Rational Integration of ZIF-8 and BiPO₄ for Energy Storage and Environmental Applications

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ABSTRACT: Environmental pollution and energy storage are among the most pivotal challenges of today's world. The development of multifunctional materials is required to address these challenges. Our study presents the rational design and synthesis of a hybrid material (ZIF-8@BiPO₄) with dual functionality: an outstanding supercapacitor electrode and an excellent photocatalyst. The ZIF-8@BiPO₄ hybrid structure was obtained by conjoining zinc ions and 2-methylimidazole ligands toward BiPO₄ by a one-pot stirring route at room temperature. The ZIF-8@BiPO₄ resulted in considerably higher specific capacitance (Cs) (489 F g⁻¹ at a scan rate of 5 mV s⁻¹; 497 F g⁻¹ at a current density of 1 A g⁻¹) than that of pure BiPO₄ (358; 443 F g⁻¹) and ZIF-8 (185; 178 F g⁻¹) under the same conditions in a three-electrode cell using the 2 M KOH aqueous electrolyte. Afterward, an asymmetric supercapacitor (ASC) device was fabricated with BiPO₄ as the anode and ZIF-8@BiPO₄ as the cathodes, acquiring an outstanding Cs of 255 F g⁻¹ at a current density of 0.5 A g⁻¹ with significant cycling stability (81% over 10,000 cycles). Moreover, the ASC has an energy density of 17.5 Wh kg⁻¹ and a power density of 13,695 W kg⁻¹, which can be considered to be at the borderline between batteries and supercapacitors. The photocatalytic activity of ZIF-8@BiPO₄ was further studied using a methylene blue (MB) dye and sildenafil citrate (SC) drug-active molecules. The degradation of MB was approximately 78% through the photocatalytic reduction after 180 min of UV irradiation. The outstanding characteristics together with the ecofriendly and low-cost preparation make ZIF-8@BiPO₄ appealing for a broad range of applications.

1. INTRODUCTION

Clean energy and clean water are among the 17 sustainable development goals set up by the United Nations General Assembly.¹ The rapid industrialization and information age brings forth the need for a sweeping type of material. In particular, graphene discovery highlighted the nano-carbon-based material’s irreplaceable impact on energy storage.²⁻⁵ By this time, there have been many studies on the singly or doped effect of activated carbon (AC), graphene, graphene oxide, carbon nanotubes (CNTs), graphical carbon nitride (g-C₃N₄), carbon dots (CDs), and carbon quantum dots.⁶⁻¹⁹ Transition metal oxides, metal sulfides, polyoxometalates, phosphates, carbonates, chalcogenides, metal–organic frameworks (MOFs) conductive polymers, and their compounds have been investigated as adequate materials for energy storage applications, and they have a domain in other areas such as catalysts, sensors, drug delivery, gas storage/separation, and other types of energy storage/
conversion systems such as batteries and fuel cells.\textsuperscript{36–47} Chiefly, metal oxides including Co\textsubscript{3}O\textsubscript{4}, Fe\textsubscript{2}O\textsubscript{3}, V\textsubscript{2}O\textsubscript{5}, RuO\textsubscript{2}, ZnO, MnO\textsubscript{2}, NiO, SnO\textsubscript{2}, TiO\textsubscript{2}, CuO, Bi\textsubscript{2}O\textsubscript{3}, etc. with high specific capacitance values and high pseudocapacitive behaviors are commonly used.\textsuperscript{64,65} Among the available metal oxides, Co\textsubscript{3}O\textsubscript{4} and RuO\textsubscript{2} come to the forefront with magnificent electrochemical reversibility and high theoretical specific capacitance, as well as remarkable cycling stability.\textsuperscript{66} However, the steep price and toxic nature of these materials limit their utilisability.\textsuperscript{67,68} To sum up, the formation of ideal SCs requires reasonably priced and environmentally friendly materials with high capacitance, besides high energy and power densities.

Recently, BiPO\textsubscript{4} materials have been widely utilized and have attracted substantial attention thanks to their ecofriendly, atomic essence, and dielectric behavior caused by high oxygen conductivity.\textsuperscript{69} The ability to be synthesized in different sizes with various morphologies such as spherical, octahedral, or rod is also a vantage of BiPO\textsubscript{4}, which enhanced its utilization in SCs and photocatalytic applications. For photocatalytic applications, the use of phosphate-containing photocatalysts, which have tremendous properties such as high electron-electron mobility of anions that promote electron and hole separation, high crystallinity, high photocatalytic oxidation performance, and good stability, has gained an important place in the literature. One of the parameters affecting the photocatalytic performance of BiPO\textsubscript{4} photocatalysts is the crystal phase of the photocatalysts. For example, it has been discovered that the hexagonal phase of BiPO\textsubscript{4} showed a lower photocatalytic performance than the monoclinic phase of BiPO\textsubscript{4}.\textsuperscript{68,69}

The competent and reversible redox reactions of Bi\textsuperscript{3+} ions and the characteristic idiosyncrasy stability of the phosphate groups engender BiPO\textsubscript{4} to demonstrate exquisite electrochemical performance. Particularly, its redox peak position in the voltage range of carbon materials (−1 to 0 V in aqueous electrolytes) utterly pointed out that it would be more feasible to be an alternative for carbon-based materials in ASCs.\textsuperscript{70,71}

