Heterogeneous Growth of UiO-66-NH_2 on Oxidized Single-Walled Carbon Nanotubes to Form "Beads-on-a-String" Composites

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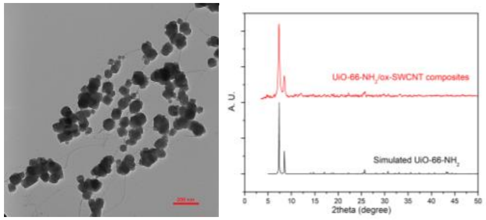
Introduction

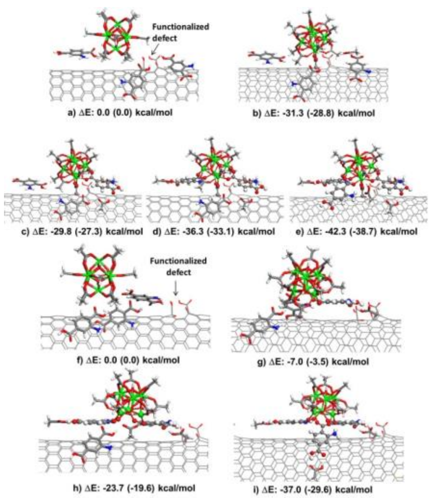
Metal-organic frameworks (MOFs) are known for their high porosity and large surface area. Most MOFs are not electrically conductive due to the lack of free charge carriers or low-energy transfer pathways in their structures, thus limiting their applications where electrical properties are desired. Extensive research has been conducted to explore the synthesis of conductive MOFs. However, for such conductive MOFs, the achieved electrical conductivity is significantly lower as compared to traditional solid-state materials. A promising approach to synthesize conductive MOFs is to hybridize them with conductive nanocarbon materials like single-walled carbon nanotubes (SWCNTs).

Morphology characterization



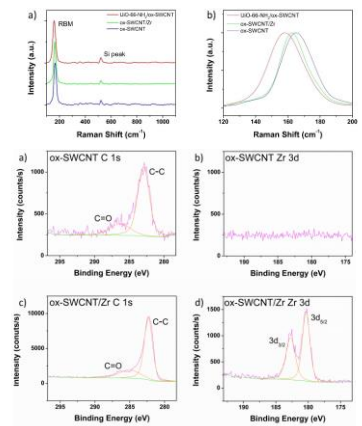
TEM and XRD of synthesized MOF/SWCNT composites. Desired "beads-on-a-string" morphology can be achieved by controlling MOF precursor concentration and adding acetic acid as modulator.

Explore synthesis pathway by DFT calculations



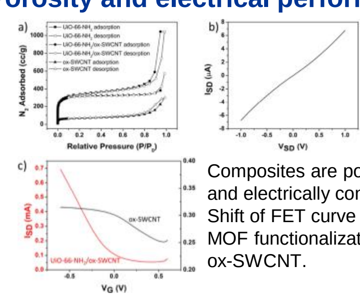
DFT calculations revealed that MOF nucleation is energetically favorable on the defect site of oxidized SWCNT (ox-SWCNT)

Characterization of Zr anchoring



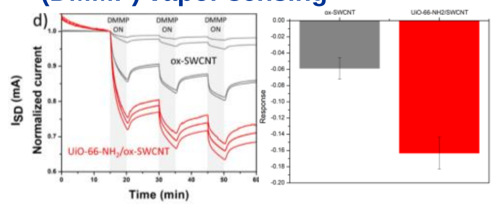
Raman and XPS spectroscopy confirmed Zr cluster anchoring on ox-SWCNT.

Porosity and electrical performance



Composites are porous and electrically conductive. Shift of FET curve implies MOF functionalization on ox-SWCNT.

Dimethyl methylphosphonate (DMMP) vapor sensing



ox-SWCNT and UiO-66-NH_2/ox-SWCNT composites devices were tested with DMMP vapor in air. MOF/SWCNT composites displayed a greater average response compared to ox-SWCNT.

Conclusions

The UiO-66-NH_2/ox-SWCNT composites combined the porosity of UiO-66-NH_2 MOF and the electrically conductivity of ox-SWCNTs. DFT calculations reveal that the carboxyl defect sites were essential for the MOF/SWCNT hybridization. Covalent bonding between SWCNTs and MOF precursors provides a general synthetic method to hybridize carboxylate type MOFs with SWCNTs and prepare electrically conductive MOF composites.

Acknowledgement

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