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Hybridizing Engineering Strategy of Decatungstate. 2. Regulated Effect of Doping Transition Metal Ions on Photocatalytic Oxidation Performance of $(nBu_4N)_4W_{10}O_{32}$

Angun Su, Mengke Chen, Zaihui Fu,* Bo Yang, Jialuo She, Feifei Wan, Chao Zhang, and Yachun Liu



and photoluminescence (PL) spectra, and cyclic voltammetry (CV) characterizations indicate that the synthetic quality, redox capacity, and visible light harvesting efficiency of TBADT, especially the separation efficiency of its photogenerated electron-hole pairs, are regulated by the metal ion dopants and gradually improved with a change of the dopant from Fe³⁺, Fe²⁺, and Co²⁺ to Ni²⁺, along with a continuous and significant



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enhancement of its photocatalytic efficiency in the visible-light-triggered selective oxidation of ethylbenzene with dioxygens in acetonitrile. The best 0.5 mol % Ni²⁺-doped TBADT can achieve a ca. 55% conversion under optimal reaction conditions and also exhibits much higher photocatalytic activity for the photo-oxidation of toluene, cyclohexane, and benzyl alcohol compared to pure TBADT. This HE strategy showcases great potential in improving the photocatalysis performance of TBADT.

1. INTRODUCTION

The selective oxidation of ethylbenzene (EB) to acetophenone (ACP) by molecular oxygen is one of the important conversions for the development of petrochemical downstream products and fine chemicals; it is also very important for the theoretical study of selective oxidation of saturated carbon– hydrogen bonds.^{1,2} Some thermal catalysis protocols with cobalt,³ carbon materials,^{4,5} and silica-based nanocomposites^{6,7} as catalysts have been developed to efficiently achieve this selective oxidation, but they usually need to employ harsh operating conditions to activate the inert molecular oxygen, which rarely leads to the chemistry being highly selective.³

Photocatalysis oxidation continues to be of interest as a potentially clean and highly selective conversion protocol for the synthesis of oxygenates owing to its mild reaction conditions. Tetrabutyl-ammonium decatungstate (TBADT), as one of the most efficient photocatalysts reported so far, has recently received considerable attention because it exhibits unique structure-dependent photo- chemical and photophysical properties. TBADT has been extensively applied in the framework of photocatalytic synthesis, especially including the photocatalytic oxidation of inert hydrocarbons by molecular oxygen (O_2) ,^{9–19} which should be due to its unparalleled reactivity.¹⁰ However, the photocatalytic performance of TBADT is still limited to its low synthetic quality, unstable structure, poor visible light harvesting efficiency,

unsatisfactory redox recycling, and photoexcited state lifetime. On the basis of the vacancy character of polyoxometalates (POMs), some efficient hybridizing engineering (HE) strategies with a photosensitizer, metal substitution, and ligand (substrate) coordination have been developed to significantly improve the photocatalytic performance of POMs.²⁰ Among these hybridized POMs, the substitution of transition metals may get a high quality of POMs, extending metal-to-POMs charge transfer and excited-state lifetimes.^{21,22} Especially, some sandwich type POMs, which are formed by sandwiching metal ions between two missing units, have exhibited unique catalysis performance in the epoxidation of olefins with $\hat{H}_2 O_2^{23,24}$ or N_2O^{25} because they are more stable than their initial structures and their redox potentials can be controlled at the molecular level by tailoring their structures and constituent elements and/or by the introduction of additional metal cations into the POM framework.²⁰ However, to the best of our knowledge, the efficient HE strategy for improving the photocatalytic performance of TBADT is still rare, which may be due to the

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unstable structure and nonvacancy character of TBADT. The only successful example is our recently reported carbon quantum dot (CQD)-hybridized TBADT with a remarkably enhanced visible-light catalytic performance.²⁶

Inspired by the above-mentioned research progress of metalhybridized POMs and CQD-hybridized TBADT, we would try to develop a simple and productive HE strategy of TBADT by transition metals here. A series of characterization and photooxidation experiments support that the doping of some cheap 3d transition metal ions Fe^{3+} , Fe^{2+} , Co^{2+} , and Ni^{2+} ions (M^{n+}) can be directly achieved in the synthesis of TBADT, and the M^{n+} ion-doped TBADT catalysts obtained by this very simple strategy have a more stable structure and stronger redox capacity than pure TBADT. More importantly, their frontier orbital energies, band gap energies, and photoexcited state lifetimes can be fine-tuned at the molecular level by the metal ion dopants, thus comprehensively resolving the above inadequacies of TBADT and showing the remarkably enhanced photocatalytic performance for the visible lightdriven selective oxidation of EB and other organic compounds with O₂. This pioneering work not only provides an effective HE strategy for the preparation of the metal ion-hybridized TBADT photocatalysts but also opens up new voyages, using inexpensive and readily available 3d transition metal ions to fine-regulate the synthetic quality, redox ability, and photophysiochemical properties of TBADT at the molecular level.

2. EXPERIMENTAL SECTION

2.1. Material and Sample Preparation. All chemicals were analytical grade and used without further purification. Sodium tungstate (Na_2WO_4 ·2H_2O), tetrabutylammonium bromide (TBABr), FeCl₃·6H₂O, FeCl₂·4H₂O, CoCl₂·6H₂O, NiCl₂·6H₂O, concentrated hydrochloric acid (36% HCl), sulfuric acid (98% H₂SO₄), phosphoric acid (85% H₃PO₄), benzenesulfonic acid (PhSO₃H), acetic acid (HAc) cyclohexane, toluene, ethylbenzene, benzyl alcohol, and acetonitrile (MeCN) were purchased from Sinopharm and used without further treatment. Distilled water was used throughout this experiment.

