Supporting Information

Inorganic-organic hybrid nano material with core-shell structure constructed by Mn-BTC and Ag$_5$[BW$_{12}$O$_{40}$] for supercapacitors and photocatalytic dye degradation

Shi Caihong$^a$, Kang Ning$^a$, Wang Chunmei$^a$, Yu Kai$^{ab,*}$, Lv Jinghua$^a$, Wang Chunxiao$^a$, Zhou Baibin$^{ab,*}$

1. Experimental section

1.1. Material and characterization methods

All reagents are commercially available and used as received without further purification. Fourier transform infrared (FTIR) spectra of compound was carried out on a Nicolet-360 spectrophotometer in the range of 400-4000 cm$^{-1}$ using KBr particles. Use Hitachi SU-70 scanning electron microscope (SEM) produced by Hitachi to analyze the morphology and content. The transmission electron microscopy (TEM) images were performed on an ultrahigh resolution scanning electron microscope (JEOL2010, Japan). Thermogravimetric analysis (TGA) is a PerkinElmer Diamond 6300 differential thermal analyzer produced in the United States, with α-Al$_2$O$_3$ as the reference material, using a platinum crucible, the heating rate is 10°C min$^{-1}$, and the heating is 25°C to 800°C, N$_2$ protects the atmosphere of the system. X-ray photoelectron spectroscopy (XPS) test equipment comes from Shimadzu Corporation, Japan, model is Axis Ultra DLD, after analyzing the element valence state and distribution of the sample. The specific surface area (BET) test instrument comes from the United States Kangta company, the model is Nova 2000E specific surface area analyzer. Powder X-ray diffraction (XRD, BRUKER D8) using Cu Kα radiation ($λ=0.154$ nm) was employed to identify the crystalline phase of the material and the range of 2θ from 20-80°. Sampling and analysis of the sample via the Varian Cary 500 UV-Vis-NIR spectrometer. Photoluminescence (PL) spectra of the samples were measured with a Hitachi F-4500 fluorescence spectrophotometer at room temperature using He–Cd laser as an excitation light source. The excitation wavelength was 325 nm.

1.2. Synthesis of K$_5$BW$_{12}$O$_{40}$·15H$_2$O

Refer to the literature, the synthesis of was slightly modified. The typical method is: 40 g Na$_2$W$_{12}$O$_{40}$·2H$_2$O and 3 g H$_3$BO$_3$ were dissolved in 60 mL distilled water. Adjusted pH to 6 with 6 M HCl solution and boiled for 2 h under magnetic stirring. Filtered to remove impurities. After that, the pH of the filtrate obtained was modulated to 2 with 6 M HCl solution and 80 g KCl was added. At this time, precipitation was generated in the solution. The solution was filtered, washed with ether to precipitation and dried to obtain 23.2 g product. It was verified that the IR spectra are basically consistent with the literature.

1.3. Synthesis of Ag$_5$[BW$_{12}$O$_{40}$]

AgNO$_3$ (0.24 g, 1.142 mmol) and K$_5$[BW$_{12}$O$_{40}$]·15H$_2$O (0.2800 g, 0.0918 mmol) were successively dissolved in
10 mL distilled water. After the evaporative crystallization, filtered and washed, the gray powdery sample of Ag$_5$[BW$_{12}$O$_{40}$] was obtained by drying it in 60°C oven for 1 day.

1.4. Electrode preparation

The active substance was prepared by mixing acetylene black with powder at a mass ratio of 1:4, and then dried in 50°C oven after 50 min of ultrasonic. 5mg of the active substance was dissolved in 150 μL ethanol solution (ethanol : water = 1:3) and dispersed ultrasonic for 40 min to prepare slurry. The nickel foam (NF) was cut to a size of 1×3 cm$^2$. Apply paste to the position of 1×1 cm$^2$ nickel foam. Dry in 50°C oven for 4 h to remove solvent. The nickel foam was laminated with a press at a pressure of 2 MPa. The mass difference before and after the nickel foam was attributed to the active substance loading.

