Supplementary materials for

Liquid Metal-based Electrosynthesis of Stratified Zinc-organic Framework

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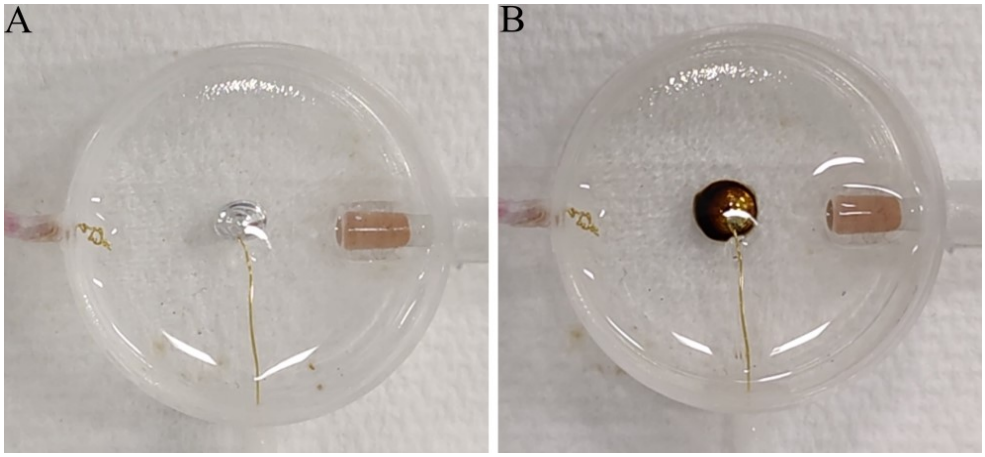

Figure S1. Voltage-induced electrocapillary effect on the interface of Ga-Zn alloy in 0.10 M NBu_4PF_6/DMF. (A) The snapshot of Ga-Zn alloy before applying potential. (B) The snapshot of Ga-Zn alloy after applying potential of -8.0 V *vs* SCE for 10 mins at 50 ℃.

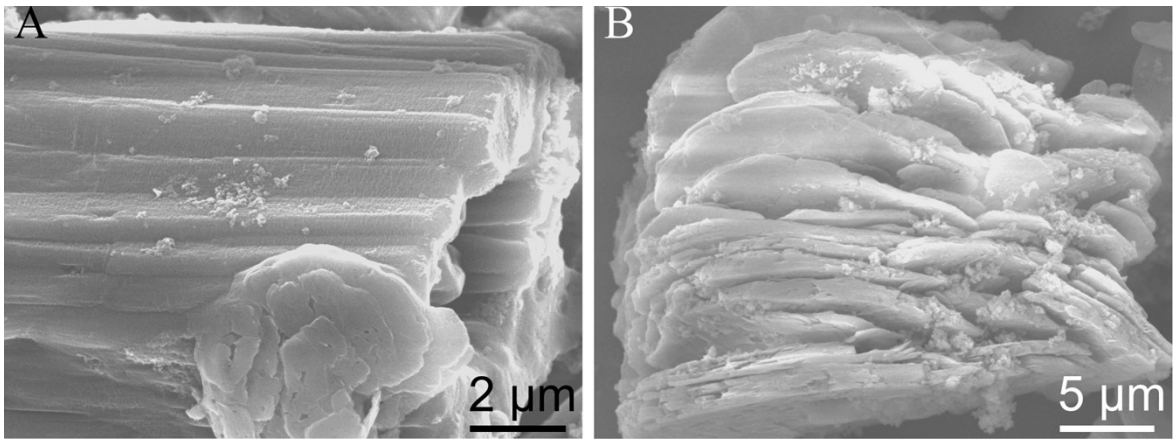

Figure S2. Potentiostatic electrosynthesis of stratified Zn-based MOF from Ga-Zn binary liquid alloy in 0.10 M NBu_4PF_6/DMF and 30 mM benzene-1,4-dicarboxylic acid. (A) SEM image of the sample produced at 0.70 V *vs* SCE. (B) SEM image of the sample produced at 1.0 V *vs* SCE.