Yet, other cutting-edge materials are MOFs due to their unique structural features such as open metal sites, high surface areas, tailored pore sizes, ultralow density, and postsynthetic modifications.\textsuperscript{72–74} Zeolitic imidazolate frameworks (ZIFs) are a subdivision of MOFs designed via the correlation of metal ion notes (like zinc or cobalt) with an organic binder in a convenient solvent. As a principle, an electronic channel is supplied by the oxidation–reduction of metal ions while the charge transfer in the framework is assisted via the linker.\textsuperscript{75} Especially, the ZIF-8 (formed by zinc ions with the linkage of 2-methylimidazole) has excellent properties such as a large surface area (BET, 1413 m\textsuperscript{2} g\textsuperscript{−1}), with a large pore size (diameter of 11.6 Å), good thermal stability (up to 550 °C), and significant chemical resistance to boiling alkaline water and organic solvents.\textsuperscript{76,77} With these multifaceted properties, it can be considered as an alternative material to TiO\textsubscript{2} and ZnO for photocatalytic applications.\textsuperscript{76}

Studies in the literature not only show that porous ZIF materials are a potential new photocatalyst class, but also trigger extensive research on ZIF photocatalysts. Compared with traditional semiconductor photocatalysts such as ZnO, TiO\textsubscript{2}, and BiW\textsubscript{6}O\textsubscript{24}, photoactive ZIFs have significant utility advantages in photocatalytic applications: (i) the well-defined crystal structures of ZIFs are useful in the study and characterization of the structure–property relationship of these solid photocatalysts; (ii) the modular nature of the ZIF synthesis allows for the rational design and fine-tuning of these catalysts at the molecular level, allowing for easy tuning of the electronic structure of ZIF catalysts; (iii) structural features of tunable active sites (i.e., metal-oxoclusters and organic binders) in ZIFs pave the way for more efficient use of photon energy; (iv) unlike typical traditional metal oxide photocatalysts, visible light photocatalytic activity can be readily introduced via linker substitutions of organic chromophores in ZIF structures like amino groups.\textsuperscript{78–80} However, poor conductivity and less cycling stability of ZIF-8 confine its usage in SCs. Thereafter, ZIFs are mainly utilized to obtain nitrogen (N)-doped porous carbon electrode materials.

To date, increasing interest has been centered on BiPO\textsubscript{4} and ZIF-8 electrode materials, and some crucial advancement has been performed. For instance, a comparison between AC and BiPO\textsubscript{4} was made by Wang et al.\textsuperscript{81} They reported a maximum specific capacitance of AC 117.3 F g\textsuperscript{−1} at a current density of 1 A g\textsuperscript{−1}, while the capacity of BiPO\textsubscript{4} was 360.56 F g\textsuperscript{−1} at the same current density and under the same potential window. Vadivel and co-workers examined a BiPO\textsubscript{4}/MWCNT (1D-1D) composite structure synthesized by a solvothermal route. The recorded maximum specific capacitance was 504 F g\textsuperscript{−1} at a scan rate of 5 mV s\textsuperscript{−1}. Moreover, they investigated the photocatalytic activity of the materials by using methyl orange (MO) as a target pollutant and notified that the BiPO\textsubscript{4}/MWCNT composite presented improved photocatalytic activity compared to pure BiPO\textsubscript{4} under UV light irradiation.\textsuperscript{60} Nithya et al. examined various pH effects on the BiPO\textsubscript{4} syntheses under various irradiation times and ultrasonication powers. A maximum specific capacitance of 1052 F g\textsuperscript{−1} (pH = 7 at 2 mV s\textsuperscript{−1}) was obtained for the BiPO\textsubscript{4} formed in the 2 h irradiation time with 60% power.\textsuperscript{79} Gao et al. scrutinized SnO\textsubscript{2} quantum dots@ZIF-8 electrochemical features as a pseudocapacitor material. The recorded maximum specific capacitance of the composite was 931 F g\textsuperscript{−1} at a sweep rate of 5 mV s\textsuperscript{−1}, while pure materials SnO\textsubscript{2} quantum dots, and ZIF-8 just had a specific capacitance of 241 and 99 F g\textsuperscript{−1}, respectively.\textsuperscript{80}

Herein, we developed a new approach to enhance the electrochemical properties of ZIF-8 addedly environmental consciousness of BiPO\textsubscript{4}. The ZIF-8@BiPO\textsubscript{4} hybrid structure was formed by compiling zinc ions and 2-methylimidazole ligands toward BiPO\textsubscript{4} by the one-pot stirring method at room temperature. Thuswise, the electrical conductivity of the composite was improved by dispersing BiPO\textsubscript{4} homogeneously within the ZIF-8 matrix. The ZIF-8@BiPO\textsubscript{4} hybrid structure with exquisite features not only served as an excellent supercapacitor cathode, resulting in high energy and power densities but also was an outstanding photocatalysis with high methylene blue (MB) dye degradation. The results show that the ZIF-8@BiPO\textsubscript{4} hybrid has a higher specific capacitance of 497 F g\textsuperscript{−1} than pure ZIF-8 (178 F g\textsuperscript{−1}) and BiPO\textsubscript{4} (443 F g\textsuperscript{−1}) at a current density of 1 A g\textsuperscript{−1} in the three-electrode system. Furthermore, the modeled ASC device implementing a ZIF-8@BiPO\textsubscript{4} cathode electrode and a BiPO\textsubscript{4} anode electrode could reach a working voltage of 1.4 V, exhibiting a maximum power density of 7067 W kg\textsuperscript{−1} with a maximum energy density of 17.5 Wh kg\textsuperscript{−1}. Meanwhile, the photocatalytic activity of the ZIF-8@BiPO\textsubscript{4} (78%) hybrid was reported to be higher than that of pure BiPO\textsubscript{4} (15%) thanks to the ZIF-8 (81%) excellent photocatalytic feature. Consequently, this multifunctional hybrid material with high photocatalytic activity and excellent...
electrochemical behaviors can be considered an example of a promising material for energy storage and water remediation applications.