1.5. Electrochemical measurement

At room temperature, CHI 660E electrochemical workstation (Shanghai Chenhua Instrument Co. Ltd.) was connected with a computer, 1 M Na$_2$SO$_4$ solution was used as electrolyte. The electrochemical properties of the synthesized compounds were tested by cyclic voltammetry (CV), galvanostatic charge/discharge (GCD) method, and electrochemical impedance spectroscopy (EIS). In the three-electrode system, nickel foam uses as the working electrode, Pt wire as the counter electrode, and Ag/AgCl (3 mol L$^{-1}$ KCl) electrode as the reference electrode. The two-electrode system uses nickel foam electrode material as a positive and negative electrode. The weight of the two nickel foam electrodes have approximately the same weight.

1.6. Photocatalytic measurement

Ultraviolet (UV) degradation experiment was carried out on 15 mg L$^{-1}$ MB, RhB, and MO three dye solutions. First, the optical absorption properties of the three compounds were tested separately. Under light avoidance conditions, 40 mg of compounds were added to 80 mL of three dyes and stirred for 50 min. 3 mL of mixture was removed every 10 min and put into a centrifuge, and the liquid supernatant was removed to measure its absorbance. The photocatalytic degradation properties of the three compounds were then tested. 40 mg of the compound was placed in 80 mL dye solution, adsorbed and stirred for 30 min in a dark room to ensure that the catalyst reached the adsorption/desorption balance. 3 mL of the solution was taken. The rest of the solution, under stirring, illuminated with a mercury lamp (125 W, 365 nm). Every about 20 minutes apart, 3 mL of solution was taken, centrifuged, and the supernatant was taken for UV spectrum to calculate the degradation rate. Simultaneously conduct five photocatalytic cycle tests.

1.7. Computational formula

The specific capacitance of the three electrodes system is calculated as follow:

$$C_s = \frac{I \times \Delta t}{m \times \Delta V} \quad \text{Equation(S1)}$$

Where $C_s$ (F·g$^{-1}$) is specific capacitance, $I$ (A) is the discharge current, $\Delta t$ (s) is the discharge time, $\Delta V$ (V) is the voltage window and $m$ (g) is the load of the active material in the electrode.

The formula for calculating the specific capacitance of two electrodes:

$$C = \frac{2I \times \Delta t}{m \times \Delta V'} \quad \text{Equation(S2)}$$

where $I$ is the current density (A), $\Delta t$ is designates the discharge time(s), $m$ signifies mass of both the
electrodes (g) and $\Delta V$ represents voltage window (V), respectively. The energy density ($E$, Wh kg$^{-1}$) and power density ($P$, W·kg$^{-1}$) calculation formulas are as follows:

\[ E = \frac{C \Delta V^2}{7.2} \quad \text{Equation(S3)} \]

\[ P = \frac{E \times 3600}{\Delta t} \quad \text{Equation(S4)} \]

EIS tests 5 mV AC voltage as the signal source, and its frequency range is $10^2$-$10^5$ Hz.

2. Results and Discussion

2.1. TG

![TG curve of Mn-BTC@Ag$_5[BW_{12}O_{40}]$](image)

**Fig S1.** TG curve of Mn-BTC@Ag$_5[BW_{12}O_{40}]$

2.2. EDX

![EDX mapping of Mn-BTC@Ag$_5[BW_{12}O_{40}]$](image)

**Fig S2.** (a)-(g) EDX mapping of Mn-BTC@Ag$_5[BW_{12}O_{40}]$

2.2. BET

![N$_2$ absorption-desorption isotherm of Mn-BTC@Ag$_5[BW_{12}O_{40}]$](image)

**Fig S3.** N$_2$ absorption-desorption isotherm of Mn-BTC@Ag$_5[BW_{12}O_{40}]$
2.3. XPS

![XPS spectra of Mn-BTC@Ag$_5$[BW$_{12}$O$_{40}$]](image)

Fig S5. XPS spectra of Mn-BTC@Ag$_5$[BW$_{12}$O$_{40}$]

2.4. Electrochemical properties

![Graphs showing CV curves and GCD curves](image)

Fig S6. (a) CV curves at different scan rates and (b) GCD curves of Ag$_5$[BW$_{12}$O$_{40}$]-NF
Fig S7. (a) CV curves at different scan rates and (b) GCD curves of Mn-BTC-NF.

Fig S8. A simulation of a symmetric SSC system.

