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#### Article

## Multinuclear Transition Metal Sandwich-Type Polytungstate Derivatives for Enhanced Electrochemical Energy Storage and Bifunctional Electrocatalysis Performances

Xinyue Ma, Kai Yu,\* Jie Yuan, Liping Cui, Jinghua Lv,\* Wenting Dai, and Baibin Zhou\*



**ABSTRACT:** Different transition metal (TM) units are introduced into a trivacant Keggin cluster to form three sandwich polytungstate derivatives,  $(H_2en)[\{K(H_2O)_{0.5}\}_2\{K_2(H_2O)_3\}\{Ni(H_2O)(en)_2\}_2\{Ni_4(H_2O)_2(PW_9O_{34})_2\}]$  (1),  $[Cu_6(Himi)_6\{As^{III}W_9O_{33}\}_2]\cdot SH_2O$  (2), and  $(H_2btp)_4[Fe^{III}_2Fe^{II}_2(H_2O)_2(AsW_9O_{34})_2]\cdot 4H_2O$  (3) (en = ethanediamine; imi = imidazole; btp = 1,3-bis(1, 2, 4-triazol-1-yl) propane). Compound 1 is a 2,3,8-connected 3D network with  $\{4^3\}_2\{4^6\cdot 6^6\cdot 8^3\cdot 6^{12}\cdot 8\}\{6\}_2$  topology based on bisupported tetra-Ni sandwich phosphotungstate and two kinds of potassium connection units. Compound 2 is a dense 12-connected 3D supramolecular network with  $\{3^{24}\cdot 4^{36}\cdot 5^6\}$  topology based on hexa-Cu(imi) sandwiched arsenotungstate. Compound 3 represents the first mixed valence tetra-Fe substituted sandwich arsenotungstate assembly. Compounds 1–3 show enhanced supercapacitor performance (618.2, 603.4, and 504.6 F·g<sup>-1</sup> at a current density of 2.4 A·g<sup>-1</sup> with 91.5%, 89.3%, and 87.8% of cycle efficiency after 5000 cycles, respectively) compared to their maternal polyoxometalates (POMs) and most reported POM-based electrode materials, which suggests that the introduction of multinuclear TM into vacant POMs is an effective method to improve the energy storage performance of POMs. In addition, compounds 1 and 3 exhibit dual-functional electrocatalytic behaviors in the reduction of iodate and the oxidation of dopamine for introduction of  $\{Ni_4\}$  and  $\{Fe_4\}$  units.

### ■ INTRODUCTION

The rapid consumption of fossil energy and the deterioration of ecological environment have given rise to the development of advanced energy storage and conversion equipment.<sup>1,2</sup> Supercapacitors as novel energy storage devices have aroused people's interest and are widely used in portable electronics, electric vehicles, and smart grids due to their long cycle lifetime, rapid energy conversion, and high energy densities.<sup>3–5</sup> Pseudocapacitors (PCs) are Faraday capacitors which can store energy through rapid reversible chemical adsorption, desorption, or redox reactions on the electrode surface. The quality of such supercapacitor devices mainly depends on the performance of the electrode material itself. At present, pseudocapacitance materials mainly include carbon-based materials,<sup>6</sup> conductive polymers,<sup>7,8</sup> and transition metal oxides/hydroxides.<sup>9,10</sup> However, the low capacitance and high cost of new carbon-based materials, as well as poor cyclic stability of conductive polymers, limit their practical application. Among the transition metal oxides, RuO<sub>2</sub> has

high theoretical specific capacity, wide voltage range, and excellent conductivity and is the best and most promising material.<sup>11</sup> But the application of such materials has been limited due to their scarce resources and high prices. Therefore, the development of cheap supercapacitor materials with good comprehensive performance is still an urgent issue.

Polyoxometallates (POMs) as a big class of nanometal oxygen clusters composed of transition metals (Mo, W, and V etc.) possess various structures, different sizes, and excellent physicochemical characteristics,<sup>12–15</sup> which endows them with wide applications in catalysis, photoelectric chemistry, and pharmacochemistry.<sup>16–19</sup> In addition, POMs can engage in fast

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Compound	1	2	3
formula	$C_{10}H_{56}K_4N_{10}Ni_6O_{77}P_2W_{18}\\$	$C_{18}H_{34}As_2Cu_6N_{12}O_{71}W_{18}$	$C_{28}H_{64}As_2Fe_4N_{24}O_{74}W_{18}$
$M_r$	5428.54	5394.84	5603.57
Crystal size, mm <sup>3</sup>	$0.17\times0.15\times0.13$	$0.19 \times 0.17 \times 0.15$	$0.18 \times 0.16 \times 0.14$
Crystal system	Triclinic	Cubic	Orthorhombic
Space group	$P\overline{1}$	Pa3	Pbca
<i>a,</i> Å	12.27(3)	21.9385	20.903(5)
b, Å	12.39(3)	21.9385	19.772(5)
<i>c,</i> Å	16.48(5)	21.9385	23.186(5)
$\alpha$ , deg	105.65(6)	90	90
$\beta$ , deg	91.29(6)	90	90
γ, deg	116.03(3)	90	90
V (Å <sup>3</sup> )	2139(10)	10559.0(6)	9583(4)
Z	1	4	4
$D_{\text{calcd}}$ kg m <sup>-3</sup>	4.213	3.394	3.884
$\mu$ (Mo K $lpha$ ), mm <sup>-1</sup>	25.711	21.407	22.892
F(000), e	2408	9464	9976
heta range, deg	2.601-24.999	3.080-24.986	2.442-27.670
Reflections collected/unique/R <sub>int</sub>	13532/7353/0.0648	12713/3098/0.0796	114471/11166/0.0743
Data/restraints/parameters	7353/962/587	3098/324/215	11166/277/680
$\mathbf{R}_1/\mathbf{w}\mathbf{R}_2 \ [\mathbf{I} \ge 2\sigma(\mathbf{I})]^a$	0.0731/0.1873	0.0838/0.1772	0.0439/0.1387
$GoF(F^2)^a$	1.073	1.066	1.051
R <sub>1</sub> /wR <sub>2</sub> (all data)	0.1181/0.1924	0.1111/0.1859	0.0749/0.1765
$R1 = \sum ( F_{o}  -  F_{c} ) / \sum \sum  F_{o} ; \ wR2 = \{ \sum [w( F_{o} ^{2} -  F_{c} ^{2})^{2}] / \sum [w( F_{o} ^{2})^{2}] \}^{1/2}.$			

