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Layered $\text{Mg}_x\text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ as Cathode Material for High Performance Aqueous Zinc Ion Batteries

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ABSTRACT: The performance of chemically intercalated V_2O_5 was found to strongly depend on the interlayer spacing, which is related to the radius of hydrated metal ion, which can be readily tuned by using different intercalated metals. Herein, we report a layered Mg-intercalated V_2O_5 as cathode material for aqueous ZIBs. The large radius of hydrated Mg^{2+} ($\sim 4.3 \text{ \AA}$, compared to $3.8 \text{ \AA}$ of commonly used Li^+) results in an interlayer spacing as large as $13.4 \text{ \AA}$ (against $11.07 \text{ \AA}$ for Li^+ intercalated V_2O_5), which allows efficient Zn^{2+} (de)insertion. As a result, the obtained porous $\text{Mg}_{0.34}\text{V}_2\text{O}_5 \cdot 0.84\text{H}_2\text{O}$ nanobelts work in a wide potential window of $0.1\text{-}1.8\text{V}$ versus Zn^{2+}/Zn , and can deliver high capacities of 353 and 264 mA h g^{-1} at current densities of 100 and 1000 mA g^{-1} , respectively, along with long-term durability. Furthermore, the reversible Zn^{2+} (de)intercalation reaction mechanism is confirmed by multiple characterizations methods.

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Given the growing utilization of renewable energy sources, demand for low-cost, safe, and eco-friendly energy storage technologies is soaring.¹⁻² Although Li-ion batteries have dominated the portable electronics market, the low abundance of Li raises questions about their long-term viability.³⁻⁴ In this regard, batteries, especially aqueous rechargeable batteries based on earth-abundant Al,⁵ Mg,⁶ Na,⁷ and Zn⁸⁻⁹ are promising candidates because of the lower cost and safer water-based electrolytes.¹⁰ Among them, aqueous zinc ion batteries (ZIBs) exhibit enormous potential owing to a series of unique advantages such as low-cost (high abundance and large-scale distribution of Zn), high safety, low redox potential, and a two-electron transfer mechanism that ensures high energy density.¹¹ Up to now, the most studied cathode materials for ZIBs have been manganese-based oxides,^{4, 11-12} Prussian blue analogs,¹³⁻¹⁴ and vanadium-based materials.¹⁵⁻²³ Among them, V-based materials, have received tremendous attention due to their low-cost, multiple redox reactions, and large interlayer spacings/tunnel that allows efficient Zn²⁺ insertion. For instance, Nazar et al. reported a Zn²⁺ intercalated V₂O₅ cathode material, namely Zn_{0.25}V₂O₅ • nH₂O (ZVO), which showed a high capacity (300 mA h g⁻¹ @ 50 mA g⁻¹) and excellent rate performance.¹⁵ Later, Mai's group reported Na_{0.33}V₂O₅ (NVO) with enhanced performance (253.7 mA h g⁻¹ @ 200 mA g⁻¹) and stability compared to pure V₂O₅.¹⁶ Our group also demonstrated that a better ZIB performance can be achieved on Ca_{0.25}V₂O₅ • nH₂O (CVO) (340 mA h g⁻¹ @ 50 mA g⁻¹) because of the larger interlayer spacing, lower molecular weight, and better conductivity than ZVO.¹⁷ Very recently, Hu et al. also demonstrated a highly durable Na₂V₆O₁₆•1.63H₂O nanowire cathode which exhibits a capacity retention of 90% over 6000 cycles at 5000 mA g⁻¹.²² Liang's group further developed several sodium vanadates²⁴ and potassium vanadates²⁵ with different compositions for ZIBs. Despite the rapid development of

ZIBs, there is still a need to search for new cathode materials with high capacity and rate performance. More importantly, the booming development always causes insufficient understanding and more attention should be paid to the fundamental insights of Zn ion storage mechanism in cathode materials.

