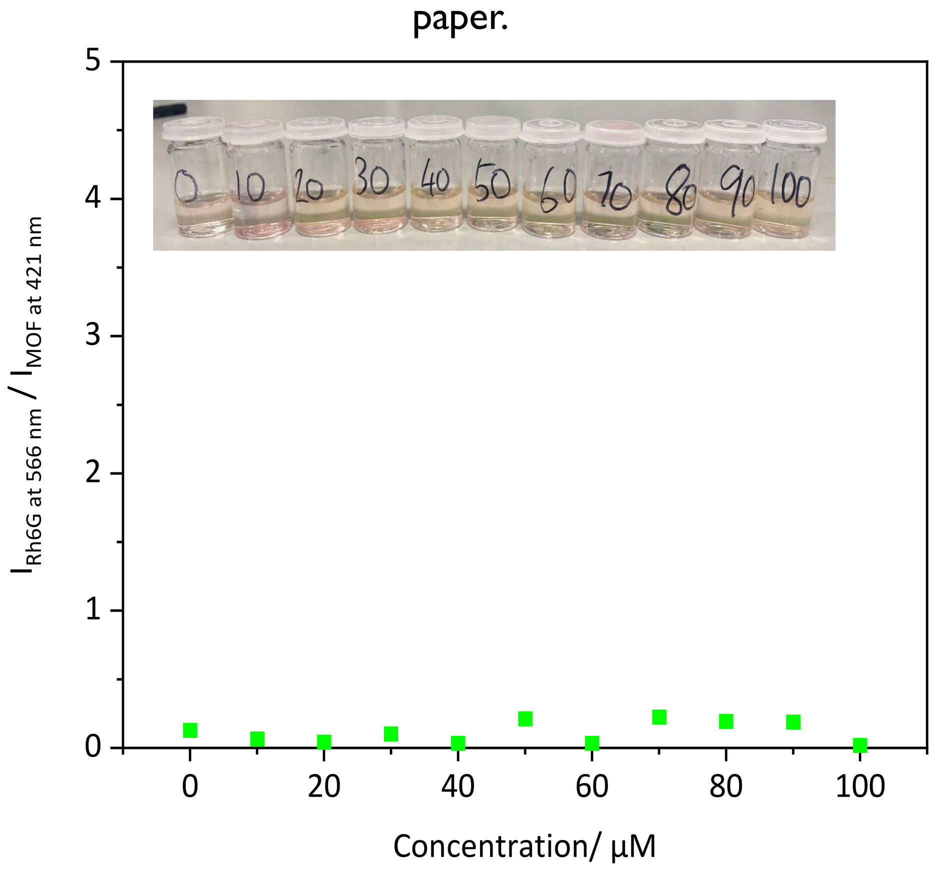

Figure 5: Fluorescence intensity ratio of Rh6G@UiO-66-NH_2-FFP with changing NO_2^- concentration. (Inset): the detection solutions after dipping Rh6G@UiO-66-NH_2-CFP for 15 minutes.

6. UiO-66-NH_2 grown on functionalised paper remains adhered.

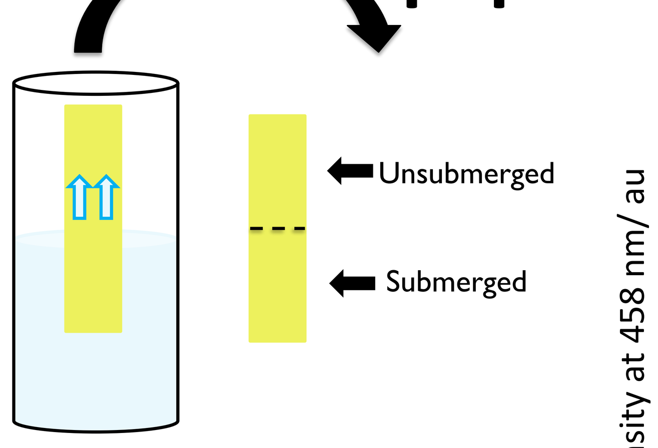

Figure 7 (above): A representation of the filter paper strip exposure process where the light blue arrows indicate the water wicking through the paper via capillary action.