Fig S9. CV curves at different scan rates of 5–100 mV s$^{-1}$ for SSC.

2.5. Photocatalytic of Mn-BTC@Ag$_5$[BW$_{12}$O$_{40}$]

Fig S10. (a-c) The absorption spectra of MO, MB, RhB with three compounds in the dark.
Fig S11. (a-c) The conversion rate of MB, MO, RhB with the same reaction time of phlocatalyst and no catalyst

Fig S12. (a-c) The absorption spectra of RhB, MB, MO with Ag₅[BW₁₂O₄₀] during the decomposition reaction under UV irradiation

Fig S13. (a-c) The absorption spectra of RhB, MB, MO with Mn-BTC during the decomposition reaction under UV irradiation

Fig S14. The IR of Mn-BTC@Ag₅[BW₁₂O₄₀] after five cycles

**Table S1.** Comparison of the properties of the Keggin POMs-based materials with several published supercapacitors
| Ref. | Electrode Material | Specific Capacitance | Cycling Stability | Current Collector | Ref. |
|------|--------------------|----------------------|-------------------|-----------------|------|
| 1 | PAni/H3PMo12O40 | 120 F g⁻¹ (0.4 A g⁻¹) | 70% (1000 cycles) | Rigid graphite plate | 4 |
| 2 | H3PMo12O40/MWCNT | 38 F g⁻¹ (1 A g⁻¹) | 91% (8000 cycles) | Porous glassy fibrous paper | 5 |
| 3 | AC/PMo12O40 | 136 F g⁻¹ (2 A g⁻¹) | 95% (5000 cycles) | Glassy carbon | 6 |
| 4 | RGO/ PMo12O40 | 51.2 F g⁻¹ (5 mA cm⁻²) | 95% (500 cycles) | Commercial flexible carbon cloth | 7 |
| 5 | PMo12−XW,40− | 140 F g⁻¹ (10 A g⁻¹) | 94.6% (1700 cycles) | Glassy carbon | 8 |
| 6 | [Ag5(brtmb)4][VW12O40−| 206 F g⁻¹ (110 A g⁻¹) | 87.5% (1000 cycles) | Glassy carbon | 9 |
| 7 | rGO-PMo12||GO-PW12 | 110 mF cm⁻² (2 mA cm⁻²) | 95% (2000 cycles) | Carbon cloth | 10 |
| 8 | [Cu (btx)4][SiW12O40] | 110.3 F g⁻¹ (3 A g⁻¹) | 87% (1000 cycles) | Glassy carbon | 11 |
| 9 | [(CuH2(C12H12N6)2)(H2O)6]2H2O | 50.0 F g⁻¹ (3 A g⁻¹) | 87.5% (1000 cycles) | Glassy carbon | 10 |
| 10 | [H(C10H10N2)Cu2][PW12O40] | 153.43 F g⁻¹ (1 A g⁻¹) | 18.2% (500 cycles) | Glassy carbon | 12 |
| 11 | AC/PMo12O40 | 183 F g⁻¹ (2 A g⁻¹) | 98% (3000 cycles) | Graphite rods | 13 |
| 12 | mPPy@GO-PMo12 | 115 mF cm⁻² (1 mV s⁻¹) | 80% (2000 cycles) | Glassy carbon | 14 |
| 13 | [Ag5(C2H3N3)4][H2SiMo12 O40]@15%GO | 230.2 F g⁻¹ (0.5 A g⁻¹) | 92.7% (1000 cycles) | Glassy carbon | 15 |
| 14 | [Ag5(C2H3N3)4][H2SiMo12O40] | 155.0 F g⁻¹ (0.5 A g⁻¹) | 78.5% (1000 cycles) | Glassy carbon | 15 |
| 15 | [Ag5(C2H3N3)4][H2SiW12O40] | 29.8 F g⁻¹ (0.5 A g⁻¹) | 78.3% (1000 cycles) | Glassy carbon | 15 |
| 16 | [CuH2(C12H12N6)3PMo12O40]−([C4H2N3]H2O)2 | 249 F g⁻¹ (3 A g⁻¹) | 93.5% (1000 cycles) | Glassy carbon | 16 |
| 17 | [Cu4(C2H3N3)4]3(PO4)2(Mo6O24) | 154.5 F g⁻¹ (3 A g⁻¹) | 91.1% (1000 cycles) | Glassy carbon | 16 |
| 18 | [Cu4H2(btx)3(PMo12O40)2]2H2O | 237 F g⁻¹ (2 A g⁻¹) | 92.5% (1000 cycles) | Glassy carbon | 17 |
| 19 | [Cu4H2(btx)3(PW12O40)2]2H2O | 100 F g⁻¹ (2 A g⁻¹) | 90% (1000 cycles) | Glassy carbon | 17 |