Because of the (de)intercalation-type storage mechanism of ZIBs, layered electrode materials are generally preferable and materials with large layer spacings are expected to possess good performance.¹⁵⁻¹⁷ Interestingly, it was reported that the interlayer spacing of chemically pre-intercalated V_2O_5 is directly proportional to the radii of hydrated ions. By screening the possible metal ions (e.g. Li^+ , Na^+ , K^+ , Ca^{2+} , Mg^{2+}), we found that the radius of hydrated Mg^{2+} (~ 4.3 Å) is much larger than others (e.g. ~ 3.8 Å for Li^+).²⁶ The Mg^{2+} intercalated V_2O_5 has a similar crystal structure to that of δ -type ZVO^{15} and CVO^{17} (**Figure 1A**). Two individual V_2O_5 layers are bound by the interlayer V-O bonds, while the hydrated Mg^{2+} ions and/or water molecules are found in the space between two bilayers.²⁷⁻²⁸ However, the molecular weight of Mg is smaller than that of Zn and Ca (both ZVO^{15} and CVO^{17} were demonstrated to be promising cathodes for ZIBs), thus higher theoretical capacity and energy density can be expected on Mg^{2+} intercalated V_2O_5 . We thus predicted that the MVO could be a promising cathode material for ZIBs.

In this work, we report the synthesis of porous $Mg_{0.34}V_2O_5 \cdot nH_2O$ (MVO) nanobelts and further demonstrate its application as a pre-cathode material in aqueous rechargeable ZIBs. We show that the as-obtained cathode can work in a wide potential window of 0.1-1.8V versus Zn^{2+}/Zn and can deliver high capacities of 353 and 264 mA h g⁻¹ at current densities of 50 and 1000 mA g⁻¹, respectively, along with excellent stability (~ 97 % capacity retention for at least

2000 cycles at a high rate of 5000 mA g⁻¹). The Zn²⁺ ion storage mechanism was thoroughly investigated and elucidated using various analytical techniques.

Figure 1. Structural characterization of MVO cathodes. (A) Crystal structure. (B) XRD pattern. (C) EDS spectrum. (D) TGA profile. (E) SEM, (F) TEM and (G) HRTEM images. (H) TEM-EDS elemental maps.

The MVO nanobelts were prepared by a simple hydrothermal method (see details in Supporting Information). As displayed in **Figure 1B**, the typical XRD pattern of MVO is dominated by (00 l) reflections, indicating a high degree of preferred orientation along c -axis. Similar diffraction patterns have also been observed in chemically pre-intercalated δ -V₂O₅.²⁹⁻³³ Essentially, these compounds originate from the parent material of V₂O₅·0.5H₂O (JCPDS #40-1297). The (001) peak is located at 2θ of $\sim 6.65^\circ$, corresponding to an interlayer spacing of 13.4 Å, which is much larger than that of ZVO (10.2 Å) or CVO (10.6 Å).¹⁷ We further carried out XRD Rietveld refinement and the structural parameters were calculated to be $a = 10.571(0)$, $b = 7.941(7)$, and $c = 13.433(2)$; $\alpha = 90.081(6)^\circ$, $\beta = 89.769(3)^\circ$, and $\gamma = 89.900(1)^\circ$ with an R factor

(R_{wp}) of 6.98% (see **Figure S1** and **Table S1**). As we discussed earlier, such a large spacing would allow efficient Zn^{2+} insertion, thus leading to a high performance. Energy disperse spectroscopy (EDS, **Figure 1C**) confirms the existence of Mg, V, and O in MVO. Inductively coupled plasma optical emission spectroscopy (ICP-OES) and thermogravimetric analysis (TGA, **Figure 1D**) were further performed to determine the amounts of Mg and crystalline water, which suggest a stoichiometric formula of $Mg_{0.34}V_2O_5 \cdot 0.84H_2O$ for the as-obtained magnesium vanadium oxide. SEM and TEM images (**Figure 1E-F**) reveal that the MVO is composed of nanobelts with a typical size of $\sim 10 \mu m$ in length and ~ 500 nm in width. High-resolution TEM (HRTEM) images (**Figure 1G** and **Figure S2**) confirm the porous structure. The measured lattice fringe of 0.22 nm can be indexed to (006) planes of MVO. Additionally, the TEM-EDS elemental mapping images (**Figure 1H**) of as-obtained MVO indicate the uniform distribution of Mg, V, and O in the MVO nanostructure. These results confirm that we have successfully synthesized porous layered MVO nanobelts with an interlayer spacing as large as 13.4 Å.

