Linear, nonlinear optical, and electrical properties of zinc oxide tetrapod/metal–organic framework hybrid structures

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Introduction

MOF@MOx hybrids have been synthetized by using the approach **MOx-to-MOF reactions** (*Freund et al. Chem. Mater. 2023*) with the aim of generating new MOF-based structures with tailored morphology, which are not achievable by standard synthetic methods.
The main features of the approach and the resulting materials are:

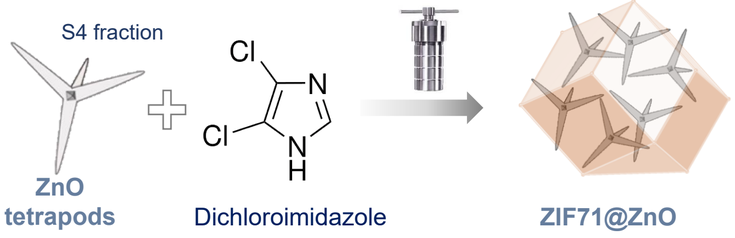
- Hybrid structures production
- The metal oxide (MOx) particles act as metal precursor
- Formation of a heterojunction at the MOx/MOF interface: expected goal enhancement of the sensor response to small concentration changes
- Increased active surface area: expected goal capture of more target molecules than MOx alone, making the sensor more sensitive.

In this work we analyze how MOF concentration changes the optical and electrical properties of ZnO tetrapods

Synthesis

MOF@MOx hybrid structures:

MOF = ZIF71; MOx = ZnO tetrapods, fraction S4



Working grid

varing **ligand amount** (MOx content is fixed; no source of Zn other than MOx**)**:

ZIF71@ZnO(S4) (1:4)
ZIF71@ZnO(S4) (1:6)
ZIF71@ZnO(S4) (1:8)

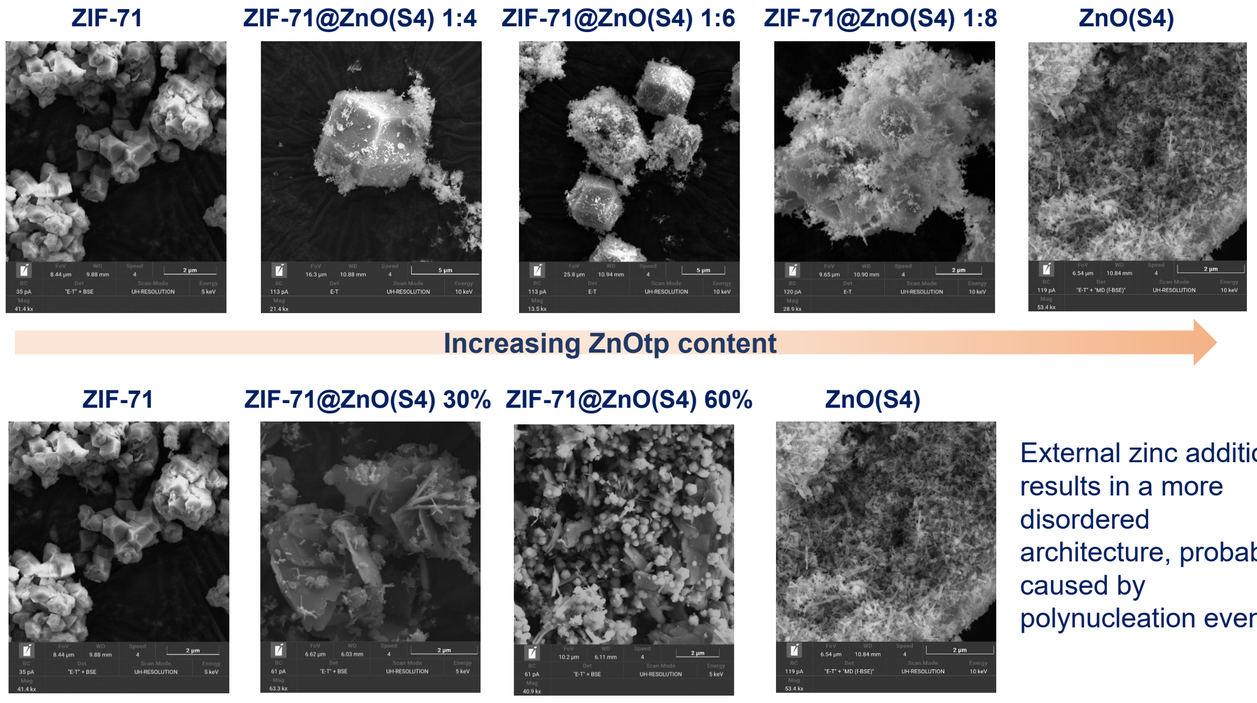
1:4 → 1= mol of ligand; 4= mol of Zn

With **additional Zn source** ($Zn(ac)_2$):