#### Table 1. Crystal Data and Structure Refinements for Compounds 1-3

multielectron conversion without changing their own structure due to their outstanding redox capacity and structural stability. Thus, they have strong electrochemical energy storage capacity and excellent electrocatalytic properties.<sup>20,21</sup> Recently, POMs have received great attention as the active material of supercapacitors. $^{22-33}$  However, the application of routine POM materials in water system supercapacitors has been hindered due to their poor electrical conductivity and great solubility in aqueous solution. In order to overcome the above shortcomings, many research groups combine POMs with conductive polymers or immobilize POMs onto carbon-based materials to prepare hybrid nanocomposites with composite features and improved supercapacitor behavior. Representative studies mainly include carbonnanotube/Cs-PMo<sub>12</sub> hybrids,<sup>22</sup> POM adsorbed activated carbon materials,<sup>23</sup> PMo<sub>12</sub>-polyaniline/graphene composites,<sup>24</sup> polymeric ionic liquid connected POM/reduced graphene oxide nanohybrids,<sup>25</sup> and {Mo<sub>132</sub>}rGO nanocomposites.<sup>26</sup> However, the above synthesis methods are complex, and it is necessary to prepare POM precursors. In addition, the exact components of the synthesized complexes are difficult to be determined. Fortunately, POM as an excellent molecular-based material has outstanding tailoring properties.<sup>27</sup> It can be connected with transition metal, organic ligands, and metal-organic complexes to form various hybrid materials and host-guest structures to adjust the stability of the solution, the specific surface area, and conductivity, so as to improve the supercapacitor performances.<sup>28-35</sup>

As one of the branches of POMs, the trilacunary Keggin  $[XW_9O_{34}]^{9-}$  (X = P, As, Sb, and Bi) is an ideal building unit that can combine a certain number of transition metals into the vacant positions between two polyoxoanions to form sandwich polytungstates with multinuclear clusters. The introduction of different transition metal units will play important roles in regulating catalysis,<sup>38–42</sup> magnetism,<sup>43–47</sup> redox properties,<sup>48–50</sup> and medicinal activity of POMs.<sup>51–54</sup> However,

property studies of sandwich polytungstate have been mainly focused on magnetic behavior, catalytic properties, and biological activity. The effects of the introduction of transition metal clusters on the energy storage performance and electrochemical behavior of these compounds have not been studied. Therefore, it is very meaningful and attractive to explore the supercapacitor and electrocatalytic properties of novel high-core sandwich polytungstate assemblies. Herein, different transition metal clusters are introduced into the trivacant Keggin cluster to yield three novel multinuclear sandwich-type polytungstates,  $(H_2en)[\{K(H_2O)_{0.5}\}_2]$ { $K_{2}(H_{2}O)_{3}$ }{ $\tilde{N}i(\tilde{H}_{2}O)(en)_{2}$ }{ $Ni_{4}(H_{2}O)_{2}(PW_{9}O_{34})_{2}$ } (1),  $[Cu_{6}(Himi)_{6}\{As^{III}W_{9}, O_{33}\}_{2}] \cdot 5H_{2}O_{2}(2), \text{ and } (H_{2}btp)_{4}$  $[Fe^{III}_{2}Fe^{II}_{2}(H_{2}O)_{2}(AsW_{9}O_{34})_{2}]\cdot 4H_{2}O$  (3) via in situ hydrothermal reaction of simple raw materials. The electrochemical energy storage performance and electrocatalytic behavior after the introduction of transition metals were studied for the first time. The result of our experiment reveals that the grafting of multinuclear TM cluster into vacant POMs is an effective method to enhance the energy storage performance and improve electrochemical properties of POMs.

#### EXPERIMENTAL SECTION

The details of general methods and materials, synthesis of compounds 1-3, X-ray crystallography, and preparation of the electrodes are given in section 1 of the Supporting Information. Details of the crystallographic data and structural determination for 1-3 are listed in Table 1.

#### RESULTS AND DISCUSSION

**Synthesis.** In the process of exploring novel transition metal substituted sandwich polytungstate assemblies, we try to introduce copper, vanadium, iron, etc. into a  $\{XW_9\}$  (X = As, P) system by a one-step hydrothermal method, as the high-core sandwich unit mentioned above is relatively difficult to be incorporated into the trivacancy Keggin system. Many factors

affect the structure of the sandwich-type derivatives during preparation. The addition of different transition metals, organic ligands, and mineralizers directly affects the type, number of substitutions, and final spatial structure of sandwich-type POMs. When the reaction of Na<sub>2</sub>MoO<sub>4</sub>·2H<sub>2</sub>O, NaAsO<sub>4</sub>, FeCl<sub>3</sub>, and 1,3-bis(1,2,4-triazol-1-yl) propane was conducted at 160 °C for 6 days at a pH range of 4-4.5, tetra-Fe-substituted compound 3 was prepared. This inspired us to change transition metal and build copper substituted arsenotungstate derivatives under similar conditions. Unfortunately, when copper salt is used to replace FeCl<sub>3</sub>, no expected crystals were obtained, which indicates that the introduction of a multinuclear copper sandwich unit requires the assistance of appropriate mineralizing agent. This may be the reason why other transition metal hexasubstituted derivatives similar to compound 2 have been reported as early as 2009,<sup>55</sup> while compounds with six-core copper have not yet been prepared. NH<sub>4</sub>VO<sub>3</sub> as excellent mineralizer can effectively activate POM clusters, so it is added to the system. Because of the simultaneous existence of copper and vanadium elements in the system, the bonding competition between them and trivacant Keggin cluster  $\{AsW_{q}\}$  must be considered. When the rigid ligand imidazolium is added to the system to control the temperature at 160 °C, the hexa-copper substituted arsenotungstate derivatives are synthesized. When imi ligands are replaced by pz and phen and the reaction temperature is reduced to 140 °C, the mixed hexa-TM ( $V^{IV}_5Cu^{II}O_6$ ) substituted arsenotungstate derivatives are obtained. It is clear that the type of ligands and the temperature of reaction are the key factors affecting the coordination activity of vanadium and copper with {AsW<sub>9</sub>} polyoxyanions. Higher reaction temperature and the addition of imi ligands are beneficial to enhance the reaction activity of Cu and reduce the reaction activity of vanadium in the {Cu/V/As/W} system. The experimental results show that the introduction of vanadium is a very difficult project, which can only be achieved with the aid of Cu<sup>2+</sup> and two rigid ligands. This is the main reason why few sandwich compounds with high nuclear vanadium substitutions have been reported. In the strategy, Cu with d<sup>10</sup> configuration and two complementary rigid ligands are easy to form multicore complexes and further form a more complex metal-organic network, which may induce Vsubstituted sandwich clusters and their extended assembly. In addition, we try to use the same one-step hydrothermal method to prepare high-core transition metal substituted sandwich-type phosphotungstate. Different transition metals and various organic ligands have been tried through a large number of parallel experiments under the reaction conditions of compound 3 by replacing sodium arsenite with phosphate or hydrogen phosphate. The results show that only when the transition metal nickel and organic ligand en are added into the system can a 4-Ni substituted 3D highly connected derivative be obtained. It is clear that phosphotungstate is not easy to be synthesized by hydrothermal synthesis of simple raw materials. On the contrary, a precursor method is more suitable for these derivatives, which can be proved by the widely reported methods of preparing for sandwich-type phosphotungstes. The synthesis strategies of the three compounds are summarized in Scheme 1.

