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## COMMUNICATION

## Motorized Janus Metal Organic Framework Crystals

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**We describe Janus metal organic framework crystals that are propelled by bubble ejection. The Janus crystals are prepared by selective epitaxial growth of ZIF-67 on ZIF-8. The Janus crystals catalyse the decomposition of H<sub>2</sub>O<sub>2</sub> to H<sub>2</sub>O and O<sub>2</sub> on the ZIF-67 surface but not on the zinc containing ZIF-8 surfaces, resulting in propulsion of the Janus crystals.**

A growing area of recent research in nano and micro-technology has been aimed towards imparting autonomous motion to functional materials.<sup>1-6</sup> Self-propulsion is a potentially desirable property for functional materials such as catalysts or absorbents, where autonomous motion through the environment can increase their effectiveness and efficiency.<sup>3-5</sup> Autonomous motors thus have many possible applications, including sensing,<sup>6</sup> environmental remediation<sup>3-5</sup> and drug delivery<sup>7</sup>.

Autonomous motors can be propelled by a variety of mechanisms,<sup>8</sup> such as surface tension gradients,<sup>2,9</sup> self-electrophoresis,<sup>10</sup> self-diffusiophoresis,<sup>11</sup> or via bubble-ejection propulsion,<sup>12</sup> using H<sub>2</sub>O<sub>2</sub> or reactive metals as fuel. Bubble-ejection using H<sub>2</sub>O<sub>2</sub> as a fuel involves the decomposition of H<sub>2</sub>O<sub>2</sub> to H<sub>2</sub>O and O<sub>2</sub>, catalyzed typically by transition metals.<sup>12</sup>

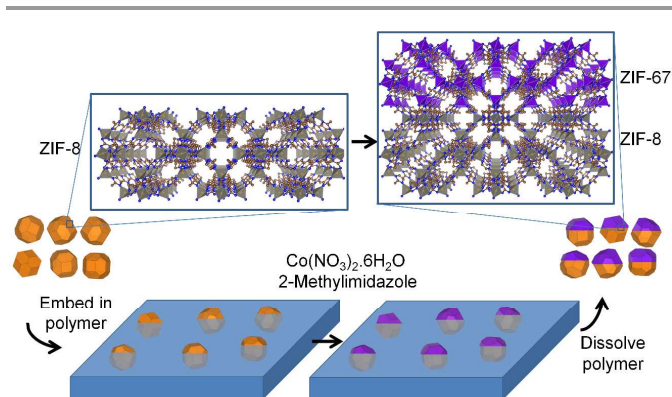
Amongst emerging functional materials, metal organic frameworks (MOFs) have proven to be extremely versatile, with many applications that would be improved by autonomous motion. Such applications include sensing,<sup>13</sup> heterogeneous catalysis,<sup>14</sup> photocatalysis,<sup>15</sup> pollutant absorption,<sup>16,17</sup> drug delivery<sup>18</sup> and bioimaging.<sup>20</sup> Adding autonomous motion to a MOF particle would thus be a desirable enhancement that could improve its function as a catalyst, carrier, absorbent or sensor.

Reports of autonomous MOF motors are currently limited to work by Ikezoe *et al.*, where the MOFs were propelled via a surface tension gradient generated by self-assembling peptides extruded from the MOF.<sup>2</sup> To our knowledge, there has been no report of a catalytic, bubble-ejection motorized MOF. Such a system could be based on hybrid catalytic/non-catalytic Janus particles whereby asymmetry of the particles imparts directionality to their motion. Further, the fabrication of Janus MOFs would not only be useful for motors, but would broaden the application range of MOF

materials.<sup>19</sup> Possible applications for Janus MOF crystals are in supraparticular assemblies,<sup>20</sup> or sensing and photonic materials.<sup>21</sup> We thus sought a scalable method for the production of Janus MOFs and we herein report the synthesis of a Janus ZIF-8/ZIF-67 micro-motor and its catalytic decomposition of H<sub>2</sub>O<sub>2</sub> for self-propulsion.