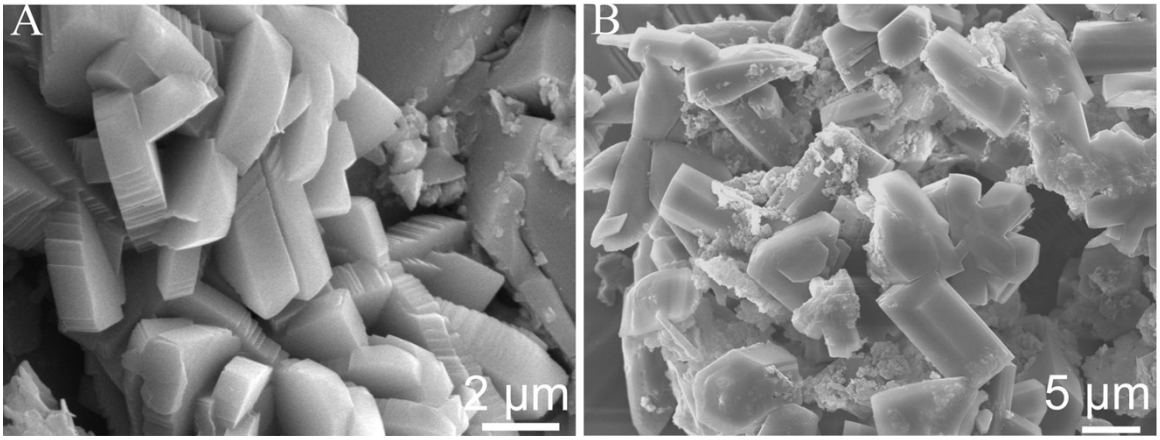

Figure S3. Galvanostatic electrosynthesis of stratified Zn-based MOFs from Ga-Zn binary liquid alloy in 0.10 M NBu_4PF_6/DMF and 30 mM benzene-1,4-dicarboxylic acid. (A) SEM image of the sample produced at 0.50 mA. (B) SEM images of the sample produced at 3.0 mA.

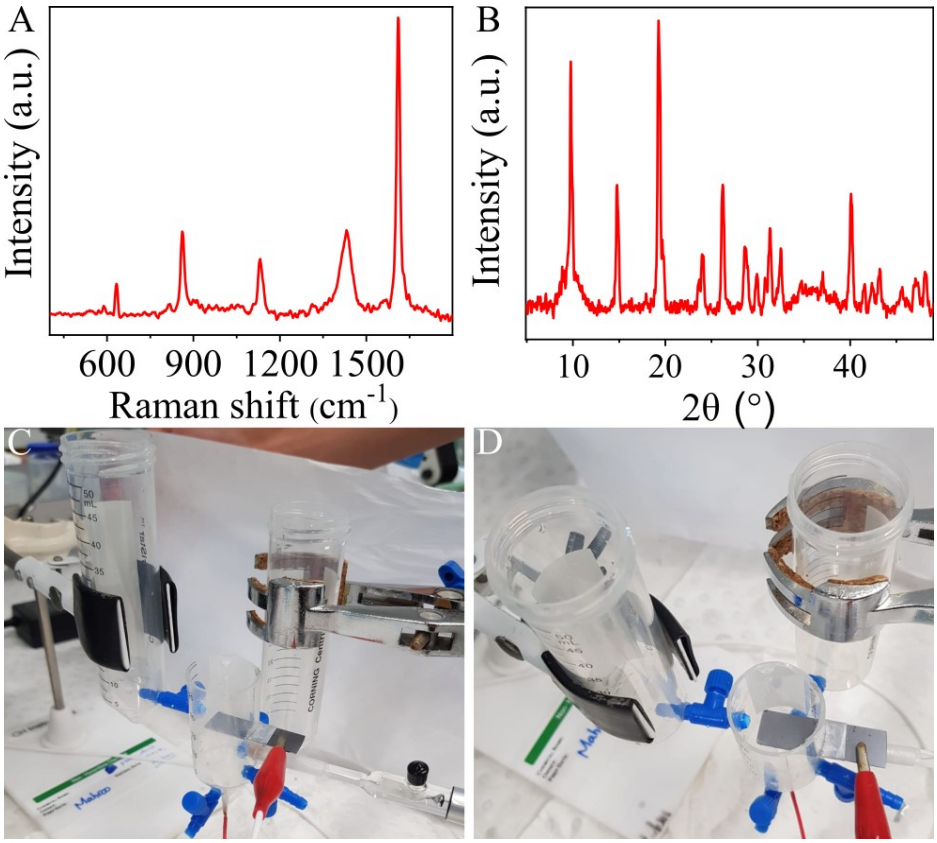

Figure S4. Stratified Zn-organic-framework electrosynthesis from Ga-Zn binary liquid alloy in (DMF and NBu_4PF_6) at 0.50 V *vs* SCE. (A) Raman spectrum of the product. (B) Powder XRD pattern of the product. (C) and (D) Side view and top view of the configuration of reactor.