2.2. Synthesis of Transition Metal lons (M^{n+})-doped TBADT Catalysts. The 3d transition metal ion Ni²⁺, Co²⁺, Fe²⁺, and Fe³⁺- doped TBADT catalysts (tagged M^{n+} -TBADT) were synthesized via a hydrothermal reaction. Typically, 6.4 g (19.4 mmol) of Na₂WO₄· 2H₂O was dissolved with 40 mL of water, followed by the addition of 13.4 mL of 3 M HCl solution containing 0.1 mmol of M^{n+} ; the acidified solution was heated to boiling for 5-10 min to obtain a decatungstate acid solution. Next, 6 M TBABr solution (20 mmol) was added to the decatungstate acid solution at 100 °C under continuous stirring, and the white solid was gradually precipitated from the reaction solution. Then, the obtained precipitate and reaction solution were transferred to a 100 mL Teflon-lined autoclave and treated at 120 °C for 12 h under autogenous pressure (about 0.19 MPa). The obtained precipitate was filtered, repeatedly washed with water and ethanol, and then dried under a vacuum at 60 °C for 24 h to yield the goal products (Mⁿ⁺-TBADT, here, the theoretical content of the doped M^{n+} ions was ca. 0.5 mol % relative to W atoms). In order to prevent Fe²⁺ oxidation to Fe³⁺, the preparation of Fe²⁺-TBADT was carried out under high pure N2 protection. The metal contents of TBADT and Mⁿ⁺-TBADT catalysts were measured by the ICP method, and the measured data are listed in Table 1. It can be seen from Table 1 that the actual W content of TBADT measured by ICP-AES analysis was 54.80 wt % and slightly lower than the theoretical W content (55.40 wt %) estimated from the molecular formula $(nBu_4N)_4W_{10}O_{32}$. And the actual W contents of most of the Mⁿ⁺-TBADT catalysts were obviously higher than the theoretical value, which should be due to the partial replacement of TBA⁺ by Mⁿ⁺. The actual doping amount of these metal ions is about 90% of their theoretical doping amount, indicating their high doping

Table 1. Metal Contents of M^{n+} -TBADT Catalysts Measured by ICP and Estimation of Their Molecular Formula

M ⁿ⁺ - TBADT	M^{n+} (wt %)	W (wt %)	M ^{<i>n</i>+} content (mol %) ^{<i>a</i>}	estimated molecular formula ^b
TBADT		54.80		
Fe ³⁺ - TBADT	0.076	56.8	0.452	$TBA_{3.865}{}^{+}Fe_{0.045}{}^{3+}W_{10}O_{32}{}^{4-}$
Fe ²⁺ - TBADT	0.079	57.51	0.469	${\rm TBA_{3.906}{}^{+}Fe_{0.047}{}^{2+}W_{10}O_{32}{}^{4-}}$
Co ²⁺ - TBADT	0.082	55.24	0.462	${\rm TBA_{3.908}}^{+}{\rm Co_{0.046}}^{2+}{\rm W_{10}O_{32}}^{4-}$
Ni ²⁺ - TBADT	0.077	58.4	0.437	$TBA_{3.912}{}^{+}Ni_{0.044}{}^{2+}W_{10}O_{32}{}^{4-}$

"The actual molar percentage of the doped M^{n+} ions relative to W atoms. ^bMolecular formula of M^{n+} -TBADT was estimated based on the following equation: the number of M^{n+} in each $W_{10}O_{32}^{4-}$ = its actual molar percentage/10, the number of TBA⁺ in each $W_{10}O_{32}^{4-}$ = $(4 - n \times \text{the number of } M^{n+} \text{ in each } W_{10}O_{32}^{4-})$.

efficiency. Powder X-ray diffraction (XRD) and transmission electron microscopy (TEM) analyses of two typical samples TBADT and Ni²⁺-TBADT indicated that the doping of Ni²⁺ ions resulted in a sharp reduction in the crystallinity of TBADT and an obvious change in the size and morphology of TBADT particles (see Figure S1 and Figure S2). The doping amount of Ni²⁺ ions in TBADT measured by attached energy dispersive spectroscopy (EDS) analysis (Table S1) was equal to its theoretical value. Additionally, UV–vis spectra in Figure S3 showed that the synthetic quality of Ni²⁺-TBADT was affected by hydrothermal treatment temperature, and the best quality could be obtained at 120 °C.

2.3. Visible-Light-Catalytic Oxidation Experiments. Visiblelight-catalytic oxidation experiments were conducted on a selfdesigned glass tube photoreactor (Figure S4, inner diameter, 1.7 cm, height, 15.5 cm) equipped with an ethanol (0-5 °C)-cooled condenser and an oxygen storage vessel (1 atm). A 35 W tungstenbromine lamp (with an UV light filter, light intensity, 535 mW/cm²), as a built-in light source, was built in a quartz glass tube (outer diameter, 1.2 cm) and then immersed in a 5.5 mL MeCN solution containing the catalyst and substrate. The whole lighting reaction was operated in the closed reactor under normal temperature and pressure and its specific operating conditions and analytical method for the oxygenated products could be found in our recent publication.² Here, each photoreaction was repeated in duplicate, and the obtained data between two parallel experiments differed by less than approximately 2%. The average results of the two parallel experiments were used in this study.