| Formula                                      | Capacity (F g$^{-1}$) | Efficiency (%) | Electrode Material |
|----------------------------------------------|-----------------------|----------------|--------------------|
| [Cu$^+$(H$_2$O)$_3$](btx)$_3$(PW$^{V_{12}}$O$_{40}$)·2H$_2$O | 82.1                  | 100            | glassy carbon     |
| [Cu$^+$(btx)$_3$(PW$^{V_{12}}$O$_{40}$)·2H$_2$O | 76.4                  | 100            | glassy carbon     |
| [Cu$^+$(btx)$_3$(SiMo$^{V_{12}}$O$_{40}$)·4H$_2$O | 138.4                 | 97             | glassy carbon     |
| [Ag$_{12}$pic(trz)$_6$][HVW$_{12}$O$_{40}$] | 93.5                  | 59.2           | glassy carbon     |
| [Ag$_{12}$pic(trz)$_6$][SiW$_{12}$O$_{40}$] | 47.8                  | 90.9           | glassy carbon     |
| [Ag(trz)]$_2$[Cu$_{12}$pic(trz)$_6$][H$_2$BW$_{12}$O$_{40}$] | 42.9                  | 86.5           | glassy carbon     |
| [Mn$_2$(BTC)$_4$](H$_2$O)$_6$ | 211.0                 | 96.0           | nickel             |
| [K$_6$(SiW$_{10}$Mn$_2$O$_{40}$)] | 137.5                 | 92.0           | glassy carbon     |
| AC/TEAPW$_{12}$ | 82                   | 93             | aluminum           |
| H$_3$PW$^{V_{12}}$O$_{40}$(BPE)$_{2.5}$·3H$_2$O | 49.2                  | 80.4           | glassy carbon     |
| H$_3$PMo$^{V_{12}}$O$_{40}$(BPE)$_{2.5}$·3H$_2$O | 137.5                 | 92.0           | glassy carbon     |
| [HPMo$^{V_{12}}$O$_{40}$]Cu$_3$(4- atrz)$_6$·H$_2$O | 231.7                 | 88.2           | glassy carbon     |
| [HPW$^{V_{12}}$O$_{40}$]Cu$_3$(4- atrz)$_6$ | 147.5                 | 95.3           | glassy carbon     |
| [H$_2$SiMo$^{V_{12}}$Mo$_3$O$_{40}$]Cu$_3$(4- atrz)$_6$·H$_2$O | 232.5                 | 98.8           | glassy carbon     |
| L$_{0.5}$[Cu$_{12}$L$_3$(SiW$_{12}$O$_{40}$)] | 159.2                 |                | glassy carbon     |
| PW$_{12}$@MIL-101 | 1124                  | 90.2           | nickel foam       |
| PW$_{12}$@MIL-101/PPy-0.15 | 158                   |                | nickel foam       |
| H[Cu$_2$(4-Hdpoy)$_2$(PMo$_{12}$O$_{40}$)(H$_2$O)$_4$]·2H$_2$O | 196.6                 |                | carbon cloth      |
| [Co(H$_2$Ptep)(HPtep)]$_2$[PW$_{12}$CoO$_{30}$]·4.5H$_2$O | 212                   | 90.2           | glassy carbon     |
| [Co(H$_2$Ptp)]$_2$[SiMo$_{2}$O$_{40}$]·2H$_2$O | 202                   | 85.8           | glassy carbon     |
| [Zn$_2$(DEP)]$_2$(H$_4$O)$_4$[H$_2$TeMo$_{6}$O$_{16}$] | 412.77                | 81.5           | glassy carbon     |
| [Co(DEP)$_2$(H$_2$O)$_2$[H$_2$(y-Mo$_{20}$O$_{36}$)]·11H$_2$O | 580                   | 73.3           | glassy carbon     |
| [Cu(DEP)]$_2$(H$_2$B$_{20}$O$_{50}$)$_{0.5}$] | 823.09                | 79.4           | glassy carbon     |
Notes and references