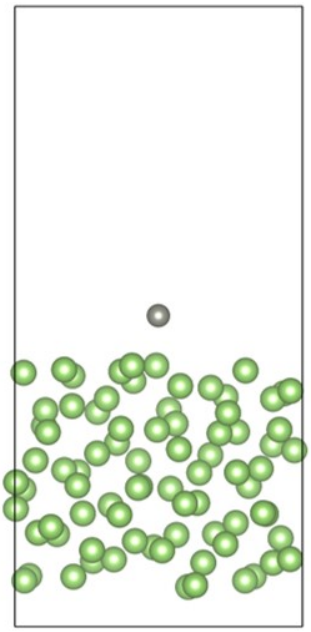

Figure S5. Initial unit cell of Ga-Zn alloy system. Note: the initial Ga-Zn alloy system was constructed from combining amorphous 80-Ga-atoms layer (simulating liquid state of Ga) and one Zn atom being placed on the surface with 10 Å of a vacuum layer.

XPS analysis: XPS analysis was carried out using Thermo Scientific K-alpha XPS spectrometer equipped with a monochromatic Al Kα source (hv= 1486.6 eV) and a concentric hemispherical electron analyzer (CHA).

Based on the XPS results (**Figure S6**), it is seen that the chemical state of Zn of stratified MOF-5 is Zn^{2+} not metallic Zn, suggesting Zn is completely ionized and bonded to the deprotonated organic linker BDC^{2-}.

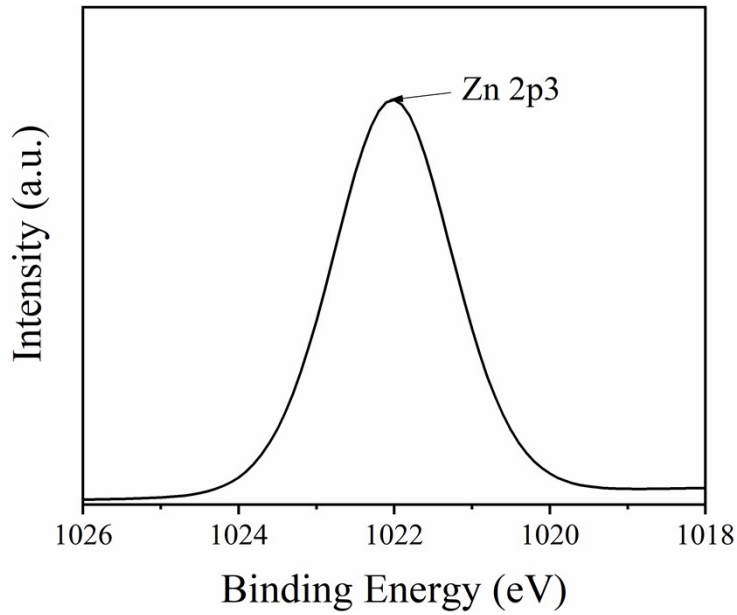

Figure S6. High-resolution XPS Zn 2p spectrum of the product synthesized at 0.50 V.

Choice of alloy concentration: In order to investigate the effect of the composition of Ga-Zn alloy, we prepared different Ga-Zn alloys with various weight percentages of Zn of 2.0 wt%, 3.6 wt%, 5.0 wt% and 100 wt%. They were all used as anodes for the electrosynthesis of stratified MOF-5 with applied potential of 0.50 V vs SCE. Afterwards, we compared the Raman spectra and XRD patterns of the products synthesized from the Ga-Zn alloys with different contents of Zn. Based on the Raman analysis (**Figure S7A**), it is seen that the intensity of five peaks reduced with increasing contents of Zn, suggesting the weaker complexations between Zn^{2+} and BDC^{2-}. Based on the XRD results (**Figure S7B**), the products made from Ga-Zn alloys with 2.0 wt%, 3.6 wt% and 5.0 wt % Zn all showed similar XRD patterns, and the product made from Ga-Zn alloy with 3.6 wt% Zn had the most distinct peaks, stating the best crystallinity. However, the product made from solid Zn shows many broad diffraction peaks that conventional MOF-5 do not have, suggesting the lack of atomic order. This observation is generally attributed to the variation in the coordination stoichiometry at the interface and hence the crystallization kinetics of MOF. Overall, the stratified MOFs produced from the Ga-Zn alloy with 3.6 wt% Zn showed relatively sharp peaks in both Raman spectra and XRD patterns, which means the stratified MOFs had well-formed structure. In addition, the Ga-Zn alloy with the eutectic Zn content of 3.6 wt% has the lowest melting point, rendering it feasible for continuous production of stratified MOFs at room temperature. The above discussions (including texts and below figures) were added into the Supplementary Information in response to your comment.