The MVO electrode (**Figure S3**) made by vacuum filtration was used as the cathode for aqueous ZIBs, where zinc foil and 3 M $Zn(CF_3SO_3)_2$ were used as anode and electrolyte, respectively. **Figure S4** shows the cyclic voltammetry (CV) plot at the scan rate of 0.2 mV s^{-1} within the voltage window of 0.1-1.8 V (vs. Zn/Zn^{2+}). We note that this working potential window is larger than other recently reported vanadium oxide based cathodes (e.g. 0.5-1.4 V for $Zn_{0.25}V_2O_5$,¹⁵ 0.6-1.6 V for $Ca_{0.25}V_2O_5$ ¹⁷), which allows to achieve higher power density. This could be due to the inferior electrocatalytic activity of the MVO electrode and the relatively more acidic electrolyte, i.e. $Zn(CF_3SO_3)_2$ that results in a lower OER kinetics as compared to that in the commonly used $ZnSO_4$ electrolyte. Indeed, the CV and linear sweep voltammetry (LSV) (**Figure S5**) curves (in a two-electrode system) further confirm the voltage window is safe and

without any hydrogen/oxygen evolution. Multiple pairs of redox peaks can be observed, indicating a multi-step reaction associated with the continuous and stepwise zinc ion (de)insertion. The galvanostatic charge-discharge curves of MVO under various current densities (from 50-3000 mA g⁻¹) are shown in Figure 2A. Obvious plateaus can be discerned during the charge/discharge process, consistent with the CV result. The rate performance of MVO is illustrated in Figure 2B, where the current density is gradually increased from 50 to 5000 mA g⁻¹ and then back to 100 mA g⁻¹. The discharge capacities at 50, 100, 500, 1000, 2000, 3000, and 5000 mA g⁻¹ are ~ 353, 330, 291, 264, 221, 167, and 81 mA h g⁻¹, respectively. Moreover, the discharge capacity recovers to 331 mA h g⁻¹ when the rate returns to 100 mA g⁻¹, suggesting an excellent rate capability. The performance reported here is better than other V₂O₅ based compounds such as ZVO (300 mA h g⁻¹ @ 50 mA g⁻¹), CVO (340 mA h g⁻¹ @ 50 mA g⁻¹), and NVO (173.4 mA h g⁻¹ @ 500 mA g⁻¹) (also see comparison in **Table S2**, Supporting Information). To further understand the Zn ion storage behavior of MVO cathode, we analyzed the electrochemical kinetics and further quantitatively separated the capacitive contribution using a previously reported simple CV method (**Figure S6**) (also see details in Supporting Information).³⁴ For instance, at a scan rate of 0.3 mV s⁻¹, 67% of the total current, namely the capacity, is capacitive in nature (Figure 2C). The current contribution ratios at other scan rates were also calculated (Figure S7). The result shows that the capacitive contribution holds the dominant position in the total capacity and the contribution ratio of capacitive to diffusive current gradually increases with the scan rate. The results indicate that the corresponding reaction is mainly limited by the electrochemical reaction rate itself but not the Zn²⁺ ion diffusion rate.^{17, 23, 35-36} Further, the *b*-value of the redox peaks are determined to be 0.73, 0.82, 0.83, 0.57, and 0.98, respectively, suggesting the dominating capacitor-like kinetics (Figure 2D).