**Structure Descriptions of 1.** Compound 1 belongs to the  $P\overline{1}$  spatial group of triclinic crystal system and contains two B- $\alpha$ -type trivacant Keggin clusters {PW<sub>9</sub>O<sub>34</sub>}, one {Ni<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>} sandwich unit, two {Ni(H<sub>2</sub>O)(en)<sub>2</sub>} complexes, one binuclear

Scheme 1. Relationship among the Structures of the Sandwich-Type Polytungstates, Transition Metal Salts, and Organic Ligands



linker {K<sub>2</sub>(H<sub>2</sub>O)<sub>3</sub>}, two {K(H<sub>2</sub>O)} cations, and one H<sub>2</sub>en ligand (Figure S1). Two {PW<sub>9</sub>O<sub>34</sub>} fragments and one {Ni<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>} unit connect each other via seven bridging O atoms of each polyoxoanion to form a tetra-Ni sandwiched cluster {Ni<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>(PW<sub>9</sub>O<sub>34</sub>)<sub>2</sub>}. In the central belt of the sandwich structure, four 6-coordinated Ni atoms (Ni1 and Ni3) are linked via a common edges mode to form a centrosymmetric tetranuclear unit {Ni<sub>4</sub>O<sub>14</sub>(H<sub>2</sub>O)<sub>2</sub>} (Figure 1b). The bond lengths of Ni–O and bond angle of O–Ni–O



Figure 1. (a) Polyhedral/ball and stick representation of the  $[\{K(H_2O)\}_2\{K_2(OH)_2(H_2O)_2\}\{Ni(H_2O)_3\}_2\{Ni_4(H_2O)_2(PW_9O_{33})_2\}]$  cluster. (b) Coordination manner of the tetra-Ni sandwich unit  $\{Ni_4O_{14}(H_2O)_2\}$  in compound 1.

are in the range of 2.02(2)-2.21(3) Å and  $88.0(10)-174.3(10)^\circ$ , respectively. The distance between adjacent Ni… Ni is 3.157 and 3.192 Å. Each Ni2 adopts hexacoordinated octahedral geometry bonds and bonds to four N derived from two en, one terminal oxygen atom of polyanion, and one water molecule to form a complex unit {Ni(H<sub>2</sub>O)(en)<sub>2</sub>}. Each such unit links with two symmetrical oxygen atoms of sandwich polyanion to yield a biarm sandwich unit [{Ni(H<sub>2</sub>O)(en)<sub>2</sub>}<sub>2</sub>-{Ni<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>(PW<sub>9</sub>O<sub>34</sub>)<sub>2</sub>}] (Figure 1a). The distances of Ni–O and Ni–N are in the range of 2.15(3)–2.24(3) Å and 2.05(4)–2.10(3) Å, respectively (Table S1).



Figure 2. (a) Polyhedral/ball and stick representation of a 2D layer of compound 1; (b) polyhedral/ball and stick representation of the 3D network of 1; (c) view of the topology of the 2D layer; (d) view of the topology of the 3D network.

Two crystallographically independent potassium atoms expand the sandwich cluster unit into an extended 3D open skeleton. Each K1 cation exhibits a deformed octahedral coordination environment with five O donors from three sandwich clusters and one water molecule. The K2 displays a distorted octahedral configuration, which is defined by two terminal oxygen atoms of sandwich polyanion and four water molecules. Two water molecules act as linkage unit connecting two symmetrical K2 atoms into a binuclear bridge unit  $\{K_2(H_2O)_6\}$ . The average distance of K–O is 2.602. Each biarmed sandwich building block links to six surrounding  $\{K1(H_2O)\}\$  caions, while each  $\{K1(H_2O)\}\$  cation connects with three adjacent sandwich units. In this way, each biarmed sandwich cluster bonds to six adjacent analogues via  $\{K1(H_2O)\}\$  linkers to result in a infinite 2D layer (Figures 2a and S2). The  $\{K_2(H_2O)_6\}$  segments of each sandwich polyanion projecting from the layer bond with the O atom of the sandwich cluster on the adjacent two layers to form a 3D framework (Figure 2b). The overall structure of compound 1 is an extended (2,3,8)-connected 3D network with  $\{4^3\}_2\{4^6,6^6,$  $8^3 \cdot 6^{12} \cdot 8$  {6}<sub>2</sub> topology based on a 3,6-connected 2D layer in view of considering  $\{K_2(H_2O)_6\}$  as 2-connected nodes,  $\{K1(H_2O)\}\$  as 3-connected nodes, and sandwich cluster as 6-connected nodes (Figure 2c and d).