2.4. Characterization. X-ray photoelectron spectroscopy (XPS) of the samples was measured on a VG Multi Lab 2000 system with a monochromatic Mg K α source operated at 20 kV. Powder X-ray diffraction (XRD) of the samples was conducted on a Rigaku 2550 Xray diffractometer using Cu K α radiation (λ = 0.15406 nm) and a graphite monochromator. Transmission electron microscopy (TEM) images of the samples were obtained from a JEOL JEM-2100 transmission electron microscope at an accelerating voltage of 200 kV. Liquid UV-vis spectra of the samples in MeCN were recorded from 200 to 800 nm on a UV-2450 spectrophotometer (Shimadzu, Japan), and their UV/vis diffuse reflectance spectra (DRS) were recorded on a U-3310 spectrophotometer (HITACHI). Their transmission FT-IR spectra were recorded from 400 to 4000 cm⁻¹ on a Nicolet Nexus 510 P FT-IR spectroscopy using a KBr disk. Photoluminescence (PL) measurements of the samples in MeCN were carried out on a fluorescence spectrophotometer (HITACHI F-7000) at room temperature. The metal contents of these samples were measured by inductively coupled plasma-optical emission spectroscopy (ICP-OES) on Optima 5300DV. Cyclic voltammetric (CV) experiments of the samples in MeCN were measured with an electrochemical analyzer (CHI 650e Chenhua Instrument Company).

	metal doping (mol %)	additive (mL, pH ^b)	MeCN (mL)	conv. ^c (mol %)	TON ^d	selectivity of products ^e (%)	
entry						α-PEA	ACP
1			5.5	16.16	6.74	29.46	70.54
2	0.5 mol % Fe ³⁺		5.5	21.31	8.52	29.00	71.00
3	0.5 mol % Fe ²⁺		5.5	26.70	12.26	31.33	68.67
4	0.5 mol % Co ²⁺		5.5	31.88	14.61	28.77	71.23
5	0.5 mol % Ni ²⁺		5.5	38.11	17.14	26.88	73.12
6	0.1 mol % Ni ²⁺		5.5	22.91	11.23	29.33	70.67
7	0.3 mol % Ni ²⁺		5.5	30.36	14.74	27.87	72.13
8	1.0 mol % Ni ²⁺		5.5	34.67	16.35	24.93	75.07
9	0.5 mol % Ni ²⁺	H ₂ O (0.5 mL)	5.0	47.22	20.19	26.22	73.78
10	0.5 mol % Ni ²⁺	12 M HCl (0.1 mL)	5.4	46.17	20.85	24.78	75.22
11	0.5 mol % Ni ²⁺	2 M HCl (0.6 mL, 0.20)	4.9	55.78	27.89	21.67	78.33
12	0.5 mol % Ni ²⁺	2 M H ₂ SO ₄ (0.6 mL, 0.15)	4.9	55.33	26.81	23.77	76.23
13	0.5 mol % Ni ²⁺	2 M H ₃ PO ₄ (0.6 mL, 1.30)	4.9	50.52	23.45	34.54	65.46
14	0.5 mol % Ni ²⁺	2 M HAc (0.6 mL, 4.60)	4.9	43.12	21.99	28.44	71.56
15	0.5 mol % Ni ²⁺	2 M PhSO ₃ H (0.6 mL, 0.50)	4.9	48.91	22.82	26.26	73.74

Table 2. Visible Light-Driven Oxygenation of Ethylbenzene with O_2 Catalyzed by M^{n+} -TBADT Samples in Various Media⁴

^{*a*}Ethylbenzene (0.5 mmol), catalyst (0.010 mmol), O₂ (1 atm), temperature (25 °C), time (12 h), using 35 W of tungsten-bromine lamp as visible light source. ^{*b*}pH values of the reaction media containing additives. ^{*c*}Ethylbenzene conversion = (\sum content (mmol) of each product measured via GC analysis/adding ethylbenzene amount (mmol)) × 100%. ^{*d*}TON = the yields of the oxygenated products (mmol)/catalyst amount (mmol). ^{*e*}Products *α*-PEA and ACP represent *α*-phenyl alcohol and acetophenone, respectively. Product selectivity = the content of this product/ \sum content (mmol) of each product × 100%.



Figure 1. Influence of various parameters on the Ni²⁺-TBADT-photocatalyzed oxidation of ethylbenzene (1.0 mmol) by O_2 in MeCN. (a) Influence of catalyst concentration (other conditions: MeCN, 5.5 mL; illumination time, 12 h). (b) Influence of illumination time (other conditions: catalyst, 0.012 mmol; MeCN, 4.9 mL; 2 M HCl, 0.6 mL). (c) Influence of HCl amount (other conditions: catalyst, 0.012 mmol; MeCN, 4.9 mL; 12 h). (d) Influence of water amount (other conditions: catalyst, 0.012 mmol; MeCN, 5.3–4.2 mL; 12 M HCl, 0.1 mL; illumination time, 12 h).

3. RESULTS AND DISCUSSION

3.1. Photocatalytic Tests. The photocatalytic performance of TBADT and its hybrid catalysts with different metal ion dopants (M^{n+} -TBADT, $M^{n+} = Fe^{3+}$, Fe^{2+} , Co^{2+} , Ni^{2+}) was assessed using the oxidation of ethylbenzene (EB, 0.5 mmol) with molecular oxygen (O_2) in MeCN under visible light illumination, and the results are listed in Table 2. As we previously reported,²⁷ TBADT showed a relatively low activity for this photo-oxidation, affording 16% EB conversion with a 6.74 turnover number (TON) and 70% acetophenone (ACP) selectivity under sustained exposure to visible light for 12 h (entry 1). Entries 2-5 show that M^{n+} -TBADT catalysts commonly exhibited an enhanced photocatalytic activity and their EB conversions presented a regular increase from 21 to 38% with a change of the metal ion dopant from Fe³⁺, Fe²⁺, and Co^{2+} to Ni^{2+} . Entries 6–8 show that as the doping of Ni^{2+} ions was enhanced from 0.1 to 1.0 mol %, the photocatalytic activity of Ni²-doped TBADT underwent a change that first increased and then decreased, which should be due to the influence of the doping amount of Ni²⁺ ions on the synthetic quality of TBADT (Figure S5). The best doping amount of Ni^{2+} ions was ca. 0.5 mol %. Entries 9–15 list the data for this photo-oxidation catalyzed by the best Ni²⁺-TBADT in the presence of water or various acidic additives. The additive water or 12 M HCl solution could further enhance the activity of this catalyst, respectively achieving 47 or 46% EB conversion (entries 9 and 10). Notably, a mixed solution of the above two additives (tagged 2 M HCl) exhibited the best promoted effect on this photocatalytic oxidation, providing ca. 55% EB conversion and as high as 78% ACP selectivity (entry 11). According to our previous study,³³ the promotion effects of these additives on photocatalysis should be due to the following reasons: Water can significantly stabilize the structure of a DT anion under light illumination and slightly improve its redox capacity. However, 12 M HCl may obviously enhance the redox capacity of the DT anion and stabilize its photoexcited states. The respective favorable effects of such two additives on the DT anion can be well combined in coexistence, thus significantly improving photocatalytic efficiency. Among the other tested acidic solution additives, 2 M H₂SO₄ solution, as a strong acid, exhibited a similar promoted effect to 2 M HCl for this photocatalysis oxidation (entries 12); 2 M H₃PO₄ and PhSO₃H solutions of moderately acidic strength, especially weakly acidic 2 M HAc solution, were behind 2 M HCl in improving EB conversion and ACP selectivity (entries 13-15).