2. EXPERIMENTAL SECTION

2.1. Materials. Bismuth nitrate pentahydrate (Bi(NO$_3$)$_3$$ \cdot $ 5H$_2$O), potassium hydroxide (KOH), nitric acid (HNO$_3$), sodium phosphate monobasic dihydrate (NaH$_2$PO$_4$·2H$_2$O), zinc nitrate hexahydrate (Zn(NO$_3$)$_2$$ \cdot $6H$_2$O), sodium dodecyl sulfate (NaC$_{12}$H$_{25}$SO$_4$)(SDS), and methanol (CH$_3$OH) were purchased from Sigma-Aldrich (Germany). 2-Methylimidazole (C$_2$H$_3$N$_2$), polyvinylidene fluoride, and n-methyl-2-pyrrolidone (NMP) were purchased from Sigma-Aldrich (USA). All chemical reagents and solvents for synthesis and analysis were utilized without further purification, and the used deionized water (DI) had 18.2 MΩ cm resistivity.

2.2. Synthesis of ZIF-8. The synthesis procedure of ZIF-8 was similar, with some small modifications reported by Bustamante et al.$^{81}$ In detail, 4 mmol Zn(NO$_3$)$_2$$ \cdot $6H$_2$O was dissolved in 20 mL of CH$_3$OH solution homogeneously. In another beaker, 32.3 mmol C$_2$H$_3$N$_2$ was also dissolved in 20 mL of CH$_3$OH with ultrasonication for 10 min. Thereafter, these two different solutions were mixed and magnetically stirred for 8 h. White ZIF-8 powders were obtained by washing three times with methanol and DI and vacuum-dried at 85 °C for 15 h.

2.3. Synthesis of BiPO$_4$. The approach of modification of BiPO$_4$ was carried out as previously reported. First, 0.5 g of NaH$_2$PO$_4$·2H$_2$O was dissolved in 50 mL of DI until a homogeneous solution was observed. Then, 5 mmol SDS was added to the solution, and the compound was ultrasonically irradiated for 15 min. In another beaker, 5 mmol Bi(NO$_3$)$_3$$ \cdot $5H$_2$O was in DI and 1 M HNO$_3$ added to the solution until pH = 10. Later, the obtained white homogeneous solution was hydrothermally treated for 24 h at 180 °C. Then, the hydrothermally treated solution was cooled down to room temperature and centrifuged after washing DI and ethanol to remove impurities. As-obtained white particles were vacuum-dried at 85 °C for 12 h and saved in a desiccator for further usage.$^{79}$

2.4. Synthesis of ZIF-8@BiPO$_4$. The composite ZIF-8@BiPO$_4$ was implemented by adding 200 mg of as-prepared BiPO$_4$ to the mixture of 20 mL of C$_2$H$_3$N$_2$·CH$_3$OH solution. The rest of the synthesis process was similar to that for pure ZIF-8. Figure 1 shows the schematic illustration of the synthesis process.

2.5. Structural Characterization. To inspect the crystallographic structures of the patterns, a Bruker AXS D8 X-ray powder diffractometer with a simple cubic lattice and Cu Kα radiation (λ = 0.15406 nm) was used, and the scan range (2θ) changing 5–90° was implemented. Fourier transform infrared spectroscopy (FTIR, Spectrum Two, PerkinElmer, USA) was applied to probe the structure and chemical bonds of the molecule. The Raman spectrum was investigated using a Raman microscope (Alpha 300 M+, WITec, Germany). The morphology of the patterns was screened using a field-emission scanning electron microscope (FESEM, Gemini 550) and a scanning transmission electron microscope (STEM, Gemini 550). Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda methods were used to analyze the pore size distribution, total pore volume (TPV), and the specific surface area (SSA) of the patterns.

2.6. Electrochemical Characterization. To obtain the working electrodes the electroactive materials (BiPO$_4$, ZIF-8, and BiPO$_4$@ZIF-8): 85 wt %, acetylene black: 10 wt % and PDVF: 5 wt % were intermingled with the inclusion of a few drops of the NMP solvent. The chosen current collector was a nickel foam in the dimensions of 1 cm × 1 cm. The oxide layer on the nickel foam was removed by cleaning 1 M HCl. The electrode was obtained by dropping the slurry on the nickel foam and drying at 85 °C for 12 h under vacuum. Roughly 1.1 mg mass of the active material was acquired.

A Gamry Reference 3000 electrochemical workstation was used to test the electrochemical measurements of the patterns in a typical three-electrode configuration by cyclic voltammetry (CV), galvanostatic charge–discharge (GCD), and electrochemical impedance spectroscopy (EIS). The electroactive materials were operated as working electrodes, Pt foil (1 × 1 cm$^2$) as the counter electrode in which the reference electrode was silver/silver chloride (Ag/AgCl). All electrochemical analysis and measurements were conducted in 2 M KOH aqueous electrolyte.

The ASC device was formed by using BiPO$_4$ as the anode and ZIF-8@BiPO$_4$ as the cathode with a glass microfiber

Figure 1. Synthesis steps of ZIF-8 and BiPO$_4$.
(Whatman) fiber as a separator. The CV, GCD, EIS, and the long-term test measurements of the asymmetric device were performed in the voltage range of $0−1.4$ V.