1. C. R. Deltcheff, M. Fournier, R. Franck, R. Thouvenot, *Inorg. Chem.*, 1983, **22**, 207-216.
2. L. X. Zheng, C. D. Wang, Y. C. Dong, H. D. Biant, T. F. Hung, J. Lu, Y. Y. Li, *Appl. Surf. Sci.*, 2016, **362**, 399-405.
3. L. G. Gong, X. X. Qi, K. Yu, J. Q. Gao, B. B. Zhou, G. Y. Yang, *J. Mater. Chem.*, 2020, **8**, 5709-5720.
4. A. K. C. Gallegos, M. L. Cantú, N. C. Pastor, P. G. Romero, *Adv. Funct. Mater.*, 2005, **15**, 1125-1133.
5. M. Skunik, M. Chojak, I. A. Rutkowska, P. J. Kulesza, *Electrochim. Acta*, 2008, **53**, 3862-3869.
6. V. Ruiz, J. Suárez-Guevara, P. Gomez-Romero, *Electrochim. Commun.*, 2014, **24**, 35-38.
7. D. P. Dubal, J. Suárez-Guevara, D. Tonti, E. Enciso, P. Gomez-Romero, *J. Mater. Chem.*, 2015, **3**, 23483-23492.
8. Y. H. Ding, J. Peng, H. Y. Lu, Y. Yuan, *RSC Adv.*, 2016, **6**, 81085-81091.
9. G. N. Wang, T. T. Chen, X. M. Wang, H. Y. Ma, H. J. Pang, *Electrochim. Acta*, 2018, **362**, 137007.
10. D. F. Chai, J. J. Xin, B. N. Li, H. J. Pang, H. Y. Ma, X. M. Wang, L. C. Tan, *ACS Appl. Mater. Interfaces*, 2019, **11**, 20845-20853.
11. D. F. Chai, C. J. Gómez-García, B. Lia, H. Panga, H. Y. Ma, C. X. Wang, M. Wang, *Dalton Trans.*, 2019, **48**, 13026-13033.
12. D. F. Chai, C. J. Gómez-García, B. Lia, H. Panga, H. Y. Ma, X. M. Wang, L. C. Tan, *ChemNanoMat*, 2019, **5**, 121409.
13. H. N. Wang, M. Zhang, A. M. Zhang, F. C. Shen, X. K. Wang, S. N. Sun, Y. J. Chen, Y. Q. Lan, *J. Solid State Chem.*, 2020, **288**, 83.8% (1000 cycles) glassy carbon
14. J. X. Wang, L. Zhang, L. J. Zhao, T. Li, S. B. Li, *J. Mol. Struct.*, 2021, **1231**, 129966.
15. T. Y. Li, P. He, Y. N. Dong, W. C. Chen, T. Wang, J. Gong, W. L. Chen, *Eur. J. Inorg. Chem.*, 2021, **2021**, 2063-2069.
16. Q. Q. Liu, X. L. Wang, H. Y. Lin, Z. H. Chang, Y. C. Zhang, Y. Tian, J. J. Lu, L. Yu, *Dalton Trans.*, 2021, **50**, 9450-9456.
17. C. X. Sun, J. Ying, Y. P. Zhang, L. Jin, A. X. Tian, X. I. Wang, *CrystEngComm*, 2022, **24**, 587-600.
27. X. Xu, Y. Q. Zhang, J. Ying, L. Jin, A. X. Tian, X. I. Wang, *CrystEngComm*, 2022, **24**, 1267-1278.
28. J. L. Zhuo, Y. L. Wang, Y. G. Wang, M. Q. Xu, J. Q. Sha, *CrystEngComm*, 2022, **24**, 579-586.
29. S. F. Ma, J. Ying, Y. P. Zhang, A. X. Tian, *CrystEngComm*, 2022, **24**, 2891-2902.