**Structure Descriptions of 2.** Compound 2 crystallizes in the *Pa* $\overline{3}$  spatial group of the cubic crystal system and consists of two trivacant Keggin B- $\alpha$ -{AsW<sub>9</sub>O<sub>33</sub>} polyoxoanions, one {Cu<sub>6</sub>(imi)<sub>6</sub>} sandwich unit, and solvent water molecules (Figures 3 and S3). In structure 2, each Cu atom adopts a pentacoordinated tetragonal pyramid configuration to link four O atoms derived from equatorial {WO<sub>6</sub>} of two {AsW<sub>9</sub>O<sub>33</sub>} clusters and one N donor of the imi molecule. Six {CuO<sub>4</sub>N} units are bonded together to generate a six-nuclear metal ring {Cu<sub>6</sub>O<sub>12</sub>N<sub>6</sub>}. Two {AsW<sub>9</sub>O<sub>33</sub>} clusters are sandwiched by the coplanar six-core unit {Cu<sub>6</sub>O<sub>12</sub>N<sub>6</sub>} via 12 terminal O atoms of two polyoxoanion clusters to yield a hexa-Cu substituted



Figure 3. Polyhedral/ball and stick representation of  $\{Cu_6(imi)_6(As^{III}W_9O_{33})_2\}$  cluster.

sandwich unit {Cu<sub>6</sub>(imi)<sub>6</sub>(AsW<sub>9</sub>O<sub>33</sub>)}. The bond lengths of Cu–O and bond angle of O–Cu–O are in the range of 2.038(18)–2.065(18) Å and 79.4(9)–147.8(14)°, respectively. The Cu–N distance is 1.99(2) Å. The distance between adjacent Cu…Cu is 3.118 Å (Table S2).

Each hexa-Cu substituted sandwich unit as basic building block links six sandwich  $\{Cu_6(imi)_6(AsW_9O_{33})\}$  clusters in ABAB mode via the H-bond interaction  $(N1\cdots O1\ 2.729)$  between the N of the central sandwich unit  $\{Cu_6O_{12}N_6\}$  and the O atoms of ambient polyoxoanion clusters (Figure S4a). Meanwhile, six other adjacent polyoxoanion clusters using the N atoms (N1) of their sandwich unit connect the symmetric O atoms (O1) of the central cluster via the same H-bonding interaction in the same way (Figure S4b). In the above connection ways, each polyoxoanion is connected with 12 surrounding analogues in the form of ABAB to result in a 3D dense packing structure (Figures S4c and 4a). The simplified structure of compound 2 is an extended 12-connected 3D net with  $\{3^{24}\cdot4^{36}\cdot5^6\}$  topology based on the fact that the 6-Cu

substituded sandwich cluster acts as a 12-connected node (Figure 4b).



Figure 4. (a) Tightly stacked 3D networks of compound 2; (b) fcu/ cubic closest packing with 12-connected  $\{3^{24} \cdot 4^{36} \cdot 5^6\}$  topology.

**Structure Descriptions of 3.** Compound 3 belongs to the *Pbca* space group of the orthorhombic crystal system, which is composed of one 4-Fe substituted sandwich POM cluster  $\{Fe^{III}_{2}Fe^{II}_{2}(H_{2}O)_{2}(AsW_{9}O_{34})_{2}\}$ , four biprotonated organic ligands  $H_{2}$ btp, and four water molecules (Figure S5). Two trivacant Keggin polyoxoanion B- $\alpha$ -{AsW<sub>9</sub>O<sub>34</sub>} are bonded together by mixed valence tetranuclear iron units  $\{Fe^{III}_{2}Fe^{II}_{2}(H_{2}O)_{2}\}$  via seven bridging O atoms of each polyoxoanion to form a tetra-Fe sandwiched cluster  $\{Fe^{III}_{2}Fe^{II}_{2}(H_{2}O)_{2}(AsW_{9}O_{34})_{2}\}$ . The sandwich units of compounds 3 and 1 are isostructural, and the coordination mode of iron in  $\{Fe^{III}_{2}Pe^{II}_{2}O_{14}(H_{2}O)_{2}\}$  is the same as that of nickel in  $\{Ni_{4}O_{14}(H_{2}O)_{2}\}$  (Figure 5). The difference is that the



Figure 5. Polyhedral/ball and stick representation of  ${Fe^{II}_{2}Fe^{II}_{2}(H_{2}O)_{2}(AsW_{9}O_{34})_{2}}$  cluster in 3.

 ${Fe^{II}_{2}Fe^{II}_{2}O_{14}(H_2O)_2}$  is a mixed valence tetranuclear unit. The bond lengths of Fe1–O3 and Fe1–O4 are 1.906(10) and 1.890(12), respectively (Table S3). The relatively shorter bond length contribution between Fe1 and O atoms results in +III valences of Fe1. The bond lengths of Fe2–O are in the range of 2.078(11)–2.254(11) Å, which yields +II valences of Fe2. The adjacent tetra-Fe sandwiched polyoxoanions with two spatial orientations are aggregated together in an ABAB manner via supramolecular interactions (O24… O30 3.032) between terminal O atoms of two sandwich-type anions to give birth to 1D chains (Figure S6). The same supramolecular interactions (O24…O30 3.032) extend adjacent 1D chains to the 2D supramolecular plane (Figure S7). In addition, isolated ligands reinforce the 2D layer via four supramolecular interactions (C9...O20 3.122, C12...O19 3.042, C18...O23 3.118, and C11...O11 3.151). The lattice water molecules link the adjacent 2D plane into the 3D supramolecular net via a pair of hydrogen bonds (O28...O2W 2.70(2) Å and O2W... O11 2.74(2) Å) (Table S4 and Figure S8).

Compounds 1-3 were synthesized by adjusting the kinds of transition metals and organic ligands under similar hydrothermal conditions, which are summarized in Scheme 1. The bond valence calculation<sup>56</sup> shows that all tungsten atoms are in +6 valence, the phosphorus, nickel, and potassium center in compound 1 are in +5, +2, and +1, respectively, the arsenic and copper atoms in compound 2 are in +3 and +5, and the arsenic, Fe1, and Fe2 centers in compound 3 are +5, +3, and +2, respectively.

**IR Spectroscopy.** The IR spectra of 1–3 (Figure S9) exhibit the obvious vibration bands of trivacant Keggin clusters.<sup>47,57</sup> The peaks at 1042, 933, 879, 756 cm<sup>-1</sup> in 1, 872, 996, 804, 714 cm<sup>-1</sup> in 2, and 862, 982, 813, 706 cm<sup>-1</sup> in 3 are indicative of the stretching vibration of  $\nu$ (P–O<sub>a</sub>) (1)/(As–O<sub>a</sub>) (2 and 3),  $\nu$ (W=O<sub>t</sub>),  $\nu$ (W–O<sub>b</sub>), and  $\nu$ (W–O<sub>c</sub>), respectively. The vibrational signals in the region of 1430–1658 cm<sup>-1</sup> are attributed to the vibration of  $\nu$ (N–H) of organic ligands in 1–3. The broad peaks at 3299–3581 cm<sup>-1</sup> are ascribed to the stretching vibration  $\nu$ (O–H) of water molecules or  $\nu$ (N–H) of protonated organic ligand.