We then employed the galvanostatic intermittent titration technique (GITT)³⁷⁻³⁸ to determine the ion diffusion coefficient of Zn^{2+} in MVO cathode (Figure 2E, F). The diffusion coefficient of MVO is determined to be 10^{-8} to $10^{-9} \text{ cm}^2 \text{ s}^{-1}$, which is higher than that of bulk V_2O_5 ³⁹ and comparable to that of nanobelt structured ZVO,¹⁵ CVO,¹⁷ $\text{Ag}_{0.4}\text{V}_2\text{O}_5$,³⁶ etc.¹² This result suggests that the porous MVO nanobelts are able to achieve fast Zn^{2+} migration, thus resulting in good rate performance. Apart from the high capacity and good rate capability, the MVO cathode also exhibits outstanding cycling stability. We measured the cycling performances at different current densities (100, 1000, and 5000 mA g^{-1}) and the results are shown in Figure 2G-I. In all cases, the capacity of MVO gradually increases at the beginning due to the activation of the electrode materials (the activation might be associated with the replacement/intercalation process, as discussed later). Similar phenomena have also been seen in ZVO and NVO.^{15-16, 39} The MVO electrodes show excellent long-term durability with negligible capacity decay at 100 mA g^{-1} for at least 200 cycles and only 5% capacity decay at 1000 mA g^{-1} for at least 1000 cycles (against the highest capacity). Even at a high rate of 5000 mA g^{-1} , 97% capacity retention can still be achieved after 2000 cycles. ICP-OES was conducted to determine the vanadium corrosion (herein, a two-electrode electrolyzer was used since it is difficult to collect the electrolyte in a coin cell) and the result shows that a very small amount of V ($\sim 0.01\%$) is detected in electrolyte after the battery was cycled at 1000 mA g^{-1} for 100 cycles. This further suggests that the MVO electrode is quite stable in $\text{Zn}(\text{CF}_3\text{SO}_3)_2$ electrolyte, which is also confirmed by the stable cycling performance.

Figure 2. Zn ion storage performance of as-obtained cathodes. (A) Galvanostatic charge-discharge plots at different current densities. (B) Rate performance. (C) CV curve with capacity separation at 0.3 mV s^{-1} . (D) The b -value of different redox peaks determined from the $\log(i)$ versus $\log(v)$ plots. (E) Charge-discharge GITT curves at a current density of 30 mA g^{-1} , and (F) the corresponding Zn^{2+} coefficients as a function of Zn^{2+} composition during the charge-discharge scan. (G-I) Cycling performances at current densities of 100, 1000, and 5000 mA g^{-1} , respectively.

In order to gain insight into the Zn^{2+} ions storage mechanism of Zn/MVO system, ex-situ XRD, Raman, XPS, EDS, SEM, and TEM characterizations were carried out. As shown in **Figure S8**, the post-characterizations of the electrode during the second cycle show that after the

first cycle, the Mg can be barely seen in the electrode material, i.e. $\text{Mg}_{0.34}\text{V}_2\text{O}_5 \cdot 0.84\text{H}_2\text{O}$, a considerable amount of Zn instead, is found after charging to 1.8 V, and the Zn/V ratio is determined to be $\sim 0.3:2$ by EDS. This result suggests that most of the Mg^{2+} has been deintercalated and further displaced by Zn^{2+} to form $\text{Zn}_{0.3}\text{Mg}_x\text{V}_2\text{O}_5$ and serve as the cathode material (x is sufficiently small because the Mg can be only detected by XPS but not EDS) after the first cycle. Such phenomenon is known as the displacement/intercalation reaction mechanism and has also been observed in $\text{Ag}_{0.4}\text{V}_2\text{O}_5$ ³⁶ and $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ ⁴⁰ for Zn ion battery as well as in $\text{Cu}_{2.33}\text{V}_4\text{O}_{11}$,⁴¹ $\text{Ag}_2\text{VP}_2\text{O}_8$,⁴² and CuTi_2S_4 ⁴³ for lithium ion battery. The deintercalated Mg^{2+} was found to deposit on Zn anode upon charge, unlike previously reported $\text{Ag}_{0.4}\text{V}_2\text{O}_5$, where Ag^+ was in situ reduced to metallic Ag and deposited on the cathode. These Mg^{2+} ions were then dissolved back in the electrolyte and served as the interaction cation along with Zn^{2+} ions upon discharge. The distribution of Mg on Zn anode was confirmed by the SEM-EDS elemental mapping (**Figure S9**). It is noteworthy that from the EDS results (conducted on the cathode during the 2nd cycle at 100 mA g⁻¹), around 1 mole Zn^{2+} was intercalated into the host materials, corresponding to a capacity of ~ 260 mA h g⁻¹ that matches the capacity shown in **Figure 2G**.