In the following experiments, the influence of various reaction parameters on the photo-oxidation of EB (1 mmol) with O_2 was checked using the best Ni²⁺-TBADT as a catalyst, and the results are shown in Figure 1. Figure 1a illuminates that the TON in pure MeCN, as expected, continuously increased from 5.1 to 17.1 when the concentration of catalyst was enhanced from 0.3 to 1.5 mol % (Figure 1a), along with a gradual increase in ACP selectivity, from 64.7 to 75.5%. Thereafter, the further increasing catalyst concentration was invalid for enhancing the TON owing to its solubility becoming worse. Figure 1b shows that TON was continuously and markedly enhanced from 11.9 to 26.7 when illumination time was prolonged from 6 to 12 h. After that, TON slowly increased to 29.9 with further prolonging the time to 24 h. On the whole, the selectivity of ACP was improved slightly by extending illumination time. Figure 1c illuminates the effect of HCl amount on photocatalytic oxidation, when the amount of HCl rose from 0.12 to 1.2 mmol, TON ascended from 18.5 to 26.7, and ACP selectivity was slowly improved from 71.2 to 78.9%, which should be due to the enhanced redox capacity of the catalyst under protonation of HCl.²⁷ After that, TON and ACP selectivity were slightly reduced with a further increase in HCl amount, which may be caused by the destruction of the catalyst structure, as supported by the following UV-vis measurement. Figure 1d shows that when the addition amount of water was enhanced from 0 to 0.5 mL, the TON continuously rose from 19.6 to 26.7. Thereafter, an attempt to further enhance the water amount to 1.2 mL contrarily resulted in a significant reduction in the TON, along with a decrease in ACP selectivity. This is likely because an excess amount of water causes the solubility of the catalyst to become worse, and a large number of the precipitated catalyst seriously affects the transmittance of visible light.

The stability of TBADT and $Ni^{\tilde{z}_+}$ -TBADT photocatalytic oxygenation systems was compared by the irradiation time dependence of TON. As shown in Figure 2, TON in the



Figure 2. A comparison of irradiation time-dependence of TON for two photocatalytic oxygenation systems (catalyst amount, 0.012 mmol; ethylbenzene, 1 mmol). 1: TBADT in pure MeCN (5.5 mL). 2: TBADT in MeCN (4.9 mL) with 2 M HCl (0.6 mL). 3: Ni²⁺-TBADT in pure MeCN (5.5 mL). 4: Ni²⁺-TBADT in MeCN (4.9 mL) with 2 M HCl (0.6 mL).

TBADT-MeCN system continuously increased with the time until about 21 h, after which, as the time went on, the increase of TON became very slow (curve 1). Notably, TON in the Ni²⁺-TBADT-MeCN system not only ascended rapidly with the time in the early stage of photoreaction (6-12 h) but also always retained an ascending trend within the examined illumination time (36 h, curve $\tilde{3}$). In the presence of 2 M HCl, the increase of TON over TBADT and especially Ni²⁺-TBADT became fast in the early stage of photoreaction (6-12 h) but obviously slow in the late stage of photoreaction (curves 2 and 4). These findings support that the hybridization of Ni^{2+} ions not only enhances the photocatalytic activity of TBADT but also can improve its stability under photoreaction conditions. On the other hand, 2 M HCl solution, as an acidic additive, may further improve the conversion efficiency of these two photocatalytic systems but slightly decreases the stability of Ni²⁺-TBADT under photoillumination, as supported by the following UV-vis spectra.

In order to further examine the effectiveness of this HE strategy, the best catalyst Ni^{2+} -TBADT was used to photocatalyze the oxidation of other substrates (1 mmol) such as cyclohexane (CYH), toluene (PhMe), and benzyl alcohol (BA) by O_2 under the same conditions as EB oxidation. As shown in Table 3, this catalyst was still active to the photo-

Table 3. Visible Light-Driven Oxygenation of Other Substrates with O_2 Catalyzed by Ni²⁺-TBADT in MeCN^a

entry	substrate	2 M HCl (mL)	conv. (mol %) ^b	TON	main products (selectivity/%)
1	toluene	-	7.57	6.53	PhCHO (79.48), BA (20.52)
2	toluene	0.6	12.25	10.65	PhCHO (78.56), BA (21.44)
3	cyclohexane	-	22.00	20.00	CY–OH (28.28), CY=O (71.72)
4 ^{<i>c</i>}	cyclohexane	0.6	34.05	30.27	CY-OH (18.47), CY=O (74.15)
5	benzyl alcohol	-	53.04	47.78	PhCHO (62.16), BA (37.84)
6	benzyl alcohol	0.6	69.66	62.20	PhCHO (47.26), BA (52.74)