**TG** Analyses. The TG analyze curves (Figure S10) of compounds 1–3 were depicted under a N<sub>2</sub> atmosphere from 50 to 900 °C. Two obvious weight losses can be detected in the TG curve of compounds 1–3. The first weight losses of 2.67% (calcd 2.63%) at 225–330 °C for 1, 14.20% (calcd 13.77%) at 160–210 °C for 2, and 1.94% (calcd 1.89%) at 160–210 °C for 3 can be attributed to the removal of all water molecules. The second weight loss of 5.45% (calcd 5.41%) at 380–650 °C for 1, 6.14% (calcd 6.64%) at 385–650 °C for 2, and 12.96% (calcd 12.91%) at 380–630 °C for 3 is attributed to the losses of organic ligands en, Himi, and H<sub>2</sub>btp, respectively.

XRPD and X-ray Photoelectron Spectra Analyses. In order to prove the purity and stability of compounds 1-3, the samples before electrochemical test were selected and immersed in 0.5 M sulfuric acid solution for 72 h. The X-ray powder diffraction of samples before and after soaking were tested, which are shown in Figure S11. Compared with the simulated PXRD diagram, the characteristic peaks of the samples did not change before and after soaking, which are in good agreement with that of the simulated XRD. The result suggests that compounds 1-3 have good stability and purity. The oxidation states of As and Cu of compound 2, as well as As and Fe of compound 3, are further determined by XPS tests, which were conducted in the energy area of As 3d5/2, As 3d3/2, Cu 2p3/2, Cu 2p1/2, Fe 2p3/2, and Fe 2p1/2 (Figure 6). The XPS spectrum of compound 2 exhibits two peaks at 39.0 and 43.2 eV in As 3d and two peaks at 933.7 and 953.8 eV in the Cu 2p region, which are attributed to  $As^{3+}$  (ref 58) and  $Cu^{2+,32}$  respectively. Two peaks at 39.9 and 44.6 eV in the As 3d for compound 3 are ascribed to As<sup>5+,59</sup> Additionally, four peaks at 724.6, 711.2, 723.5, and 709.6 eV in Fe 2p are attributed to  $Fe^{3+}$  and  $Fe^{2+}$  ions, respectively.<sup>60</sup> The oxidation number of all elements coincides with the calculated results of the valence bond.

**SEM and EDS Analyses.** The element composition and surface topography of compounds 1-3 were studied by



Figure 6. XPS spectrum of As (a), Cu (b) of compound 2 and As (c), Fe (d) of compound 3.

scanning electron micrographs (SEM) and energy dispersive spectroscopy (EDS). As shown in Figures 7 and S12–S15, compounds 1–3 are rectangular bulk crystals with a size of about 130 × 80 × 15, 140 × 70 × 30, and 180 × 120 × 60  $\mu$ m<sup>3</sup>, respectively. The elements C, N, O, P, W, K, and Ni in compound 1, C, N, O, As, W, and Cu in compound 2, and C,



Figure 7. EDS elemental mappings of W, O, Ni, P, N, K, and C for compound 1.

N, O, As, W, and Fe in compound 3 are detected and evenly distributed from the figure of EDS mapping and microanalysis.

**Capacitive Performance Compounds 1–3.** The electrochemical performances of 1–3-based glassy carbon electrode (1–3-GCE) were carried out in a trielectrode system with 0.5 M sulfuric acid electrolyte. The cyclic voltammetry (CV) curves of 1–3-GCE in the potential window range of -0.6-0.6V (potentials vs Ag/AgCl) at scanning rates from 25 to 200 mV s<sup>-1</sup> are shown in Figure 8. The CV curves of 1–3-GCE



Figure 8. Cyclic voltammograms (CV) curves of 1-GCE (a), 2-GCE (b), and 3-GCE (c) in 0.5 M sulfuric acid solution at 25, 50, 75, 100, 125, 150, 175, and 200 mV s<sup>-1</sup> (inset shows plots of the anodic and cathodic peak currents vs scan rates). (d) Comparative diagrams of CV curves of 1-, 2-, and 3-GCE at 20 mV s<sup>-1</sup>. Potentials vs Ag/AgCl.

exhibit three pairs of reversible redox peaks with mean-peak potentials  $E_{1/2} = (E_{pa} + E_{pc})/2$ , -115 (II–II'), -345 (III–III'), and -585 (IV–IV') mV for 1, -120 (II–II'), -333 (III–III'), and -578 (IV–IV') mV for 2, and -105 (II–II'), -325 (III–III'), and -529 (IV–IV') mV for 3, which could be assigned to continuous two-electron redox processes of W atom in sandwich-type polytungstate clusters.<sup>61</sup> The redox reaction of the W center of compounds 1–3 is similar. The transformation mechanism of compound 1 as a representative can be described as the following:<sup>26</sup>

$$\{ Ni_{4}(H_{2}O)_{2}(PW_{9}O_{34})_{2} \}^{10^{-}} + 2e + 2H^{+} \leftrightarrow \{ H_{2}Ni_{4}(H_{2}O)_{2}(PW^{VI}_{7}W^{V}_{2}O_{34})_{2} \}^{10^{-}}$$
(1)

$$\{H_2Ni_4(H_2O)_2(PW^{V1}_7W^V_2O_{34})_2\}^{10^-} + 2e + 2H^+ \leftrightarrow \{H_4Ni_4(H_2O)_2(PW^{V1}_5W^V_4O_{34})_2\}^{10^-}$$
(2)

$$\{H_4 Ni_4 (H_2 O)_2 (PW^{VI}_5 W^{V}_4 O_{34})_2 \}^{10-} + 2e + 2H^+ \leftrightarrow \{H_6 Ni_4 (H_2 O)_2 (PW^{VI}_3 W^{V}_6 O_{34})_2 \}^{10-}$$
(3)