2.7. Photocatalytic Degradation Studies on ZIF-8@BiPO$_4$.

Photocatalytic degradation experiments were carried out by using MB dye and sildenafil citrate (SC) as model pollutants under ultraviolet (UV) irradiation. The degradation of MB or SC was performed by exposure to a UV irradiation source (400 W UV lamp at $\lambda=380$ nm) from the top of the reactor. For each experiment, 100 mg of the catalyst was added into a glass beaker containing 100 mL of prepared MB or CS aqueous solution at a concentration of 10 mg L$^{-1}$. To establish an adsorption–desorption equilibrium between the pollutant and the photocatalyst, the prepared solution was magnetically stirred in the dark for 60 min and then subjected to UV light for 180 min. During UV exposure, MB or CS solution (1 mL) with a catalyst at certain time intervals was withdrawn and then centrifuged to remove the solid catalyst for analysis. Thereafter, the concentration of MB in the solution was measured by UV–vis absorption spectroscopy at 664 nm and CS concentration in the solution was measured by the ultraperformance liquid chromatography method with diode array detection (UPLC-DAD).

Finally, the percentage degradation of MB was calculated by eq 1:

$$\text{degradation (\%)} = \left( \frac{C_0 - C_t}{C_0} \right) \times 100$$  (1)

where $C_0$ (mg L$^{-1}$) is the initial equilibrium concentration of MB at 664 nm and $C_t$ (mg L$^{-1}$) is the concentration of MB at 664 nm at the given time “$t$” min$^{-1}$.

3. RESULTS AND DISCUSSION

3.1. Structural and Morphological Studies.

Figure 2 presents the structural and chemical characterization of the synthesized hybrid material. To analyze the phase and structure of the as-prepared materials, X-ray diffraction (XRD) measurements were implemented. In Figure 2a (red line), the peaks at 2 theta values of 7.25, 10.44, 12.67, 14.71, 16.35, 18.01, 21.99, 24.50, 25.75, 29.68, 30.58, and 31.50$^\circ$ are referred to (011), (002), (112), (022), (013), (222), (114), (233), (134), (044), (244), and (235) planes of ZIF-8, respectively.

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In Figure 2a (black line), the peaks at 2 theta values of 17.04, 18.70, 21.32, 21.93, 25.33, 25.42, 27.25, 28.39, 29.17, 30.14, 30.57, 31.18, 34.5, 37.12, 38.69, 41.56, 42.18, 42.62, 43.05, 46.28, 46.98, 48.38, 48.98, 50.82, 51.96, and 53.18$^\circ$ referring to (011), (002), (112), (022), (013), (222), (114), (233), (134), (044), (244), and (235) planes of ZIF-8, respectively.

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synthesized BiPO₄ has a monoclinic phase compatible with the 120 ort he12re (JCPDS #15-0767). In Figure 2a (blue line), XRD results of the composite material ZIF-8@BiPO₄ are shown in which all of the characteristic peaks of both ZIF-8 and BiPO₄ can be detected obviously. The narrow and strong peaks indicate that the structure has highly crystalline properties.

The chemical configuration and chemical bonding of the samples were determined by applying FTIR. In Figure 2b (red line), the peak at 3135 cm⁻¹ is related to the N−H stretching band of the 2−methyl−imidazole ligand. The bands belonging to methyl groups lie around 2938 cm⁻¹ (imidazole aliphatic C−H) and 1570 cm⁻¹ (C−H stretching). The absorption bands between 1420 and 1307 cm⁻¹ can be ascribed to C−N stretching, and the band located at 1145 cm⁻¹ corresponds to C−N vibration. An axial deformity is apparent at 1570 cm⁻¹ as the C==N band. The bands around 673 and 690 cm⁻¹ can be related to Zn−N stretching. The results are compatible with the literature.

In Figure 2b (black line), the bands depicted around 523 and 602 cm⁻¹ belong to symmetric stretching and asymmetric bending vibrations of P−O, and the occurred bonds between 904 and 1064 cm⁻¹ can be confirmed to be the O−P−O linkage possessing BiPO₄. Moreover, in Figure 2b (blue line) FTIR results of the composite material owing all of the characteristic peaks of ZIF-8 and BiPO₄ are seen obviously.

The Raman spectra of the materials are demonstrated in Figure 2c,d. In Figure 2c, the monitored peaks at 100−300 cm⁻¹ belong to symmetric bending vibrations of Bi−O, and those around 558−615 cm⁻¹ correspond to v₂ and v₄ bending vibrations of PO₄ groups. Furthermore, the screened peaks at 983 and 1055 cm⁻¹ are responsible for the v₁ symmetric and v₃ as the C==N band. The bands around 673 and 690 cm⁻¹ can be related to Zn−N stretching. The results are compatible with the literature.

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antisymmetric vibration modes of PO₄ in BiPO₄.²⁸ In Figure 2d (red line), Raman spectra of ZIF-8 are shown. The peak of C–H is depicted at 1504 cm⁻¹, the peaks between 1119 and 1184 cm⁻¹ belong to C–N stretching, and the peaks around 643 and 952 cm⁻¹ can be ascribed to the imidazolium ring.²⁸ Additionally, the peak of Zn–N is depicted at 282 cm⁻¹. Figure 2d (blue line) shows the Raman spectra of the composite material ZIF-8@BiPO₄ including all characteristic peaks of raw materials. The peaks around 176–281 cm⁻¹ belong to symmetric bending vibrations of Bi–O and those around 644–687 cm⁻¹ correspond to ν₁ and ν₄ bending vibrations of PO₄ groups, respectively. The depicted peaks at 984 and 1042 cm⁻¹ are responsible for the ν₁ symmetric and ν₃ antisymmetric vibration modes of PO₄ in BiPO₄. Moreover, the peak of Zn–N is depicted at 284 cm⁻¹. The broad peak around 649–952 cm⁻¹ might be acceptable of the peaks of the imidazolium ring. Additionally, the peaks between 1147 and 1185 cm⁻¹ refer to C–N stretching, and the peak at 1460 belongs to the C–H bond.