ZIF71@ZnO(S4) 30%
ZIF71@ZnO(S4) 60 %

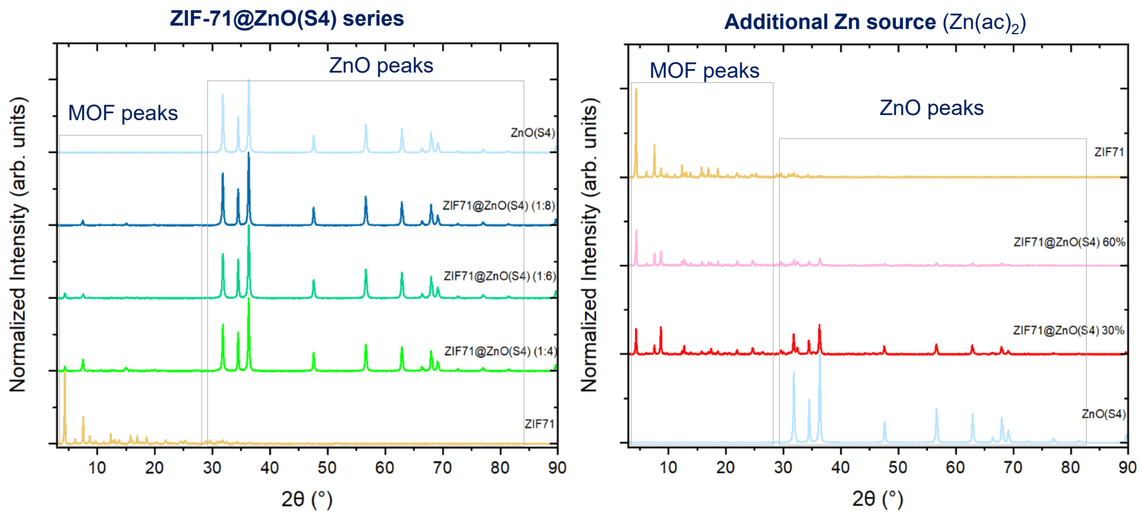
30% stands for the percentage of MOF in the whole MOF@MOx

Materials morphology

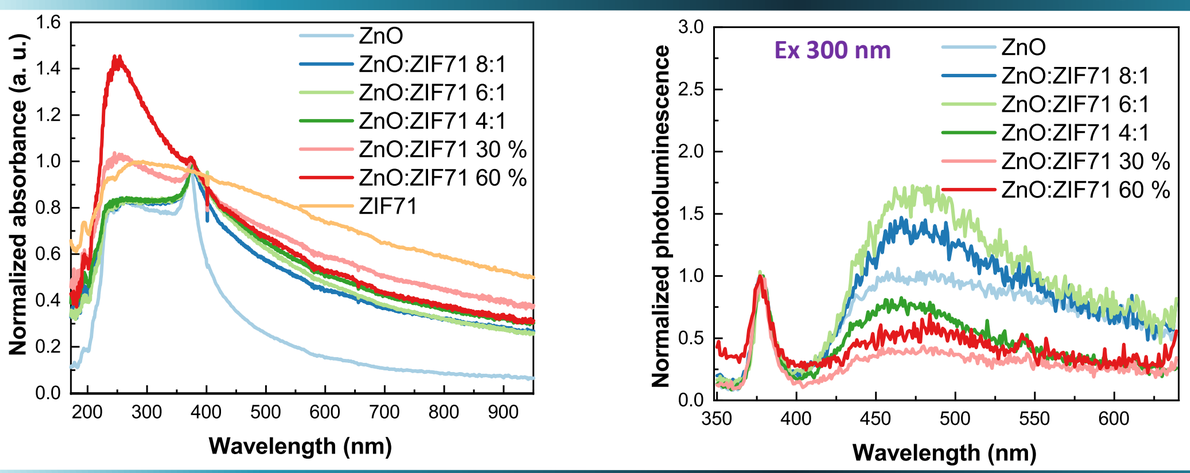


External zinc addition results in a more disordered architecture, probably caused by polynucleation events