Additional quasi-irreversible peaks (I/I') in 1–3-GCE with  $E_{1/2}$  395, 80, and 425 mV in the positive voltage direction represent the characteristic peaks associated with the transition metal Ni,<sup>62</sup> Cu,<sup>63</sup> and Fe<sup>64</sup> redox couples, respectively. Different from the rectangular shape of a dual-layer capacitor, the above three compounds exhibit quasi-reversible multiple pairs of oxidation–reduction peaks, which indicates that they are typical pseudocapacitance active material. When the scan

speed gradually increases from 25 to 200 mV  $s^{-1}$ , the shape of the CV curve remains substantially constant but shows an increase in current density, which illustrates the outstanding Faraday process on the electrode surface and good rate performance of sandwich-type polytungstates.<sup>33,65</sup> From the CV curve, we can also see that the cathode peak and anode peak move slightly in the direction of negative and positive potential, respectively, which may be caused by the polarization effect of the electrode. As shown in the inset of Figure 8, the linear relations between the current of all redox peaks and sweeping rate demonstrates the kinetics of interfacial Faraday reaction and the rapid electron transfer speed.<sup>29-35</sup> The contrast diagrams of CV curves between 1-3-GCE and their respective parents' POM: Na<sub>9</sub>[PW<sub>9</sub>O<sub>34</sub>]·7H<sub>2</sub>O-GCE ({PW<sub>9</sub>}-GCE), and Na<sub>8</sub>[A- $\alpha$ -HAsW<sub>9</sub>O<sub>34</sub>]-GCE ({AsW<sub>9</sub>}-GCE) in the voltage range of -0.6-0.6 V at scanning rate of 25 mV·s<sup>-1</sup> are recorded in Figure S16. Compared with CV of {PW<sub>9</sub>}-GCE and {AsW<sub>9</sub>}-GCE, CV curve of 1-GCE, 2-GCE, and 3-GCE exhibit bigger encircled area than that of their parent-GCE at the same scanning speed, which suggests that they have larger capacitance than that of their parent POMs. Extended CV area indicates enhanced capacitance performance due to the introduction of multicore transition metals cluster. In addition, as shown in Figure 8d, the CV area of 1-3-GCE is in the order of: 1-GCE > 2-GCE> 3-GCE, indicating that compounds 1 and 2 have a larger capacitance than that of compound 3. As a result, the introduction of the transition metal complex and the construction of the 3D channel assembly can also improve the supercapacitors performance of sandwich-type polytungstate to some extent.

The galvanostatic charge–discharge at different current densities of 1–3-GCE was conducted in the potential range of –0.6–0.6 to further evaluate the electrochemical energy storage performance of synthetic compounds. As shown in Figure 9, the GCD curves of 1–3-GCE exhibit the voltage platform corresponding to the CV shape, which indirectly reflects the Faraday redox behavior derived from tungsten and the transition metal clusters of sandwich-type polytung-state.<sup>29–35</sup> The specific capacitance ( $C_s$ ) values are 618.2, 593.2, 564.8, 555.6, and 512.4 F·g<sup>-1</sup> for 1-GCE, 603.4, 586.8,



**Figure 9.** GCD curves of 1-GCE (a), 2-GCE (b), and 3-GCE (c) at current densities of 2.4, 4.8, 9.6, 14.4, and 19.2  $\text{Ag}^{-1}$ . (d) Comparison of specific capacitance of 1–3-GCE and parent POM: {AsW<sub>9</sub>O<sub>33</sub>} and {PW<sub>9</sub>O<sub>34</sub>} at different current densities.

548.0, 513.6, and 493.2  $F \cdot g^{-1}$  for 2-GCE, and 504.6, 480.4, 464.7, 444.2, and 424.9  $F \cdot g^{-1}$  for 3-GCE at the current densities of 2.4, 4.8, 9.6, 14.4, and 19.2  $A \cdot g^{-1}$ . The areal capacitances (*C*<sub>a</sub>) are 182.4, 175.0, 166.6, 163.9, and 151.2 mF· cm<sup>-2</sup> for 1-GCE, 178.0, 176.0, 161.7, 151.5, and 145.5 mF· cm<sup>-2</sup> for 2-GCE, and 147.4, 141.5, 102.6, 87.3, and 78.1 mF· cm<sup>-2</sup> for 3-GCE at the same current density as above. In the case of high current density (19.2), the  $C_s$  and  $C_a$  of 1-3-GCE can still remain very large values (512.4  $F{\cdot}g^{-1}$  and 151.2 mF  ${\cdot}$  $cm^{-2}$  (1), 493.2 F·g<sup>-1</sup> and 145.5 mF·cm<sup>-2</sup> (2), 424.9 F·g<sup>-1</sup> and 78.1 mF·cm<sup>-2</sup> (3)), which reflects the prominent rate capability of the sandwich-type polytungstate. With the increase of current density, the sequential slight decrease of the  $C_s$  and  $C_a$  values (Figure 9d) can be attributed to the loss of efficiency of polytungstate in the redox process under large current.<sup>29,34</sup> In addition, consistent with the results of CV area comparison, the  $C_{\rm s}$  values of 1–3-GCE are higher than that of their contrast compounds ( $\{PW_{q}\}$ -GCE and  $\{AsW_{q}\}$ -GCE), which further illustrates that the  $C_s$  of synthetic derivatives can be increased by introducing multinuclear transition metals into vacancy POM clusters. The  $C_s$  values of 1-3-GCE are higher than that of amorphous POM-based nanocomposites, such as carbonnanotube/Cs-PMo12 hybrids,<sup>22</sup> POM adsorbed activated carbon materials,<sup>23</sup> PMo<sub>12</sub>-polyaniline/graphene composites,<sup>24</sup> polymeric ionic liquid connected POM/reduced graphene oxide nanohybrids,<sup>25</sup> and {Mo<sub>132</sub>}-rGO nanocomposite.<sup>26</sup> The higher specific capacitance of compounds 1-3 may be related to the ordered arrangement of the internal structure of the crystal, which can lead to more rapid and efficient transfer of the electrons on the electrode surface. Meanwhile, the  $C_s$  values of 1–3-GCE are also higher than that of most reported POMs crystal materials (Table \$5).<sup>29-37</sup> The superiority of the capacitance performance may be due to the introduction of transition metal cluster units, which leads to more abundant redox reactions in multicore sandwich-type POMs clusters.