^aSubstrate (1.0 mmol), catalyst (0.012 mmol), acetonitrile, O_2 (1 atm), temperature (25 °C), time (12 h), using 35 W of tungstenbromine lamp as visible light source. ^bThe calculated substrate conversion based on the main oxygenation products. ^cChlorocyclohexane (selectivity,7.38%) was also detected out.

oxidation of three such compounds in pure MeCN; about 7.6% PhMe, 22% CYH, and 53% BA were converted to the corresponding oxygenated products, manly including BA and benzaldehyde (PhCHO) for PhMe, cyclohexanol (CY–OH) and cyclohexanone (CY=O) for CYH, and benzoic acid (PhCOOH) for BA. The conversions of these three substrates just coincided with their gradually decreasing side chain C–H bond energies.²⁸ Also, the photo-oxidation of these substrates catalyzed by Ni²⁺-TBADT was promoted dramatically in the presence of 2 M HCl solution, and the conversions of PhMe, CYH, and BA increased by approximately 5, 12, and 15%, respectively. These results were far superior to those previously reported in pure TBADT photocatalysis.²⁷

3.2. Study on the Mechanism of Transition Metal Ion-Hybridized TBADT. XPS. The chemical states for the surface atoms of pure TBADT and its two typical hybrids with Ni²⁺ or Fe³⁺ ions were investigated by X-ray photoelectron spectroscopy (XPS), and the high resolution XPS spectra for the surface W and O atoms of TBADT and Ni²⁺-TBADT are shown in Figure 3. The survey XPS spectra of three samples

and the high resolution XPS spectra for Fe³⁺-TBADT, as well as the composition of the surface elements of three samples, could be found in Figure S6 and Table S2, respectively. As shown in Figure 3a, the two energy peaks for W $4f_{5/2}$ and W 4f_{7/2} in pure TBADT appeared at 37.06 and 34.94 eV, respectively; the doping of Ni²⁺ caused these two peaks to shift about 0.7 eV to higher energy regions, simultaneously leading to an energy peak at 531.17 eV for O 1s of TBADT being shifted to a low energy region of 530.19 eV (Figure 3b). Figure S6f,g shows that Fe³⁺ ions exhibited a weaker doping effect than Ni²⁺ in regulating the energy peaks of W and O atoms of TBADT (+0.66 eV shift for W energy peaks and -0.89 eV shift for O energy peak). This indicates that the doping of transient metal ions can induce electronic deviation from W to O atoms, thus resulting in an increase of the binding energy (BE) of the W atom and a decrease of the BE of the O atom. This may be due to the fact that, compared to the TBA⁺ ion, the transient metal ion has a much smaller ionic radius and a higher positive valence, so it is tightly bound to the $[W_{10}O_{32}]^{4-}$ anion via its enhanced positive electric field and coordination with W=O or W-O bonds, thus inducing the above electronic deviation process. And the coordination effect of Ni2+ ions seems to contribute more to the adjustment of the XPS spectrum of TBADT than that of Fe^{3+} ions, as supported by the following FT-IR spectra. Notably, Figure S6 showcases that the XPS signals for the W, O, C, and N atoms of TBADT could be found clearly in the survey XPS spectra of three samples, but the XPS signals of the doped Ni and Fe ions were hardly found in the survey spectra of two hybrids (Figure S6b and e). And the TEM image of Ni²⁺-TBADT in Figure S2b clearly displays that after doping Ni²⁺ ions, TBADT units could interconnect to each other to form large aggregates with various sizes and morphologies. These findings likely support that most doped transient metal ions as bridging ions can connect multiple $[W_{10}O_{32}]^{4-}$ anions to each other to form a sandwich structure. The composition of the surface elements of these two hybrids obtained by XPS analyses showed that the surface Ni (0.33 mol %) content was much lower than the surface Fe (0.66 mol %) content (Table S2), suggesting that Ni^{2+} ions are significantly better than Fe³⁺ ions in terms of inducing a sandwich structure.

UV-Vis Spectra. Figure 4 is the liquid UV-vis absorption spectra of TBADT and its hybrids with Fe³⁺, Fe²⁺, Co²⁺, and Ni²⁺ in MeCN. A UV-vis spectrum of TBADT exhibited two characteristic bands at 250–350 nm (curve 1 of Figure 4a), consistent with literature reports.^{29,30} A band at 320 nm is



Figure 3. High resolution XPS spectra for W and O atoms of pure TBADT and Ni²⁺-TBADT.



Figure 4. (a) UV-vis spectra of TBADT and M^{n+} -TBADT ($M^{n+} = Fe^{3+}$, Fe^{2+} , Co^{2+} , Ni^{2+} ; 1.2×10^{-4} M) in MeCN. Inset is a magnified view of their structural bands at 320 nm. (b) Ni²⁺-TBADT in various media containing 1 mmol cyclohexane after visible light irradiation for 12 h.

assigned to the oxygen to tungsten charge transition (LMCT) of four linear W–O–W bridge bonds in the $[W_{10}O_{32}]^{4-}$ structure, ^{29,30} and another weak band at 265 nm originates from an LMCT process of the unstable structural subunit $[W_5O_{16}]^{2-31}$ or the keggin structural $[H_2W_{12}O_{40}]^{6-.32}$ The UV–vis spectra of four hybrid samples were very similar to that of TBADT; the doping of metal ions hardly affected the center wavelengths of the above two bands (see curves 2–4 in Figure 4a), but it could strengthen the structural band at 320 nm to some extent (see inset in Figure 4a). A ratio ($R = I_{320nm}/I_{265nm}$) for the integral areas of two such LMCT bands may reflect the synthetic quality of TBADT, ³³ and the calculated R values for pure TBADT and Fe³⁺, Fe²⁺, Co²⁺, and Ni²⁺-doped TBADT samples were ca. 0.72, 0.73, 0.76, 0.76 and 0.77, respectively (see Table 4), indicating that the metal ion