N₂ adsorption–desorption isotherms were applied to scrutinize the porosity of the structures seen in Figure S1. In comparison with BiPO₄, ZIF-8 and ZIF-8@BiPO₄ display much more adsorbed amount of N₂ gas, indicating the existence of micropores (Figure S1a). Pure ZIF-8 has the largest SSA-TPV 407.66 m² g⁻¹; 0.50771 cm³ g⁻¹, while the SSA-TPV of BiPO₄ and ZIF-8@BiPO₄ is 2.79 m² g⁻¹; 0.00447 cm³ g⁻¹, 275.73 m² g⁻¹; 0.35118 cm³ g⁻¹, respectively. The addition of ZIF-8 enhanced the average pore size value of BiPO₄; thus, BET results and pore sizes of ZIF-8@BiPO₄ are higher than those of pure BiPO₄. In Figure S1b, the pore size distribution of the patterns is demonstrated. The obtained average pore sizes of ZIF-8, BiPO₄, and ZIF-8@BiPO₄ are 11, 8, and 15 nm, respectively.

In Figure 3, the surface morphology of the patterns screened by FESEM and STEM techniques is demonstrated. While ZIF-8 has a regular polyhedron shape (Figure 3a–d), BiPO₄ mostly has irregular cubic-like shapes with agglomerated particles (Figure 3b–e). The composite ZIF-8@BiPO₄ also shows
(Figure 3c–f) both polyhedron and irregular agglomerated cubic-like morphology interwoven with each other. Energy-dispersive spectrometry (EDS) was utilized to identify the composition of the ZIF-8@BiPO₄ structure. In Figure 3g, individual elemental mapping images of C, N, O, P, Bi, and Zn and EDS images are shown indicating that ZIF-8@BiPO₄ combination was achieved successfully.

3.2. Electrochemical Studies. 3.2.1. CV Studies. The electrochemical characterization results are summarized in Figure 4. Figure 4a–c displays CV of the electrodes in a three-electrode system at different scan rates (20, 50, 100 mV s⁻¹) in 2.0 M KOH (vs Ag/AgCl) electrolyte. ZIF-8 CV curves were examined in the potential range of −0.01 to 0.55 V (vs Ag/AgCl), while BiPO₄ working potential was between −1.2 and 0.2 V (vs Ag/AgCl), and ZIF-8@BiPO₄ CV curves were scanned between −1.2 and 0.65 V (vs Ag/AgCl). All of the materials have conspicuous redox peaks expressing the pseudocapacitive nature of the materials. By polarization with the scan rate increment, there is a shift toward the larger potential range on the anodic area while cathodic peak shift was toward the lower potential range. Regardless of the increment of the current density with the scan rate, all of the patterns yet had obvious redox peaks, which confirmed gratifying charge/discharge reversibility. The frequent redox reactions transpiring at the electrode/electrolyte interface conduct to redox peaks of the patterns to enhance with the increased scan rates.

The specific capacitance values of the electrodes at various scan rates were measured based on the following equation:

$$C_s = \frac{\int I(V) \Delta t}{\nu \times m \times \Delta V}$$  \hspace{1cm} (2)

The area under the CV curves is designated by \(\int I(V) \Delta t\), the scan rate is shown as \(\nu\) (mV s⁻¹), \(m\) (g) presents the mass of the active material, and \(\Delta V\) (V) typifies the applied potential window.

Due to the distinctness of the potential range of the electrodes, it was inconvenient to synthesize the obvious differences from CV graphs. However, the specific capacitances measured from eq 1 declared that composite ZIF-8@BiPO₄ has the highest specific capacitance value of 489 F g⁻¹ at a scan rate of 5 mV s⁻¹. The maximum specific capacitance values of ZIF-8 and BiPO₄ at the same scan rate are 185 and 358 F g⁻¹, respectively. Although there were distinct differences from rising 5 to 20 mV s⁻¹ for all electrodes, this disparity lessens with increasing scan rates as shown in Figure 5a. At high scan rates, there were not many differences between electrochemical features of pure BiPO₄ and composite material ZIF-8@BiPO₄.

The specific capacitance of the electrodes was reckoned from the charge–discharge curves by the following equation.

$$C_s = \frac{I \times \Delta t}{m \times \Delta V}$$  \hspace{1cm} (3)

where \(I\) (A) typifies the discharge current, \(\Delta t\) (s) is the average discharge time, the mass of the active material abbreviated as \(m\) (g), and \(\Delta V\) (V) represents the GCD applied potential window. The current density \(J\) (A g⁻¹) was meant the ratio of discharge current \(I\) (A) to the mass of the active material \(m\) (g).