The cycle stability of GCD is the key parameter to evaluate the durability and lifetime of a supercapacitor electrode. The cycling performances of 1-3-GCE, {PW<sub>9</sub>}-GCE, and {AsW<sub>9</sub>}-GCE are depicted in Figure 10a at a certain current density



**Figure 10.** Capacitance degradation of 1-GCE, **2**-GCE, and **3**-GCE during 3000 cycles at a current density of 2.4 mA·cm<sup>-2</sup>. (b) EIS contrast spectra of 1-GCE, **2**-GCE, **3**-GCE, and parent POM:  $\{AsW_9O_{33}\}$  and  $\{PW_9O_{34}\}$  (Inset: the magnification part of the high frequency range for the EIS spectra).

(2.4 A·g<sup>-1</sup>) and voltage range (-0.6-0.6 V). After 1000 cycles, the C<sub>s</sub> values of 1–3-GCE decreased by approximately 7.56%, 8.33%, and 10.72%, respectively, and then by a small amount as the number of cycles increased. The capacitance retention rates of 1–3-GCE are 91.5%, 89.3%, and 87,8%, respectively, while those of {PW<sub>9</sub>}-GCE and {AsW<sub>9</sub>}-GCE are only 82.1% and 83.4% after 5000 cycles. Compounds 1–3 show better



Figure 11. EIS control spectra of 1-GCE (a), 2-GCE (b), and 3-GCE (c) before and after circulation (Inset: the magnification part of the high frequency range for the EIS spectra).

cyclic stability than their maternal POM, suggesting that the grafting of multinuclear transition metal units into trivacant Keggin cluster improves the stability and cycle life of polytungstate. In addition, compared with the cyclic stability of compounds 1-3, it is found that the highest capacitance retention rate of compound 1 is more than 90%, which can be ascribed to its spatial structure characteristics. Compound 1 is a complicated high-connected 3D framework based on tetra-Ni substituted sandwich-type phosphotungstate. A large number of covalent bonds in its structure reinforce the skeleton of polytungstate, effectively alleviate the volume changes caused by Faraday redox reaction, and thus improve the cyclic stability of electrode materials during charge and discharge.

To further evaluate the relationship between capacitive performance and the resistance of the polytungstate electrode materials, the EIS spectra of compounds 1-3 and two control compounds were tested and shown in Figure 10b. As shown in the insertion diagram, the intercept between the Nyquist curve of 1-3-GCE and the X axis in the high frequency domain is 3.83, 4.20, and 4.35, respectively. The values are smaller than those of {PW<sub>9</sub>}-GCE and {AsW<sub>9</sub>}-GCE, which means that they have smaller ohmic resistance  $(R_s)$  than their parent POM. In addition, the radius of their curved semicircle is also smaller than that of the two control compounds indicating that they have lower charge transfer resistance  $(R_{ct})$  than their parent POM. Meanwhile, the slope of 1-3-GCE in the low frequency region is larger than control compounds, suggesting that compounds 1-3 have lesser ion diffusion resistance  $(Z_w)$ than their mother POM. The results of comparison among compounds 1-3 show that the order of three resistance values  $(R_{s}, R_{ct}, Z_w)$  is 1-GCE < 2-GCE < 3-GCE, suggesting that compounds 1 and 2 have smaller internal and diffusion resistance than compound 3. The above EIS analysis results can be interpreted as follows: (1) The introduction of the multinuclear transition metal endows the obtained sandwichtype derivative with a more abundant electron transfer process, which enhances Faraday reaction and reduces the inherent electrodes of three electrode materials. (2) The introduction of metal complexes (Ni(en)<sub>2</sub> and Cu(imi)) in compounds 1 and **2** provides a rich  $\pi$  electron system and accelerates the electron transfer in the electrode materials. (3) The 3D channel structure of compound 1 allows rapid diffusion of the electrolyte and provides a site for efficient conversion of ions/electrons. The EIS contrast diagrams before and after 5000 cycles of 1–3-GCE are shown in Figure 11. The Warburg resistance  $(Z_w)$  and  $R_s$  values of three compounds increase slightly after 5000 cycles, while the shape of the Nyquist plots was basically the same before and after cycles, so the  $R_{ct}$  values hardly changed much after 5000 cycles. These results further

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confirm the outstanding cyclic stability and reversible redox performance of compounds 1-3.

**Bifunctional Electrocatalytic Properties.** Dopamine (DA) is a substance widely existing in the human body that can transmit neural information. Whether DA in the brain maintains balance is of great significance to regulate the uncertain mood of the human body. Lack of DA can cause increased muscle tone and sluggish movement, including quiescent tremors, which can lead to depression, Parkinson's disease, or heart disease.<sup>66</sup> Therefore, it is of great significance to monitor its content in the human body by an electrochemical method to assist in clinical diagnosis of related diseases. In addition, the exploration of iodate  $(IO_3^{-})$  content is also of great significance in medicine and the food industry. So the organic biomolecule DA and inorganic IO<sub>3</sub><sup>-</sup> were selected as substrates for redox reactions to further study the electrocatalytic behavior of sandwich derivatives formed by the introduction of different transition metals.

As depicted in Figure 12, with the increase of DA concentration, the anodic peak current of the Ni(II) and



**Figure 12.** Cyclic voltammograms of 1-GCE (a) and 3-GCE (b) in 0.5 M  $H_2SO_4$  solution containing DA at different concentrations (from bottom to top: bare-GCE, 0, 0.5, 1.0, 1.5, 2.0 mM; Scan rate: 30 mV·s<sup>-1</sup>). Potentials vs Ag/AgCl.

Fe(III) waves of 1-GCE and 3-GCE increased sharply, illustrating the catalytic activities of 1-GCE and 3-GCE for the oxidation of DA.<sup>21</sup> It can be seen from the insertion figure that there is a linear relationship between the added DA concentration and anode peak (I) current, reflecting nearly equal current stride and each addition of DA, which further demonstrates the stability and effective electrocatalytic activity of 1-GCE and 3-GCE to oxidation of DA.<sup>66</sup> On the contrary, with the addition of DA, the Cu peak of 2-GCE is almost unchanged suggesting that it has no catalytic effect on the oxidation of DA (Figure S17). The above results indicate that the transition metal summit due to the introduction of multicore TM improves the oxidation capacity of polytung-state, and the effects of different transition metals on the oxidation capacity are also different.