Table 4. Data for the Relative Intensity of Structural Band, First Oxidation Potential, Frontier Orbital Energy Level, and Band Gap Energy of TBADT and Mⁿ⁺-TBADT Hybrids

sample	R ^a (eV)	$ E_{Ox}^{b} $ (V)	HOMO ^c (eV)	LUMO ^d (eV)	E_{g}^{e} (eV)
TBADT	0.72	-1.73	-3.09	-0.02	3.07
Fe ³⁺ -TBADT	0.73	-1.71	-3.11	-0.11	3.00
Fe ²⁺ -TBADT	0.76	-1.69	-3.13	-0.15	2.98
Co ²⁺ -TBADT	0.76	-1.68	-3.14	-0.19	2.95
Ni ²⁺ -TBADT	0.77	-1.66	-3.16	-0.24	2.92

^{*a*}*R* indicates a ratio (I_{320nm}/I_{265nm}) of the integral areas of two LMCT bands in Figure 4a. ^{*b*}*E*_{Ox} indicates the more negative oxidation potentials measured by cyclic voltammetry. ^{*c*}HOMO = $-[E_{Ox} - (-0.02) + 4.8]$ eV. ^{*d*}LUMO = HOMO + *E*_g. ^{*e*}Estimated *E*_g from the DRS spectra in Figure 7.

dopants can improve the synthetic quality of TBADT to some extent, and the divalent transition metal ions, especially including Ni²⁺, show a good improved effect. And the synthetic quality of TBADT could be adjusted by the doping level of metal ions, as shown in Figure S5. Figure 4b shows that when Ni²⁺-TBADT in pure MeCN was irradiated by visible light for 12 h, the structural band at 320 nm was reduced obviously owing to photodegradation, and its decay was decelerated in the presence of water but accelerated with 12 M HCl, consistent with the results previously reported in pure TBADT.^{27,33} Notably, the addition of 2 M HCl markedly changed the UV–vis spectrum of Ni²⁺-TBADT, generating three new bands at 220–400 nm. But this spectral change did not occur in our previously reported TBADT-2 M HCl–

MeCN system.²⁷ These three bands should be attributed to the interaction of the leached NiCl₂ with HCl, as supported by an UV–vis spectrum of NiCl₂–2 M HCl–MeCN solution (Figure S7). This indicates that the doped Ni²⁺ ions are easily exchanged by a large number of protons ionized in 2 M HCl, leading to their severe leaching from the sandwich type TBADT.

FT-IR Spectra. Figure 5 illustrates that the FT-IR spectra of TBADT and Mⁿ⁺-TBADT hybrids were very similar to each other, consisting of the characteristic peaks at 500–1000 cm⁻¹ and 1200–3000 cm⁻¹ (Figure 5a), which are respectively attributable to the $[W_{10}O_{32}]^{4-}$ anions and tetrabuthylammonium cations. Three characteristic peaks of TBADT appeared at 968, 900, and 804 cm⁻¹ are ascribed to the stretching vibrations of its $W=O_t$, W-O-W, and $W-O_e-W$ bonds, respectively, which can be indicative of the structural character of the $[W_{10}O_{32}]^{4-.27}$ The magnified view of these three peaks clearly shows that a perceptible red shift of the stretching vibration frequency of the W–O_b–W and especially $W=O_t$ bonds could be noticed in the metal-ion-containing hybrids, and a slightly larger red-shift appeared in the divalent metal-ion-containing hybrids, supporting a coordination of transient metal ions with the $W-O_b-W$ and especially $W=O_t$ groups of $[W_{10}O_{32}]^{4-}$ anions, which is confirmed by the following control test. As shown in Figure S8, the above redshift phenomenon disappeared when 2 M HCl was added to the FT-IR testing procedure of Ni²⁺-TBADT. This should be due to the fact that the severe leaching of Ni²⁺ ions from the hybridized catalyst, as supported by the UV-vis spectral results of Figure 4b, easily occurs in the presence of 2 M HCl, thus resulting in the loss of the above-mentioned coordination effect.

Photoluminescence (PL) Spectra. The PL spectral technique, as a forceful tool to evaluate the stability (or lifetime) of the photoexcited state,³⁴ was used to study the photocatalytic systems of TBADT and its hybrids. As previously reported by us,^{26,33} a PL spectrum of TBADT displayed a strong and broad PL peak at 350–550 nm in MeCN under 320 nm light excitation; the doping of M^{n+} ions in TBADT resulted in a remarkable decay of this PL signal. Moreover, such decay was gradually strengthened with a change of the dopant from Fe³⁺, Fe²⁺, and Co²⁺ to Ni²⁺ (Figure 6a). This strong fluorescence quenching effect supports the idea that the doping of M^{n+} ions, like our previously reported CQD doping,²⁶ can significantly stabilize the photoexcited state of TBADT, and such a stable effect is regulated by the



Figure 5. FT-IR spectra (a) of pure TBADT(1), Fe^{3+} -TBADT (2), Fe^{2+} -TBADT (3), Co^{2+} -TBADT (4), and Ni^{2+} -TBADT (5). (b) The magnified view of their FT-IR spectra in 1200–500 cm⁻¹.



Figure 6. (a) PL spectra of TBADT and M^{n+} -TBADT composites $(3.0 \times 10^{-4} \text{ M})$ in pure MeCN. 1: Pure TBADT, 2–5: M^{n+} -TBADT (M = Fe³⁺, Co²⁺, Ni²⁺, Fe²⁺). (b) PL spectra of Ni²⁺-TBADT (3.0 × 10⁻⁴ M) in MeCN containing additives. 1: pure MeCN. 2: MeCN (5.0 mL) and H₂O (0.5 mL). 3: MeCN (5.4 mL) and 12 M HCl (0.1 mL). 4: MeCN (4.9 mL) and 2 M HCl (0.6 mL).