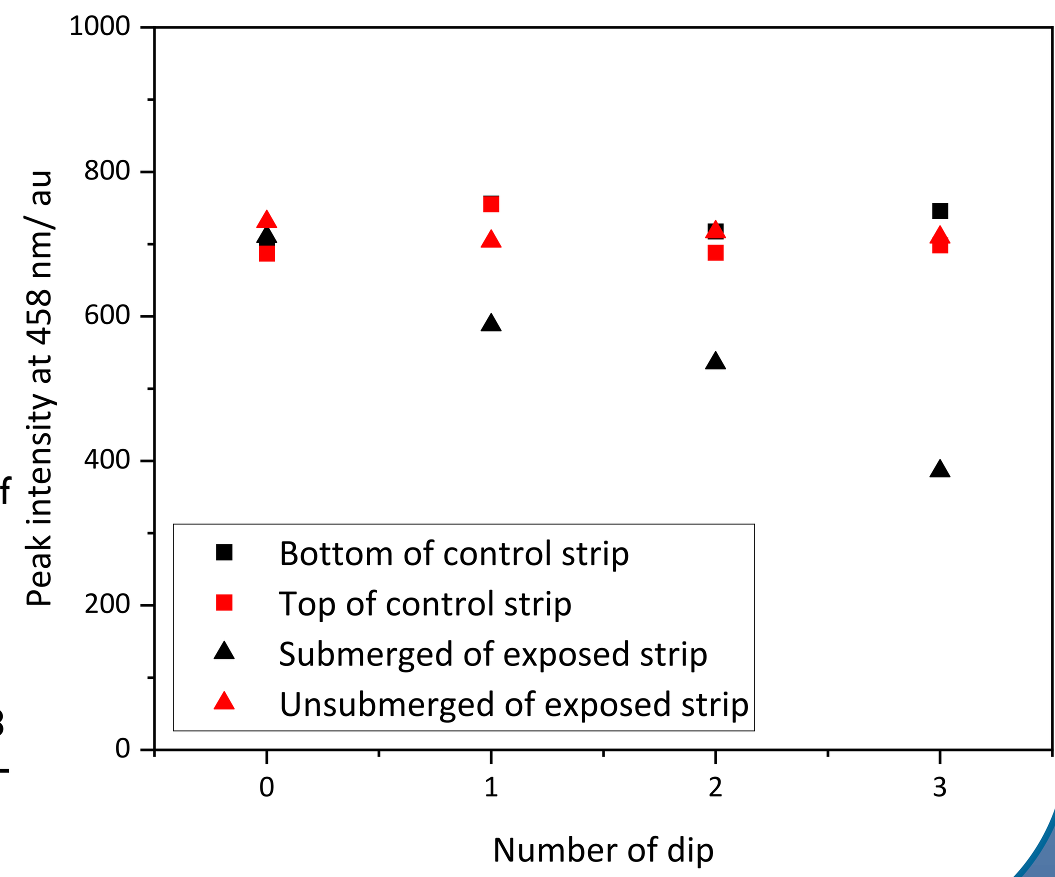

Figure 8 (right): Peak intensity at 458 nm of different strip sections of UiO-66-NH_2-CFP after multiple exposures to water or as a control.