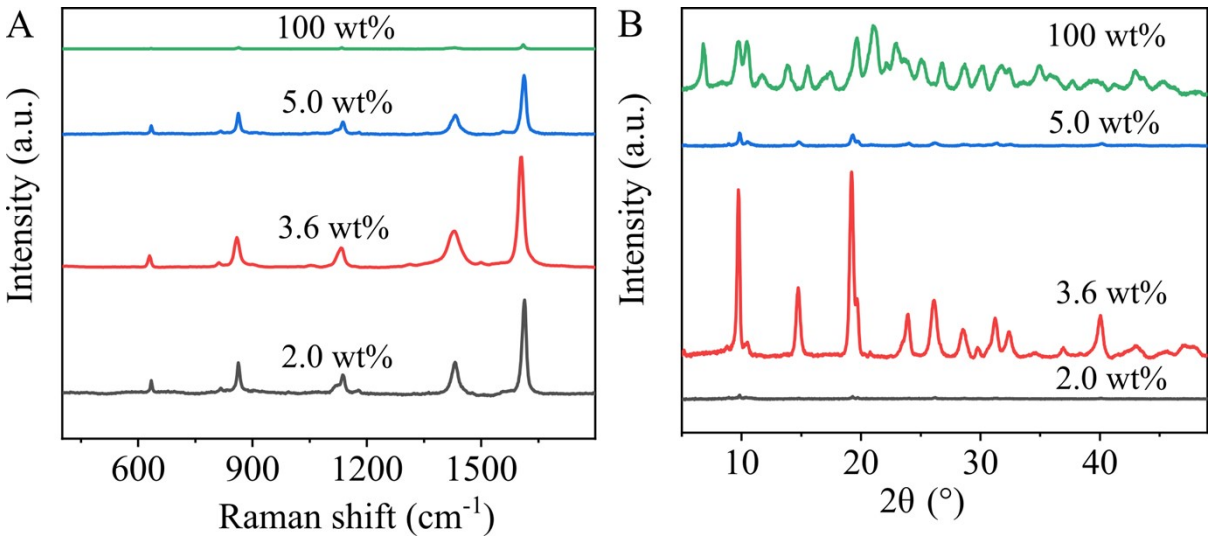

Figure S7. Characterizations of the products synthesized from Ga-Zn alloy with different weight percentage of Zn at applied potential of 0.50 V. (A) Raman spectra of the products. (B) XRD patterns of the products.

Choice of electrolyte concentration: The use of electrolyte is to enhance the conductivity of the solution to accelerate the reaction. The concentration of the electrolyte affects the magnitude of the current. Here, we chose 0.10 M NBu_4PF_6 since it can ensure the reaction to proceed at a reasonable rate. In order to investigate the effect of the electrolyte concentration, we prepared a series of electrolyte solutions with different concentrations, including 0.050 M, 0.10 M 0.20 M NBu_4PF_6, with the same concentration of 30 mM organic linker (H_2BDC) in dimethylformamide (DMF). Afterwards, we obtained the chronoamperometric curves of the reactions at 0.50 V with different concentrations of the electrolytes. As shown in **Figure S8**, it is observed that the current increases with increasing the concentration of the electrolyte. Specifically, with concentration of electrolyte increasing from 0.050 M to 0.10 M, the current density increases significantly from 1.0 $mA \cdot cm^{-2}$ to 2.0 $mA \cdot cm^{-2}$, while the current density only has a minor rise from 2.0 $mA \cdot cm^{-2}$ to 2.4 $mA \cdot cm^{-2}$ when the concentration increases from 0.10 M to 0.20 M. Overall, we believe that the 0.10 M NBu_4PF_6 is the optimal concentration for the electrolyte since it maintains a reasonable currents without using excessive amount of electrolyte.