The (de)insertion mechanism in $\text{Zn}_{0.3}\text{Mg}_x\text{V}_2\text{O}_5$ (after the first cycle) was investigated via XRD during the third cycle (**Figure 3**). The structural changes accompanying Zn^{2+} (de)intercalation are complex. Two solid-solution regimes ($0.8 > x > 0$ and $1.4 > x > 0.8$) are separated by a phase transition exist (at $x \approx 0.8$). Firstly, during the discharge process, up to $x \sim 0.8$ (1.8-0.8V), only a small contraction of interlayer spacing is observed (**Figure 3C**). This is because of the inserted Zn^{2+} with structural water (solvation effect) will screen the interlayer electrostatic repulsion as the Zn^{2+} content increases. Further, the formation of hydrogen bonds

among Zn^{2+} , H_2O , and lattice oxygen that pulls the bilayers closer. After the charging process, these peaks nearly recover to their initial position, demonstrating that the structural change of $\text{Zn}_{0.3}\text{Mg}_x\text{V}_2\text{O}_5$ upon the charge/discharge process is highly reversible, which ensures good cycling stability. It is noteworthy that as demonstrated previously, the water (both crystal water and the water in the electrolyte) plays a critical role which can enhance the zinc ion transport, electrochemical activity, as well as the reversibility.^{15, 22, 35, 44} In our case, combined with the XRD results (**Figure 3**), we believe Zn^{2+} ions are intercalated into the gallery as a complex along with water. We observed that the interlayer spacing of Zn^{2+} intercalated MVO is around 13.2 Å, while the spacing of the parent material $\text{V}_2\text{O}_5 \cdot 0.5\text{H}_2\text{O}$ is 8.75 Å. The ~4.45 Å difference in interlayer spacing suggests that the Zn^{2+} ions are likely intercalated as a complex with water molecules because the radius of the hydrated Zn^{2+} is around 4.3 Å whereas is ~0.7 Å for Zn^{2+} with no hydration. The water-based shielding layer reduces the “effective charge” of Zn^{2+} . In the meantime, it also increases the distance between Zn^{2+} and the neighboring oxygen ions of the MVO layers, resulting in the reduced electrostatic bond strength, which is also the reason why it exhibits a high diffusion coefficient.^{22, 35} Beside the diffraction peaks of $\text{Zn}_{0.3}\text{Mg}_x\text{V}_2\text{O}_5$, we also observed a new phase that emerges upon discharge process from 0.6 to 0.3 V. Unfortunately, due to the complex dual ion-intercalation process, we are unable to identify this specific compound. However, the diffraction peaks with almost equal interval in 2theta degree (~ 6.3°, 12.7°, 19.2°, and 25.8°) suggest a layered structure and we therefore speculate that the new phase is likely the layered $\text{Zn}_{(z+0.3)}\text{Mg}_x\text{V}_2\text{O}_5$, where $1.4 > z > 0.8$. We further performed Raman analysis of MVO at different charge/discharge states. As shown in Figure 4A, we can observe that two peaks between 400-600 cm^{-1} gradually weakened during the discharge process and then strengthened after fully charged to 1.8 V, which is associated with the (de)insertion of the Zn^{2+} . Notably, two