The individual charge–discharge curves of the electrodes at different current densities were graphed in Figure 4d–f. While ZIF-8 could reach a maximum specific capacitance of 178 F g⁻¹ at a current density of 1 A g⁻¹, the highest specific capacitances of BiPO₄ and ZIF-8@BiPO₄ were 443 and 497 F g⁻¹ at the same current density, respectively. Although there were 0.2 V differences between BiPO₄ (\(V_c = 0.2\) V) to ZIF-8@BiPO₄ (\(V_c = 0.4\) V), the composite material still had higher specific capacitances than pure materials. In Figure 5b, the specific capacitance variations with current densities are depicted. Significantly, there was not a conspicuous discrepancy on specific capacitances between pure BiPO₄ and ZIF-8@BiPO₄ at high current densities such as 10 and 20 A g⁻¹.

To further determine the long-term cycling stability of the electrodes long-term chronopotentiometry analysis was applied at a current density of 20 A g⁻¹ up to 5000 cycles. In Figure 5c, the retained specific capacitance value of the electrodes is demonstrated. The retention of ZIF-8 (78%) was recorded more less than the retention of BiPO₄ (89%). Satisfyingly, the capacity efficiency of ZIF-8@BiPO₄ was higher than others (91%) indicating that the composite material has better cycling stability.

3.2.3. Electrochemical Impedance Spectroscopy. To test the kinetics of ion and charge transfer action of the materials, EIS was performed. In Figure S2, individual Nyquist plots in low- and high-frequency ranges are shown. The comparison of EIS in low- and high-frequency ranges (inset displays the equivalent circuit model) in 2 M KOH solution is graphed in Figure 5d, e in the frequency range of 0.01–100 kHz with an amplitude of 5 mV.

When the ion diffusion resistance is determined by the low-frequency region, the high-frequency region is responsible for the charge transmission. The vertical line in the low-frequency area affirms the ideal capacity performance of the patterns. Ion diffusion among the electrode and electrolyte causes another line called the Warburg line which makes 45°angle among that vertical line and the x-axis.

The charge transport resistance (\(R_c\)) of the electrodes ZIF-8, BiPO₄, and ZIF-8@BiPO₄ was 0.80, 0.56, and 0.76 mΩ, respectively. The equivalent series resistance (\(R_e\)) for the electrode BiPO₄ (1.04 Ω) was lower than that of ZIF-8 (1.72 Ω), although there was not a noticeable discrepancy between BiPO₄ (1.04 Ω) and ZIF-8@BiPO₄ (1.16 Ω). As declared, BiPO₄ has the minimum and ZIF-8 has the highest values of \(R_c\) and \(R_e\).

3.2.4. Electrochemical Performances of an ASC. To further test the operation of the electrodes in practical applications, a two-electrode system ASC was fabricated by using ZIF-8@BiPO₄ as the cathode and BiPO₄ as the anode material with a glass microfiber filter separator presoaked in 2 M KOH. The optimal mass balance of anode and cathode
electrodes \( \frac{M_+}{M_-} \) was calculated to be \( \sim 1.3 \) by the following equation:  

\[
\frac{M_+}{M_-} = \frac{C_- \times \Delta V_-}{C_+ \times \Delta V_+} \tag{4}
\]

where \( M \) represents the mass of the active material, \( C \) symbolizes specific capacitance, and \( \Delta V \) signifies the potential window for the anode and cathode electrodes.

In Figure 6, electrochemical features of the ASC device are illustrated. Figure 6a shows individual CV curves of anode BiPO\(_4\) \([-1.2 \text{ to } 0.2 \text{ V (vs Ag/AgCl)}]\) and cathode ZIF-8@BiPO\(_4\) \([-1.2 \text{ to } 0.65 \text{ V (vs Ag/AgCl)}]\). Figure 6b demonstrates the CV curves of the ASC device in different potential windows ranging from 0.8 to 1.4 V at a scan rate of 100 mV s\(^{-1}\). The determined suitable potential window was 0–1.4 V. CV curves of the ASC device in the cell voltage limit of 1.4 V at the different scan rates (30–50–100 mV s\(^{-1}\)) are also shown in Figure 6c. At both cathodic and anodic scans, the reduction and oxidation peaks can be detected, and these peaks are more conspicuous at lower scan rates. This could be predicated on the deintercalation process that appears at the surface of the electrodes.

The specific capacitance \( C_{sp} \) of the ASC cell, the energy density \( E \), and the power density \( P \) were reckoned up according to the following equations:

\[
C_{cell} = \frac{4 \times I \times \Delta t}{m \times \Delta V} \tag{5}
\]

\[
E = \frac{C_{cell} \times \Delta V^2}{4 \times 3.6} \tag{6}
\]

\[
P = \frac{3600 \times E}{\Delta t} \tag{7}
\]

The GCD behavior of the ASC device at various current densities is shown in Figure 6d. Well-proportioned charge and discharge curves indicate a fast \( I-V \) reaction.
maximum and minimum specific capacitance values by using eq 5 were 255 F g$^{-1}$ at a current density of 0.5 A g$^{-1}$ and 57 F g$^{-1}$ at a current density of 50 A g$^{-1}$ as illustrated in Figure 7a.

To check the kinetics of ion and charge transfer reaction of the ASC device, EIS analysis was employed. The Nyquist plot of the ASC was graphed in Figure 6e in the frequency range of 0.01 – 100 kHz at open circuit potential. The obtained $R_c$ and $R_d$ values are 2.87 Ω and 6.91 mΩ, respectively.

Additionally, to test the long-term cycling stability of the ASC device, a constant current density of 10 A g$^{-1}$ was applied up to 10,000 cycles as shown in Figure 6f. The retention of the specific capacity of the ASC device was 81% of its initial capacity after 10,000 cycles, indicating that the formed ASC device shows good cycling stability.