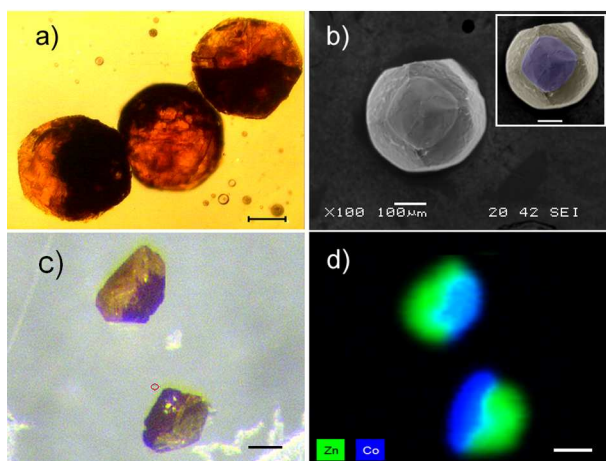
The zeolitic imidazolate framework, ZIF-8, [Zn(MeIm)<sub>2</sub>]<sub>n</sub>,<sup>22</sup> was chosen for several reasons. Firstly, highly crystalline, monodispersed ZIF-8 can be obtained via controlling nucleation and growth rates through the use of modulators and surfactants.<sup>23</sup> Further, ZIF-8 is also isostructural to ZIF-67, [Co(MeIm)<sub>2</sub>]<sub>n</sub>,<sup>24</sup>; both have a sodalite topology with tetrahedral, divalent metal centers bridged by 2-methylimidazolate ligands. As it has been shown that heteroepitaxial growth of isostructural MOFs can be used to create hybrid crystals,<sup>25,26</sup> we hypothesized that ZIF-67 could also be grown epitaxially on a ZIF-8 crystal surface to introduce and create a redox active (Co<sup>II</sup>) / redox inactive (Zn<sup>II</sup>) hybrid material. Lastly, ZIF-8 can undergo a wide array of post-synthetic modifications to expand the functionality of the MOF. Post-synthetic modifications include ligand<sup>27</sup> and metal exchange,<sup>28</sup> as well as surface or bulk functionalization with catalytic noble metals<sup>29</sup> and semiconductors.<sup>30</sup>

ZIF-8 single crystals were synthesized by modified literature methods (see ESI for experimental details).<sup>13b</sup> Briefly, Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and 2-methylimidazole in a 1:2 molar ratio were dissolved in DMF. Polyvinylpyrrolidone (PVP) and acetic acid were added to control the crystal nucleation and growth rate. The size of the crystals was controlled by varying the amount of PVP and acetic acid used. Crystals between 200 to 500 μm in diameter were selected for further experiments. The ZIF-8 crystals were then partially embedded in a poly(methyl methacrylate) (PMMA) film to passivate part of the crystal surface. ZIF-8 is known to assemble at a water-oil interface and MOF-polymer colloidosomes fabricated using such an interface have been reported by Huo *et al.*<sup>31</sup> Trapping solids at a water-organic interface is an effective and simple route to fabricating Janus particles.<sup>32,33</sup> Polymer films with partially embedded ZIF-8 crystals could be prepared by suspending ZIF-8 at the interface between water and a 10 wt% solution of PMMA in ethyl acetate and then allowing the ethyl acetate to evaporate (Figure 1).



**Figure 1.** Schematic illustration of procedure for making Janus MOF crystals, where ZIF-8 crystals are partially embedded in PMMA (blue). Subsequent modification of the exposed portion and removal of the polymer affords Janus particles.

The polymer films containing ZIF-8 were immersed in an aqueous ZIF-67 precursor solution at 80 °C. Within a few hours, purple deposits, identified as ZIF-67 by powder X-ray diffraction, were observed on the entire film. To selectively grow ZIF-67 on the ZIF-8 crystals, either PVP was added as a modulator or the solvent was changed to H<sub>2</sub>O:DMF (1:1 vol). Both measures were able to effectively suppress nucleation on the polymer surface such that purple deposits were no longer seen on the polymer surface and were only observed on the ZIF-8 crystals (see ESI for experimental details). Simple removal of the polymer film with ethyl acetate yielded Janus ZIF-8/ZIF-67 crystals (Figure 2). X-ray fluorescence (XRF) elemental mapping and energy-dispersive X-ray spectroscopy (EDS) confirmed the presence and location of both Zn and Co on the Janus particles (Figure 2 and Figure S1 - S2).

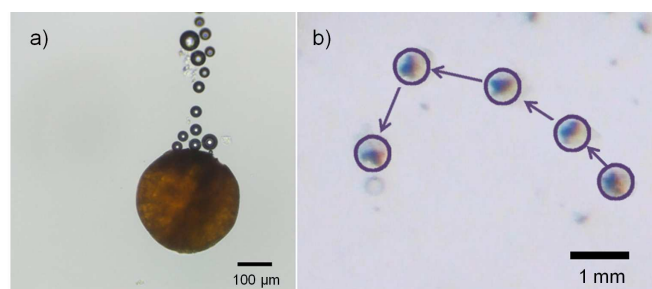


**Figure 2.** a) Optical microscope photograph and b) SEM image of Janus ZIF-8/ZIF-67 crystal, SEM image false colored (insert) to highlight the two different MOFs; c) Video capture and d) XRF elemental map of Janus particle cross-section. All scale bars represent 100  $\mu$ m.