As shown in Figure 13a-c, with the increase of  $IO_3^-$  concentration, the anode peak current of all W decreases and



**Figure 13.** Cyclic voltammograms of 1-GCE (a), 2-GCE (b), and 3-GCE (c) in 0.5 M  $H_2SO_4$  solution containing  $IO_3^-$  at different concentrations (from top to bottom: bare-GCE, 0, 0.5, 1.0, 1.5 mM; Scan rate: 30 mV·s<sup>-1</sup>). Potentials vs Ag/AgCl. (d) Histogram of the CAT vs concentration of  $IO_3^-$  or DA for 1–3-GCE. (I<sub>p</sub> values of cathodic peak VI for  $IO_3^-$  and anodic peak I for DA at a scan rate of 30 mV·s<sup>-1</sup>.)

the cathode peak current increases correspondingly. In addition, the same linear relationship between  $IO_3^-$  concentration and cathode peak (II', III', and IV') current indicates stable and effective electrocatalytic activity of 1-3-GCE for the reduction of  $IO_3^{-}$ .<sup>67</sup> In contrast, no obvious response was observed for the reduction of  $IO_3^-$  and oxidation of DA at a bare-GCE without active materials (Figures 12 and 13). The reaction mechanism of 3-GCE on DA and  $IO_3^-$  as a representative can be deduced and shown in the five sections of the Supporting Information.

The catalytic efficiencies (CAT) of 1-3-GCE were computed via the CAT formula.<sup>68</sup> The bar chart of CAT% for 1-3-GCE vs concentrations of DA or  $IO_3^-$  is shown in Figure 13d. The order of CAT of 1-3-SCE for iodate reduction and DA oxidation is 3-GCE > 1-GCE > 2-GCE, which suggests that the catalytic performance of tetra-Fe substituted arsenotungstate is better than that of tetra-Ni substituted phosphotungstate and 6-Cu substituted arsenotungstate. It can be seen from the comparison results that the implantation of metal complexes in compounds 2 and 3D structural advantages of compound 1 are not reflected in the electrocatalytic efficiency, which indirectly reflects that the difference in electrocatalytic performance of three sandwich-type derivatives is mainly determined by the types of TM sandwich unit. The electrocatalytic advantage of compound 3 can be attributed to the higher redox peak position of Fe center and the better synergistic effect between the mixed valence tetranuclear iron cluster { $Fe^{III}_{2}Fe^{II}_{2}(H_2O)_{2}$ } and the W center in the POM cluster. In summary, compounds 1 and 3 show dual-functional electrocatalytic behavior for reduction of IO<sub>3</sub><sup>-</sup> assigned to W centers and oxidation of DA attributed to Ni/Fe centers, which are new potential bifunctional electrocatalytic sensor materials.

The electrocatalytic stability studies have shown that after 60 cycles, the CVs of reduced  $IO_3^-$  and oxidized DA have hardly changed (Figures S18 and S19), which indicates that 1-3-

GCEs have better catalytic stability and the catalytic activity could be well maintained during repeating electrocatalytic reactions.

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In conclusion, different TM units are introduced into trivacant Keggin POMs to yield tetra-Ni, hexa-Cu, and tetra-Fe substituted sandwich-type polytungstate derivatives. Synthetic compounds exhibit better supercapacitor performance than their parent POMs and most reported POM-based electrode materials, which suggests that the introduction of multinuclear transition metal into vacant POMs is an effective method to improve electrochemical supercapacitor performance of POMs. In addition, compounds 1 and 3 are potential dualfunctional electrochemical sensing materials and exhibit excellent catalytic behavior in the reduction of inorganic iodate and the oxidation of organic biological molecules dopamine for introduction of  $\{Ni_4\}$  and  $\{Fe_4\}$  units. This work not only enriches the types of sandwich-type POMs but also provides a useful strategy for enhancing the energy storage performance and improving the electrocatalytic oxidation ability of POMs.

#### ASSOCIATED CONTENT

#### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.0c00382.

Experimental Section, structural figures (Figures S1– S8), structural data (Tables S1–S5), physical characterization (Figures S9–S19), and electrocatalytic reaction mechanism of 3-GCE (PDF)

#### **Accession Codes**

CCDC 1945872–1945874 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data\_request/cif, or by emailing data\_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

#### AUTHOR INFORMATION

#### **Corresponding Authors**

- Jinghua Lv Key Laboratory for Photonic and Electronic Bandgap Materials, Ministry of Education, School of chemistry and chemical engineering, Harbin Normal University, Harbin 150025, P. R. China; Phone: (+86) 0451-88060334; Email: wlljh1964@163.com; Fax: (+86) 451-8806-0653
- Baibin Zhou Key Laboratory for Photonic and Electronic Bandgap Materials, Ministry of Education, School of chemistry and chemical engineering and Key Laboratory of Photochemical Biomaterials and Energy Storage Material, Heilongjiang Province, Harbin Normal University, Harbin 150025, P. R. China; ● orcid.org/0000-0001-8304-5092; Phone: (+86) 0451-88060334; Email: zhou\_bai\_bin@163.com; Fax: (+86) 451-8806-0653

#### Authors

- Xinyue Ma Key Laboratory for Photonic and Electronic Bandgap Materials, Ministry of Education, School of chemistry and chemical engineering and Key Laboratory of Photochemical Biomaterials and Energy Storage Material, Heilongjiang Province, Harbin Normal University, Harbin 150025, P. R. China
- **Jie Yuan** Harbin Medical University Daqing Campus, Daqing 163319, Heilongjiang, China
- Liping Cui Key Laboratory for Photonic and Electronic Bandgap Materials, Ministry of Education, School of chemistry and chemical engineering and Key Laboratory of Photochemical Biomaterials and Energy Storage Material, Heilongjiang Province, Harbin Normal University, Harbin 150025, P. R. China
- Wenting Dai Key Laboratory for Photonic and Electronic Bandgap Materials, Ministry of Education, School of chemistry and chemical engineering and Key Laboratory of Photochemical Biomaterials and Energy Storage Material, Heilongjiang Province, Harbin Normal University, Harbin 150025, P. R. China

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.inorgchem.0c00382

#### Notes

The authors declare no competing financial interest.

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