The connection between energy and power densities of the ACS is demonstrated in the Ragone plot in Figure 7b. For the fabricated ASC device, the obtained maximum energy density was 17.5 Wh kg$^{-1}$ at a power density of 178 W kg$^{-1}$ and a boosted power density of 13,695 W kg$^{-1}$, giving an energy density of 2.9 Wh kg$^{-1}$. The detailed results are tabularized in Table 1.

### Table 1. Energy and Power Densities of the ASC at Different Current Densities

| Power Density (A g$^{-1}$) | Energy Density (Wh kg$^{-1}$) | Power Density (W kg$^{-1}$) | Energy Density (Wh kg$^{-1}$) |
|---------------------------|-------------------------------|-----------------------------|-------------------------------|
| 0.5                       | 255                           | 10                          | 561                           |
| 1                         | 204                           | 15                          | 460                           |
| 5                         | 51                           | 20                          | 251                           |
| 10                        | 44                           | 30                          | 18                           |

To illuminate the photocatalytic process of the ZIF-8@BiPO$_4$ hybrid material, the UV–vis spectrum of ZIF-8@BiPO$_4$ was measured, and the Tauc plot was applied to the determine band gaps by using the obtained UV–vis spectra (Figure S5). It was found that ZIF-8, BiPO$_4$, and ZIF-8@BiPO$_4$ have a maximum absorption peak centered at 360, 330, and 355 nm wavelengths, respectively. As the band gaps for ZIF-8
and BiPO$_4$ were calculated as 2.80 and 3.41 eV, the band gap for Zif-8@BiPO$_4$ was found as 2.40 and 3.87 eV. ZIF-8 and BiPO$_4$ demonstrate a narrow and wide band gap, respectively, and Zif-8@BiPO$_4$ exhibits a slightly wider band gap compared with the directly generated BiPO$_4$ sample due to the movement of the O$_2p$ state at the top of the valence band to the low-energy direction caused by the produced O$_{vac}$.

Reusability is an important feature to evaluate the stability of catalysts. The reusability performance of Zif-8@BiPO$_4$ hybrid catalysts was evaluated using MB dyestuff with repeated uses. Zif-8@BiPO$_4$ hybrid catalysts did not perform consistently over three cycles of photodegradation. After three cycles, the photocatalytic reusability of the hybrid catalysts decreased significantly. It has been determined that the decrease in the degradation value obtained at the end of the third cycle is about 30% (1st cycle: 78% and 2nd cycle: 54%).

4. CONCLUSIONS

To conclude, we have developed a hybrid material by synergetic integration of ZIF-8 and BiPO$_4$ nanoparticles for addressing the pressing challenges in energy storage and water remediation applications. The electrochemical features of the formed electrodes were optimized in 2 M KOH electrolyte in a three-electrode cell configuration. The Cs of hybrid material ZIF-8@BiPO$_4$ (489 F g$^{-1}$ at a scan rate of 5 mV s$^{-1}$; 497 F g$^{-1}$ at a current density of 1 A g$^{-1}$) was substantially higher than that of pristine materials BiPO$_4$ (358, 443 F g$^{-1}$) and ZIF-8 (of ~185, 178 F g$^{-1}$) under the same conditions. The ASC device fabricated by using BiPO$_4$ as the anode and ZIF-8@BiPO$_4$ as cathode electrodes received an excellent Cs of 255 F g$^{-1}$ at a current density of 0.5 A g$^{-1}$. The cycling stability of the ASC was also as high as 81% over 10,000 cycles. Additionally, the acquired highest energy and power densities were 17.5 Wh kg$^{-1}$ and 13,695 W kg$^{-1}$, respectively. Thereafter, the degradation of MB was examined for the use of photocatalysis implementation. After 180 min of UV irradiation, the degradable amount of MB was obtained as 78%. These results show that the as-prepared environmentally kind, reasonably priced, multifunction hybrid material can find an execution area on supercapacitors and photocatalytic applications.
ASSOCIATED CONTENT

Supporting Information
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Notes
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REFERENCES

(1) Anonymous . 17 goals of Sustainable Development; United Nations Department of Economic and Social Affairs. https://sdg.un.org/goals (accessed March 2, 2022).

(2) Satpathy, S.; Das, S.; Bhattacharyya, B. K. How and Where to Use Super-Capacitors Effectively, an Integration of Review of Past and New Characterization Works on Super-Capacitors. J. Energy Storage 2020, 27, No. 101044.

(3) Zhu, Q.; Zhao, D.; Cheng, M.; Zhou, J.; Owusu, K. A.; Mai, L.; Yu, Y. A New View of Supercapacitors: Integrated Supercapacitors. Adv. Energy Mater. 2019, 9, No. 1901081.

(4) Poonam; Sharma, K.; Arora, A.; Tripathi, S. K. Review of Supercapacitors: Materials and Devices. J. Energy Storage 2019, 21, 801–825.

(5) Vangari, M.; Pryor, T.; Jiang, L. Supercapacitors: Review of Materials and Fabrication Methods. J. Energy Eng. 2013, 139, 72–79.

(6) Berrueta, A.; Ursa, A.; Martin, I. S.; Efekhari, A.; Sanchis, P. Supercapacitors: Electrical Characteristics, Modeling, Applications, and Future Trends. IEEE Access 2019, 7, 50869–50896.

(7) Zhi, M.; Xiang, C.; Li, J.; Li, M.; Wu, N. Nanostructured Carbon-Metal Oxide Composite Electrodes for Supercapacitors: A Review. Nanoscale 2013, 5, 72–88.