Figure 7. UV-vis DRS spectra of TBADT and Mⁿ⁺-TBADT hybrids (a) and their Tauc plots (b)

type and valence of metal ions, presenting an increasing sequence of $Ni^{2+} > Co^{2+} > Fe^{2+} > Fe^{3+}$, in agreement with the above photoreaction results. The influence of the additives on the PL intensity was further investigated using Ni^{2+} -TBADT as a representative sample, as shown in Figure 6b; the PL intensity of this doped sample was slightly enhanced in the presence of water but reduced in the presence of 2 M and especially 12 M HCl, which was consistent with our previously reported results in a pure TBADT photocatalysis system.³³

Bandgap Energy. In order to obtain bandgap energy (E_g) , the UV/vis diffuse reflectance spectra (DRS) of pure TBADT and M^{n+} -TBADT hybrids were measured, and the recorded

DRS spectral curves are shown in Figure 7a. It is seen from Figure 7a that the DRS spectrum of TBADT showed a slightly and gradually bathochromic shift of optical absorption from approximately 400 to 500 nm with a change of the dopant from Fe³⁺, Fe²⁺, and Co²⁺ to Ni²⁺. The Tauc plots of the samples (Figure 7b) were obtained from treating their DRS spectral curves, and the E_g values calculated by Tauc's equation³⁵ are listed in Table 4. The E_g values of M^{n+} -TBADT hybrids were slightly lower than that of TBADT and presented a decreasing sequence of Ni²⁺ < Co²⁺ < Fe²⁺ < Fe³⁺, indicating that under the doping of these metal ions, the visible light harvesting efficiency of TBADT is improved to some

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Figure 8. Cyclic voltammograms (CVs) of TBADT and its hybrid (2.4×10^{-3} M) in MeCN (10 mL) containing 0.1 M tetrabutylammonium hexafluorophosphate under anhydrous anaerobic conditions at a scan rate of 100 mV/s. (a) TBADT; (b) Ni²⁺-TBADT.

Scheme 1. Proposed Mechanism for the Doped Mⁿ⁺ Significantly Enhanced Visible Light-Driven Photocatalysis Activity of TBADT



extent, and its band gap energy can also be fine-tuned at the molecular level.

Frontier Orbital Energy Levels. According to the literature suggestion method,^{23,35} the cyclic voltammograms (CVs) of TBADT and Mⁿ⁺-TBADT hybrids in MeCN were recorded under anhydrous anaerobic conditions at a scan rate of 100 mV/s with a ferrocene/ferrocenium couple as the standard³⁶ (-0.02 V shown in Figure S9). Figure 8 gives the CV curves of two typical samples, TBADT and Ni²⁺-TBADT (the CV curves of other three hybrids could be found in Figure S9). The CV curve of TBADT in Figure 8a exhibited two pairs of strong redox waves at -2.0 to -0.8 V attributable to the redox process between W⁶⁺ and W⁵⁺ ions,³⁷ supporting the multielectron redox process of TBADT. These two pairs of redox waves for the hybrids presented a different degree of shift toward the positive potential. The more negative oxidation potential (E_{Ox}) is recommended to estimate the HOMO energy by the calculation formula $(-[E_{Ox} - (-0.02) + 4.8])$ proposed in the literature,^{38,39} and the corresponding LUMO energy is also estimated by the sum of the HOMO energy and the above measured bandgap energy. Table 4 lists the data for the E_{Ox} HOMO, and LUMO energy levels of TBADT and M^{n+} -TBADT hybrids. In that, the E_{Ox} potential of TBADT gradually but slowly increased with a change of the dopant from Fe³⁺, Fe²⁺, and Co²⁺ to Ni²⁺, along with a decrease in its frontier orbital energy levels. Moreover, the LUMO energy level was reduced more obviously than the HOMO energy level. This indicates that the doping of these transient metal ions can improve the redox capacity of TBADT through lowering its frontier orbital energy levels, and this improved effect presented an increasing sequence of Ni²⁺ > Co²⁺ > Fe²⁺ > Fe³⁺. Furthermore, this improved effect was also found in the CV measurements of these samples in MeCN-2 M HCl media (see Figure S10).

DISCUSSION

According to the present characterization results, we propose that, under an electrostatic force, the 3d transient metal ions in a hybrid can be surrounded by multiple $[W_{10}O_{32}]^{4-}$ anions to form the sandwich structure via their coordination with the $W-O_b-W$ and especially $W=O_t$ groups (see Scheme 1). This coordination effect can provide an extra ligand field stabilization energy (LFSE), thereby helping to improve the structural stability of TBADT (reflecting the improved synthetic quality of a catalyst), as previously reported in sandwich type POMs.^{16–18} Furthermore, the frontier orbital energy levels and band gap energy of TBADT are slightly reduced by this coordinated effect, thereby enhancing its redox

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capacity and visible light harvesting efficiency. More importantly, this coordination mode may be conductive to accelerating a transfer of the photogenerated electrons toward the doped metal ions, thus playing a unique role in stabilizing the photoexcited state of TBADT. According to classical coordination field theory, LFSE in the weak field and high spin state, which can be indicative of the stability of transient metal complex, is gradually enhanced from 0 to 1.2 Dq with increasing the d electron number of the centered metal ion from 5 to 8.⁴⁰ On the basis of this regulation, the coordination ability of the centered metal ions in the hybridized TBADT presents an enhancing sequence of Ni²⁺(d⁸) > Co²⁺(d⁷) > Fe²⁺(d⁶) > Fe³⁺(d⁵), thus leading to a continuous improvement of the above hybridization effects, as supported by the current photoreaction and characterization results.

