

# Nanocellulose-Paper-Based Analytical Devices with MOFs/Heterojunction Structures for Multiplex SERS Detection

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**Abstract**— Metal-organic frameworks (MOFs) as surface-enhanced Raman scattering (SERS) substrates exhibit selectivity towards analytes with different energy levels. However, due to the energy level mismatch, the multiplex SERS detection on the same substrate has not been developed yet. In this study, we demonstrated nanocellulose-paper-based analytical devices (NanoPADs) with both *in-situ* ZIF-8/Zn(OH)<sub>2</sub> and ZIF-67/Co(OH)<sub>2</sub> structures. As a proof-of-concept, we independently detected two common environmental pollutants, methyl orange and Rhodamine 6G, on NanoPADs under different incident light wavelengths, achieving limits of detection as 10<sup>-7</sup> M, respectively. Our work potentially advances high-sensitive and multiplex SERS-based device development.

## I. INTRODUCTION

Metal-organic frameworks (MOFs) have received considerable attention as surface-enhanced Raman scattering (SERS) substrates due to their molecular selectivity [1]. However, the existing MOFs-based SERS substrates are restricted by their charge transfer (CT) mechanism and can only detect analytes with specific energy levels [2]. There is a need to develop MOFs-based SERS substrates for multiplex detection. Thus, we developed nanocellulose-paper-based analytical devices (NanoPADs) with two MOFs/heterojunction structures to detect both methyl orange (MO) and Rhodamine 6G (R6G).

## II. METHODS

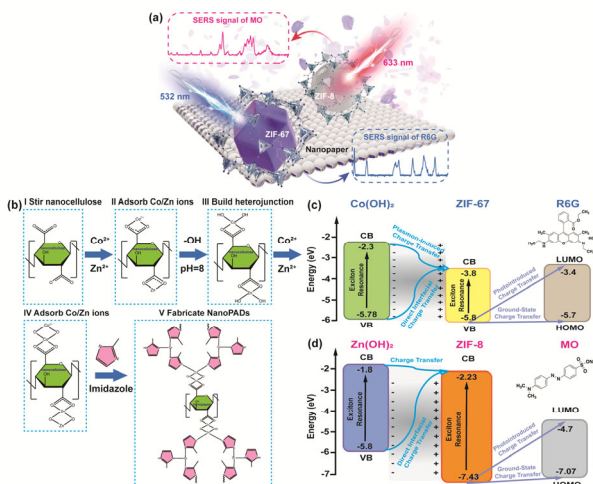


Figure 1. Fabrication of NanoPADs and energy level diagram of systems.

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We developed NanoPADs generated with both *in-situ* ZIF-8/Zn(OH)<sub>2</sub> and ZIF-67/Co(OH)<sub>2</sub> systems, by shifting incident laser length from 633 nm to 532 nm for initiating photo-induced CT between ZIF-8 to MO and ZIF-67 to R6G (Figs. 1(a) and 1(b)). In our MOFs/heterojunction structures, hydroxides provide additional CT to MOFs to enhance SERS signals. Figs. 1(c) and 1(d) show the energy level diagrams of ZIF-67/Co(OH)<sub>2</sub> and ZIF-8/Zn(OH)<sub>2</sub> systems under illumination at 532 nm and 633 nm, respectively. The R6G probe's HOMO and LUMO values are -5.70 eV and -3.40 eV, respectively. The electrons in the valence band (VB) of ZIF-67 (-5.80 eV) injected into LUMO of R6G molecules (-3.40 eV). The electron absorption threshold for the R6G molecule is about 555-579 nm, so ZIF-67 to R6G works under 532 nm laser. Besides, for the ZIF-8-MO system, the process follows the CT mechanism of semiconductor-to-molecule. The electrons in the VB of ZIF-8 (-7.43 eV) injected into LUMO of MO molecules (-4.70 eV) under 633 nm laser.

## III. RESULTS

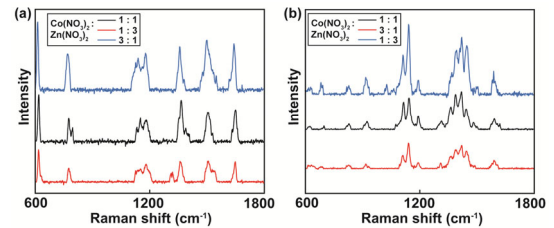


Figure 2. SERS detection results of R6G and MO on different NanoPADs.

In the preparation of NanoPADs, we first chose equivalent Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (1.5 g for each, pH=8.0). Then, we adjusted the ratio of Co and Zn ions to 3:1 and 1:3 to fabricate different NanoPADs. At these ratios, characteristic peaks of MO and R6G could be successfully detected. Figs. 2(a) and 2(b) illustrate the Raman spectra of R6G and MO on NanoPADs under 532 nm and 633 nm laser, respectively. Their limits of detection are achieved as 10<sup>-7</sup> M, respectively.

## IV. DISCUSSION & CONCLUSION

The NanoPADs still retain the molecular selectivity of MOFs and relatively high sensitivity in multiplex SERS detection, potentially advancing SERS-based device development.

## REFERENCES

- [1] H. Sun *et al.*, "Stabilizing photo-induced vacancy defects in MOF matrix for high-performance SERS detection," *Nano Res.*, vol. 15, pp. 5347–5354, 2022.
- [2] H. Sun *et al.*, "Metal–Organic Frameworks as Surface Enhanced Raman Scattering Substrates with High Tailorability," *J. Am. Chem. Soc.*, vol. 141, no. 2, pp. 870–878, 2019.