7. UiO-66-NH_2 grown on filter paper did not give predicted response to NO_2^-.

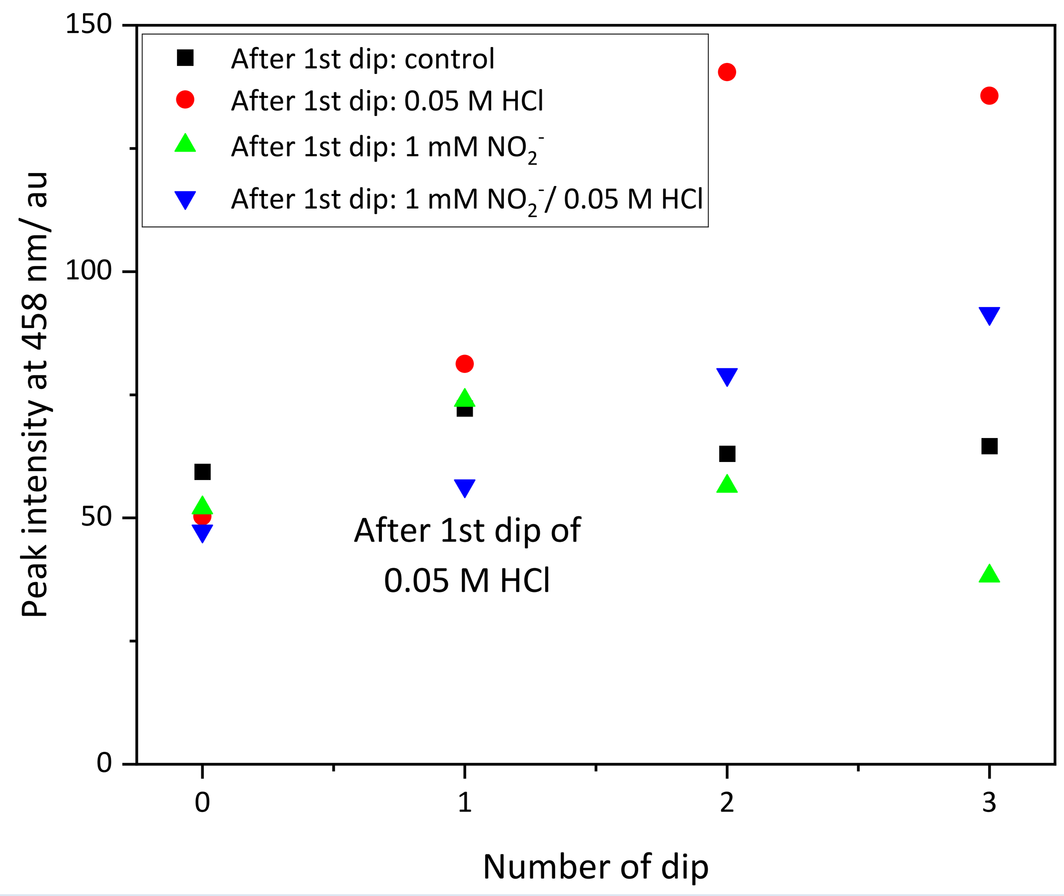

Figure 9 (left): Peak intensity at 458 nm of submerged strip section of UiO-66-NH_2-CFP after multiple exposures to different detection solutions.

- The presence of H^+ in the detection solution results in an enhancement of emission of the MOF grown on filter paper.

8. Conclusion of this research

- Rh6G@UiO-66-NH_2 gave a quantitative response to NO_2^- in solution but then showed interference (contrast to the literature) and had difficulty adhering to functionalised filter paper.
- UiO-66-NH_2 adhered to functionalised filter paper, but did not yield expected quenching effect with an excess of NO_2^- (1 mM).

9. Future works of this research

- Determine the quantity of MOF growth using solvothermal method and investigate response to NO_2^- with another growing technique (dip-coating),
- Use a MOF with a visual colour change response (Co-based MOF) to gaseous ammonia (convert ammonium in water into gaseous ammonia using NaOH), then measure RGB value for quantification of ammonium.[5]

References.

1) M. A. P. Mahmud, et al., *Chemosphere, 2020*, **259**, article: 127492, 2) S. Deng, et al., *Journal of Hazardous Materials, 2024*, ***463***, *article: 132898, 3)* X. Hao, et al., *Journal of Solid State Chemistry*, 2020, **287**, article: 121323, 4) T. Hashem et al., *ACS Applied Nano Materials*, 2019, **2**, 5804-5808, 5) T. Leelasree et al., *Chemistry of Materials*, 2023, **35**, 416-423.