Quantification of Zn and Co in the Janus particles by inductively coupled plasma mass spectrometry (ICP-MS) and XRF show a Zn:Co atom ratio of  $19 \pm 3:1$ . The ZIF-67 was likely to have grown as a thin film on the ZIF-8 surface and little transmetalation occurred. Hence the bulk of the crystals consisted mainly of ZIF-8. Both ZIF-8 and ZIF-67 have the same space group (*I*-43*m*) and almost identical cell parameters (ZIF-8:  $a = 16.9910$  Å; ZIF-67:  $a =$

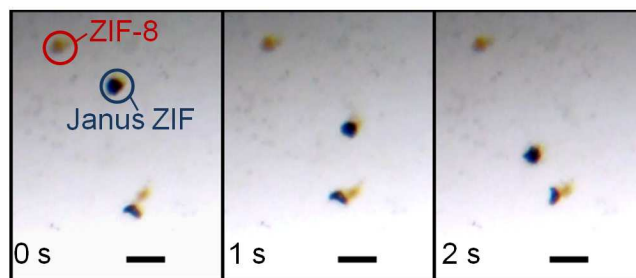
$16.9589$  Å). X-ray diffraction showed that the Janus MOF remained highly crystalline (Figure S3), with well-defined spots in the diffraction pattern. This suggests little lattice mismatch between the core ZIF-8 and the ZIF-67.<sup>26</sup> Bulk characterization by powder X-ray diffraction of the ground Janus crystals indicated the presence of no other crystalline phase besides the ZIFs (Figure S3). Our results suggest that the same synthetic strategy can be applied to other isostructural MOFs which have been reported.<sup>34</sup>

When the Janus crystals were placed in a hydrogen peroxide solution, bubbles immediately evolved at their visibly darker sides, which were identified as the cobalt containing regions. No bubbles were observed at the non-catalytic, zinc containing area (Figure 3a). In 5% H<sub>2</sub>O<sub>2</sub> solution, the Janus crystals were propelled by the bubbles and moved at speeds of up to  $\sim 0.2$  mm/s. (Figure 3b, See also Video 1).



**Figure 3.** a) Optical microscope picture of Janus crystal in H<sub>2</sub>O<sub>2</sub> solution. Oxygen bubbles can be seen evolving selectively at the darker, cobalt rich region of the crystal; b) tracking image of Janus crystal in 5% H<sub>2</sub>O<sub>2</sub> at 5 second intervals.

Higher concentrations of H<sub>2</sub>O<sub>2</sub> resulted in more vigorous bubbling and greater propulsion. Janus particles in 10% H<sub>2</sub>O<sub>2</sub> moved at speeds of up to 1 mm/s (Figure 4, Video 2). ZIF-8 crystals were added as a control and no bubbling was observed on their surfaces. Hence the ZIF-8 crystals remained stationary while the Janus crystals were propelled. The motion of pure ZIF-67 crystals was also observed and was much less directional due to vigorous bubbling on all sides of the crystal (Video 3). When the Janus crystals were exposed to H<sub>2</sub>O<sub>2</sub>, the edges of the crystals were etched and the crystallinity visibility deteriorated.



**Figure 4.** Time lapse picture of ZIF-8 crystal (circled in red) and Janus crystal (circled in blue) in 10% H<sub>2</sub>O<sub>2</sub> solution at 1 second intervals. ZIF-8 crystal does not move while Janus crystal moves in a circular path.

Since MOFs contain organic ligands that are susceptible to oxidative degradation by H<sub>2</sub>O<sub>2</sub>, it is expected that the crystallinity of the Janus particles decreases. SEM images of the Janus particles that had been in 5% H<sub>2</sub>O<sub>2</sub> revealed significant surface degradation over 5 hours (Figure S5). However, X-ray diffraction experiments showed that the bulk particles remained crystalline after 5 hours of exposure

to H<sub>2</sub>O<sub>2</sub> (Figure S6). No other crystalline phases were detected by X-ray diffraction and the surface degradation of the crystal likely yields amorphous material. XRF elemental mapping of the Janus particles showed that elemental distribution remained unchanged from exposure to 5% H<sub>2</sub>O<sub>2</sub> after 5 hours (Figure S7 and S8). The concentration of Co ions leached into solution was analyzed by ICP-MS. The Co content was found to be 3 ± 2 ppm when 1 mg of Janus particles was soaked in 5 ml of 5% H<sub>2</sub>O<sub>2</sub> for 12 hours, indicating a low amount of Co leaching.

In summary, we have fabricated Janus ZIF-8/ZIF-67 crystals by partially embedding ZIF-8 crystals in polymer films, followed by epitaxial growth of ZIF-67 on the ZIF-8. The Janus crystals catalytically decompose H<sub>2</sub>O<sub>2</sub> on the ZIF-67 surfaces and are propelled by oxygen bubbles. We envision that further post-synthetic modification to the ZIF-8/ZIF-67 system is possible to impart additional functionality, such as including guest molecules in the pore space. Additionally, the method of passivation and epitaxial growth can be extended to other MOFs to make Janus or patchy structures, which can be used for motors or even supra-particle assembly.<sup>20</sup>

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## Notes and references

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Electronic Supplementary Information (ESI) available: Experimental details, XRF images, XRD patterns, EDX data FTIR spectra See DOI: 10.1039/c000000x/

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