peaks between 800-1000 cm^{-1} Raman shift emerged and strengthened upon discharge and then disappeared as Zn^{2+} extraction. These two peaks are related with $\text{V}=\text{O}$,⁴⁵ and can be ascribed to the new phase and similar phenomenon can be found in other works.^{16, 46-47} This result is also in good agreement with the XRD analysis. **Figure S10** reveals that the porous structure is well maintained upon the charging/discharging process. The HRTEM images further suggest that the contraction of the lattice spacing of (006) plane is highly reversible (**Figure 4B-D**), which matches with the XRD result. Moreover, the SEM images of the electrodes after 200 and 2000 cycles also reveal that there are no obvious morphology changes (**Figure S11**). Finally, ex-situ XPS analysis was used to further substantiate the above results. As shown in Figure 4E, no signal can be detected in Zn 2p region in the original electrode, while sharp and strong peaks can be observed in the fully discharged sample, which indicates the successful insertion of Zn^{2+} ions. In contrast, in fully charged state (Zn^{2+} extraction), the intensities of the Zn 2p peaks are very weak, indicating most of Zn^{2+} are extracted from the electrode.^{16, 23} This again agrees with the XRD and TEM result. Additionally, the evolution of V 2p XPS peaks confirms the reversible electrochemical reduction of V-O-V upon charge/discharge. As depicted in **Figure 4F**, the peaks at binding energies of 515.8 and 517 eV can be assigned to V^{4+} and V^{5+} species, respectively, which confirms partial reduction of the V_2O_5 framework due to the pre-intercalated Mg^{2+} .^{46, 48} Analysis of the discharged cathode revealed a third contribution at 515.4 eV that corresponds to V^{3+} species, along with an increase in V^{4+} and a decrease in V^{5+} as a result of Zn^{2+} intercalation and consequent reduction of V_2O_5 framework. The peaks of V^{4+} and V^{5+} components shift slightly to higher binding energies of 516.4 eV and 517.4 eV (V 2p_{3/2}), respectively. The reason for such a blue shift may be linked to the intercalation of the Zn^{2+} ions and the concomitant bonding rearrangements at the $\text{V}^{4+}/\text{V}^{5+}$ sites, the exact nature of which still remains unclear.¹⁵

After the charging process, the V^{5+} again becomes the dominant species, similar to that of the fresh electrode in the initial state. This, together with the XRD, Raman, EDS, SEM, and TEM results, confirm the high reversibility and outstanding stability of the resultant $Zn_{0.3}Mg_xV_2O_5$ upon charge/discharge.

Figure 3. *Ex situ* XRD characterization of the resultant $Zn_{0.3}Mg_xV_2O_5$ cathode upon charging-discharging process. (A, C) The ex-situ XRD patterns of the resultant $Zn_{0.3}Mg_xV_2O_5$ electrodes at different charge/discharge states, and (B) corresponding galvanostatic charge-

discharge profile at 200 mA g⁻¹. (D) The XRD patterns of MVO electrodes discharged to 0.6 V and charged to 0.3 V.

Figure 4. *Ex situ* structural and compositional characterizations of the resultant $\text{Zn}_{0.3}\text{Mg}_x\text{V}_2\text{O}_5$ cathode during the charging-discharging process. (A) Raman spectra collected at different charge/discharge states. (B-D) HRTEM images at (B) initial, (C) fully discharged, and (D) charged states, respectively. (E, F) XPS spectra of (E) Zn 2p and (F) V 2p regions in original, fully discharged, and charged states.

Based on these findings and discussion, we proposed the storage mechanism as shown in **Figure 5** and the electrode reactions as follows:

The 1st cycle on the cathode:
discharge:

charge:

Figure 5. Schematic illustrations of Zn²⁺ storage mechanism upon electrochemical charge and discharge processes.

The subsequent cycles:

The reactions on the zinc anode:

The overall reaction after first cycle can be depicted as:

Given the abundant Zn²⁺ and the trace amount of Mg²⁺, the contribution of Mg²⁺ intercalation might be small, the overall reaction therefore can be simplified as

5 In summary, we have developed a high-performance cathode material for aqueous ZIBs
6
7 characterized by relatively large interlayer spacing. The resultant $\text{Zn}_{0.3}\text{Mg}_x\text{V}_2\text{O}_5$ cathodes can
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9 deliver a high capacity of 352 mA h g⁻¹ at 100 mA g⁻¹ along with excellent rate performance and
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11 cycling stability (~97 % capacity retention for at least 2000 cycles at 5000 mA g⁻¹). Extensive
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13 characterization of the cathode material at different charge/discharge states revealed that the
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15 structure of the cathode is highly reversible and highly stable. The replacement/intercalation
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17 mechanism demonstrated here is quite different from the previously reported CVO and NVO,
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19 which provides more information and gives a new insight into the reactions of aqueous ZIBs.
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27 ASSOCIATED CONTENT
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31 **Supporting Information.** The following files are available free of charge.
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34 Experimental details, additional supporting data, and comparison of performance, as noted in the
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36 main text (PDF)
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50 **Notes**
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