(8) Abu Eldahab, Y. E.; Saad, N. H.; Zekry, A. Enhancing the Design of Battery Charging Controllers for Photovoltaic Systems. Renew. Sustain. Energy Rev. 2016, 58, 646–655.

(9) Mahlia, T. M. I.; Saktisahdan, T. J.; Jannifar, A.; Hasan, M. H.; Matseslar, H. S. C. A Review of Available Methods and Development on Energy Storage; Technology Update. Renew. Sustain. Energy Rev. 2014, 33, 532–545.

(10) Ke, Q.; Wang, J. Graphene-Based Materials for Super capacitor Electrodes — A Review. J. Materiomics 2016, 37–54.

(11) Wang, H.; Wang, Q.; Hu, B. A Review of Developments in Energy Storage Systems for Hybrid Excavators. Autom. Constr. 2017, 80, 1–10.

(12) Li, T.; Ma, R.; Lin, J.; Hu, Y.; Zhang, P.; Sun, S.; Fang, L. The Synthesis and Performance Analysis of Various Biomass-Based Carbon Materials for Electric Double-Layer Capacitors: A Review. Int. J. Energy Res. 2020, 44, 2426–2454.

(13) Qiu, M.; Sun, Z. T.; Sang, D. K.; Han, X. G.; Zhang, H.; Niu, C. M. Current Progress in Black Phosphorus Materials and Their Applications in Electrochemical Energy Storage. Nanoscale 2017, 9, 13384–13403.

(14) Chen, X.; Xu, G.; Ren, X.; Li, Z.; Qi, X.; Huang, K.; Zhang, H.; Huang, Z.; Zhong, J. A Black/Red Phosphorus Hybrid as an Electrode Material for High-Performance Li-Ion Batteries and Supercapacitors. J. Mater. Chem. A Mater. 2017, 5, 6581–6588.

(15) Ma, D.; Li, Y.; Yang, J.; Mi, H.; Luo, S.; Deng, L.; Yan, C.; Rauf, M.; Zhang, P.; Sun, X.; Ren, X.; Li, J.; Zhang, H. New Strategy for Polysulfide Protection Based on Atomic Layer Deposition of TiO2 onto Ferroelectric-Encapsulated Cathode: Toward Ultrastable Free-Standing Room Temperature Sodium–Sulfur Batteries. Adv. Funct. Mater. 2018, 28, No. 1705537.

(16) Hulstutjer, J. D.; Wasala, M.; Richie, J.; Barron, J.; Winchester, A.; Griffith, S.; Yang, C.; Xu, W.; Song, L.; Kar, S.; Talapatra, S. High Performance Graphene-Based Electrochemical Double Layer Capacitors Using 1-Butyl-1-Methylpyrrolidinium Tris (Pentafluoroethy1) Trifluorophosphate Ionic Liquid as an Electrolyte. Electronics 2018, 7, 229.

(17) Li, Z.; Huang, T.; Gao, W.; Xu, Z.; Chang, D.; Zhang, C.; Gao, C. Hydrothermally Activated Graphene Fiber Fabrics for Textile Electrodes of Supercapacitors. ACS Nano 2017, 11, 11056–11065.

(18) Dang, Y. Q.; Ren, S. Z.; Liu, G.; Cai, J.; Zhang, Y.; Qiu, J. Electrochemical and Capacitive Properties of Carbon Dots/Reduced Graphene Oxide Supercapacitors. Nanomaterials 2016, 6, 212.

(19) Jiang, Y.; Jiang, Z.; Shi, M.; Liu, Z.; Liang, S.; Feng, J.; Sheng, R.; Zhang, S.; Wei, T.; Fan, Z. Enabling High Surface and Space Utilization of Activated Carbon for Supercapacitors by Homogeneous Activation. Carbon 2021, 59–563.

(20) Wang, A.; Sun, K.; Xu, R.; Sun, Y.; Jiang, J. Cleanly Synthesizing Botten Potato-Based Activated Carbon for Super-capacitor by Self-Catalytic Activation. J. Cleaner Prod. 2021, 283, No. 125385.

(21) Thomas, B. N.; George, S. C. Production of Activated Carbon from Natural Sources. Trends Green Chem. 2015, 1, 7.

(22) Xiang, C.; Li, M.; Zhi, M.; Manivannan, A.; Sources, N. W. A Reduced Graphene Oxide/Co3O4 Composite for Supercapacitor Electrode. J. Power Sources 2013, 226, 65.

(23) Wu, H.; He, D.; Wang, Y. Facile One-Step Process Synthesized Reduced Graphene Oxide/Mn3O4 Nanocomposite for a Symmetric Supercapacitor. Mater. Lett. 2020, 268, No. 127613.
Application in Energy Storage Devices. *New J. Chem.* 2020, 44, 7369−7375.

(94) Jung, S.; Thi Huong, P.; Sahani, S.; Tripathi, K. M.; Park, B. J.; Han, Y. H.; Kim, T. Biomass-Derived Graphene-Based Materials Embedded with Onion-Like Carbons for High Power Supercapacitors. *J. Electrochem. Soc.* 2022, 169, No. 010509.

(95) Sankar Das, G.; Youn Hwang, J.; Jang, J.-H.; Malika Tripathi, K.; Kim, T. Biomass-Based Functionalized Graphene for Self-Rechargeable Zinc−Air Batteries. *ACS Appl. Energy Mater.* 2022, 5, 6663−6670.