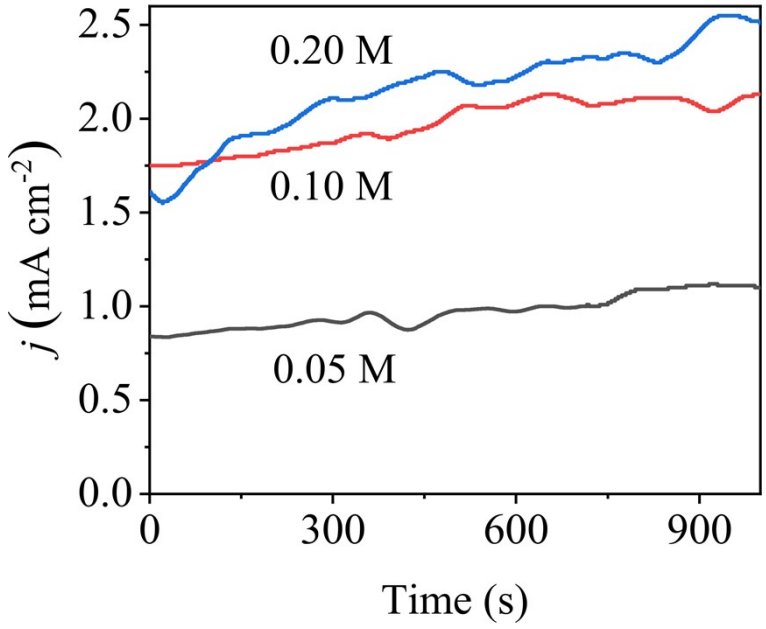

Figure S8. Chronoamperometric curves of electrosynthesis at different electrolyte concentrations.

Electrochemical impedance spectroscopy analysis: The electrochemical impedance was obtained at 0.50 V during the MOF formation at potential perturbation of 50 mV from 1000 kHz to 100 Hz. The Nyquist plot (**Figure S9**) shows a semicircle at high frequencies. Based on the Nyquist plot, the series resistance (R_s) and charge transfer resistance (R_{ct}) were 5.38 Ω and 98.5 Ω, respectively. Both low values of R_s and R_{ct} suggest the high conductivity of the electrode and the relatively low charge transfer resistance of the reaction.

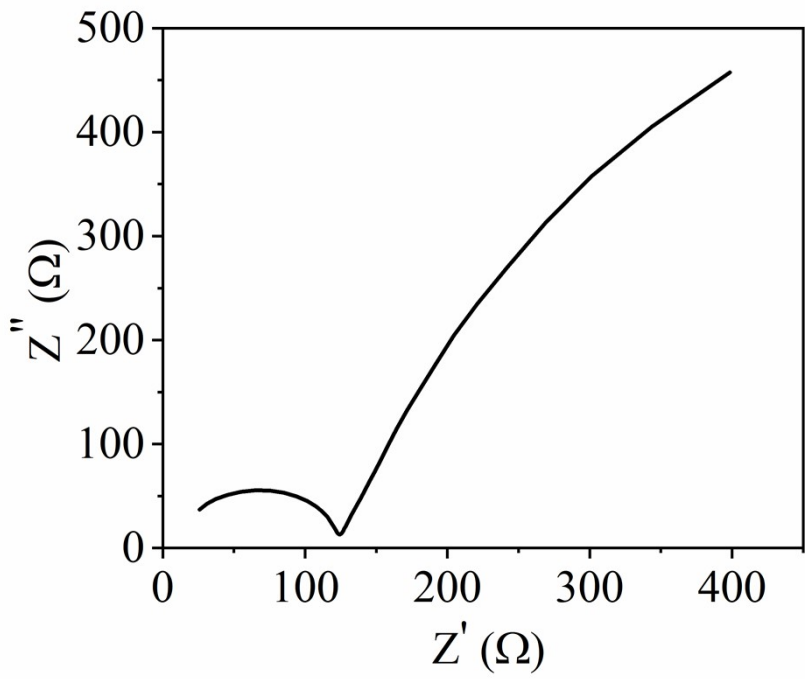

Figure S9. Nyquist plot obtained from the electrosynthesis of the product at 0.50 V (recorded from 1000 kHz to 100 Hz at the amplitude of 50 mV).