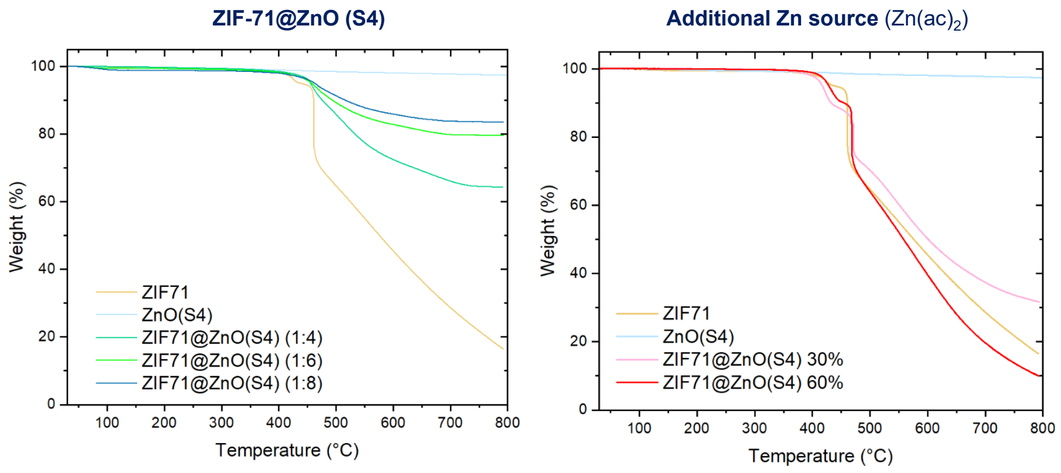
XRD



UV-Vis absorption and photoluminescence spectroscopy

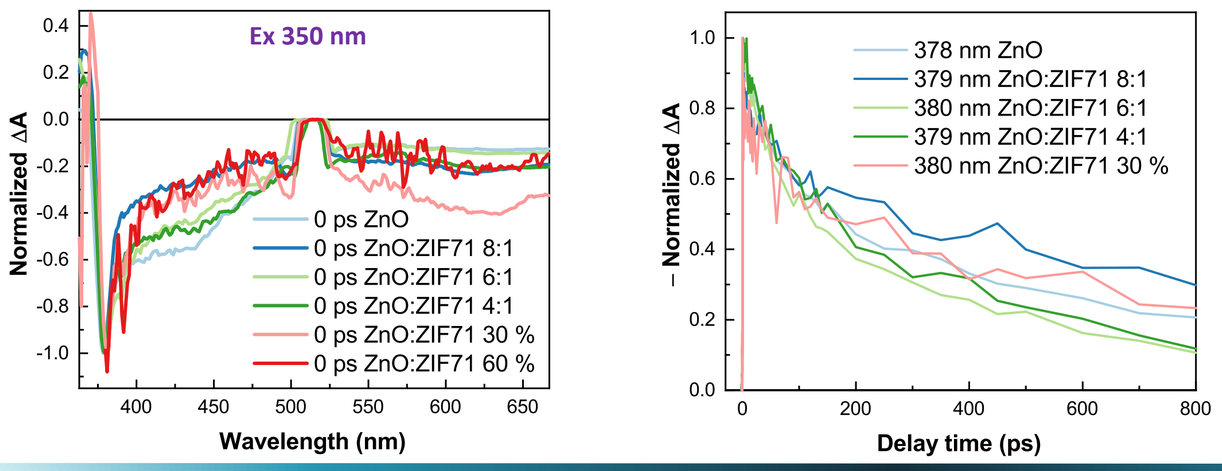


Thermogravimetry

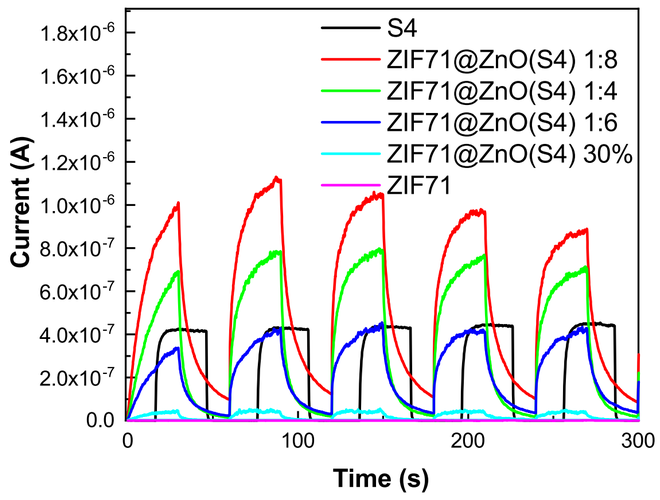


The thermogravimetric profiles are in all cases fully consistent with the formation of the MOF in the intended proportion.

Transient absorption spectroscopy



Photocurrent



Conclusions

- Novel ZIF-71@ZnO composites were successfully synthesized, and their electro-optical properties were systematically investigated.
- SEM analysis confirms the successful integration of polyhedral ZIF-71 crystals with ZnO tetrapods, demonstrating the formation of the ZIF-71@ZnO composite.
- The incorporation of ZIF-71 modifies the defect-states, leading to changes in defect-related optical transitions relaxation dynamics.
- The optical response of ZnO tetrapods can therefore be effectively tuned through integration with the ZIF-71 metal–organic framework.
- These findings demonstrate that ZIF-71@ZnO composites are promising materials for future optoelectronic and photocatalytic applications.

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