According to the present results and the previous studies,⁴¹⁻⁴⁴ the mediated mechanism of metal ion dopant on the visible light catalytic activity of TBADT was proposed as follows (Scheme 1): Photoirradiation of the $[W_{10}O_{32}]^{4-}$ anion (mainly using UV light) induces electron transfer from its bridge oxygen-based highest occupied molecular orbital (HOMO) to tungsten atom-based lowest unoccupied molecular orbital (LUMO), thus generating its locally excited state. And the latter can rapidly decay in less than 30 ps to the actual state (tagged wO), which is a relaxed excited state, probably of triplet multiplicity. The wO species with a redox potential of +2.44 V vs a saturated calomel electrode (SCE),⁴⁵ as a super strong oxidant, is able to directly oxidize inactive hydrocarbons (RH) to yield its one electron reduced species $[W_{10}O_{32}]^{5-}$ and a carbon centered radical species (R[•]) via a hydrogen atom abstraction or electron transfer pathway. The following reoxidation of the $[W_{10}O_{32}]^{5-}$ to its starting $[W_{10}O_{32}]^{4-}$ (catalysis cycling) and the formation of the oxygenated products can be achieved under the participation of O₂.⁴¹⁻⁴⁴ Evidently, the visible light catalytic activity of TBADT should be proportional to the above-described hybridizing effects of a transient metal ion and presents a gradual and significant enhancement with increasing the hybridizing effects of a transient metal ion from Fe³⁺, Fe²⁺, and Co^{2+} , to Ni^{2+} .

4. CONCLUSION

In summary, for the first time, we have developed a novel and productive hybridizing engineering (HE) strategy for the 3d transition metal ion-doped nonlacunary TBADT that, as a highly efficient catalyst, is used to photocatalyze the selective oxidation of inactive hydrocarbons by O2 under mild conditions. This HE strategy provides a good solution to overcome the inherent defects of TBADT that are related to low synthetic quality, poor visible light response, unsatisfactory redox capacity, and photoexcited state lifetime in its photocatalysis applications. Furthermore, it also has an advantage to finely adjust the synthetic quality, redox capacity, and photophysicochemical property of TBADT by varying the type and valence state of the transient metal ion. By this HE strategy, we are interested in synthesizing other transient metal and rare earth metal ion single or cohybridized TBADT catalysts and investigating the relationship of their structure, redox, and optical properties with their photocatalytic performances, as well as exploring their potential applications in other important visible-light-catalysis reactions.

ASSOCIATED CONTENT

③ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.0c00390.

XRD patterns, TEM images and EDS spectra, UV-vis spectra and XPS analysis, FT-IR spectra, and cyclic voltammograms (PDF)

AUTHOR INFORMATION

Corresponding Author

Zaihui Fu – National and Local United Engineering Laboratory for New Petrochemical Materials and Fine Utilization of Resources, Key Laboratory of Resource Fine-Processing and Advanced Materials of Hunan Province and Key Laboratory of Chemical Biology and Traditional Chinese Medicine Research (Ministry of Education of China), College of Chemistry and Chemical Engineering, Hunan Normal University, Changsha 410081, China; orcid.org/0000-0002-3382-0836; Phone: +86 731 88872576; Email: fzhhnnu@126.com; Fax: +86 731 88872531

Authors

- Anqun Su National and Local United Engineering Laboratory for New Petrochemical Materials and Fine Utilization of Resources, Key Laboratory of Resource Fine-Processing and Advanced Materials of Hunan Province and Key Laboratory of Chemical Biology and Traditional Chinese Medicine Research (Ministry of Education of China), College of Chemistry and Chemical Engineering, Hunan Normal University, Changsha 410081, China; Hunan University of Medicine, Huaihua 418000, China; ◎ orcid.org/0000-0002-5129-5916
- Mengke Chen National and Local United Engineering Laboratory for New Petrochemical Materials and Fine Utilization of Resources, Key Laboratory of Resource Fine-Processing and Advanced Materials of Hunan Province and Key Laboratory of Chemical Biology and Traditional Chinese Medicine Research (Ministry of Education of China), College of Chemistry and Chemical Engineering, Hunan Normal University, Changsha 410081, China
- Bo Yang National and Local United Engineering Laboratory for New Petrochemical Materials and Fine Utilization of Resources, Key Laboratory of Resource Fine-Processing and Advanced Materials of Hunan Province and Key Laboratory of Chemical Biology and Traditional Chinese Medicine Research (Ministry of Education of China), College of Chemistry and Chemical Engineering, Hunan Normal University, Changsha 410081, China
- Jialuo She National and Local United Engineering Laboratory for New Petrochemical Materials and Fine Utilization of Resources, Key Laboratory of Resource Fine-Processing and Advanced Materials of Hunan Province and Key Laboratory of Chemical Biology and Traditional Chinese Medicine Research (Ministry of Education of China), College of Chemistry and Chemical Engineering, Hunan Normal University, Changsha 410081, China
- Feifei Wan National and Local United Engineering Laboratory for New Petrochemical Materials and Fine Utilization of Resources, Key Laboratory of Resource Fine-Processing and Advanced Materials of Hunan Province and Key Laboratory of Chemical Biology and Traditional Chinese Medicine Research (Ministry of Education of China), College of

I

Chemistry and Chemical Engineering, Hunan Normal University, Changsha 410081, China

- **Chao Zhang** National and Local United Engineering Laboratory for New Petrochemical Materials and Fine Utilization of Resources, Key Laboratory of Resource Fine-Processing and Advanced Materials of Hunan Province and Key Laboratory of Chemical Biology and Traditional Chinese Medicine Research (Ministry of Education of China), College of Chemistry and Chemical Engineering, Hunan Normal University, Changsha 410081, China
- Yachun Liu National and Local United Engineering Laboratory for New Petrochemical Materials and Fine Utilization of Resources, Key Laboratory of Resource Fine-Processing and Advanced Materials of Hunan Province and Key Laboratory of Chemical Biology and Traditional Chinese Medicine Research (Ministry of Education of China), College of Chemistry and Chemical Engineering, Hunan Normal University, Changsha 410081, China

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.inorgchem.0c00390

Notes

The authors declare no competing financial interest.

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