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Engineered Cadmium and Manganese Nanomaterials: Performance Evaluation in Energy Storage and Catalytic Systems

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Abstract:
Cd and Mn nanomaterials engineered have become promising in the two fields of energy storage and catalytic systems. This paper provides a detailed comparison of the electrochemical and catalytic activity of pure CdO, pure MnO_2, and Cd -Mn nanocomposites synthesized through the controlled precipitation and calcination techniques. These materials were described by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and electrochemical impedance spectroscopy (EIS). The storage performance of energy was estimated by measuring lithium-ion battery (LIB) and supercapacitor, and the catalytic performance was estimated by measuring oxidative degradation of model organic pollutants in ambient conditions. Cd-Mn composite nanomaterial showed a high level of specific capacitance of 310 F/g at 1 A/g current density, which is better than CdO of 180 F/g and MnO_2 of 240 F/g. The Cd-Mn composite was found to have a reversible specific capacity of 380 mAh/g in battery usage and exhibited catalytic degradation efficiency of 88 and 84 with organic dyes and nitro-aromatic compounds, respectively. This was due to the synergistic effect of Cd and Mn components, growth in the surface area (72-98 m 2/G), and electron transfer kinetics. These findings demonstrate that Cd-Mn nanomaterials are an efficient multifunctional material that can solve energy and environmental problems at the same time.

Keywords: nanomaterials, cadmium, manganese, energy storage, supercapacitors, batteries, catalysis, electrochemical performance.

1. INTRODUCTION

The international shift to sustainable energy infrastructure and eco-cleaning requires the creation of new functional materials with high functionality, allowing them to solve various technological issues (Kumar et al., 2023). Lithium-ion batteries (LIBs) and supercapacitors are used as energy storage systems and are essential in the integration of renewable energy as well as in the portability of electronics (Park & Kim, 2022). At the same time, pollutant degradation catalytic systems are still critical in protecting the environment (Chen et al., 2023). But it has been seen that it is difficult to come up with materials that perform in both fields.

Metal oxide nanomaterials have attracted much interest because of their controllable electronic behaviors, large surface area-volume ratios, and the ability to exist in multiple oxidation states that can be used in various functional cases (Zhang and Liu, 2021). Single metal oxides have drawbacks: cadmium oxide (CdO) has moderate specific capacity as a battery anode and low catalytic activity; manganese dioxide (MnO_2) has high catalytic properties and supercapacitive behavior and low cycle stability in battery systems (Patel et al., 2022). The synthesis of these materials in strategic composites as nanomaterials may also be employed to utilize synergistic effects that would overcome the weaknesses of individual materials.

Cadmium oxide has a number of benefits in terms of energy storage, such as a narrow band gap (2.2 eV), good electrical conductivity, and high theoretical specific capacity (Rahman & Hassan, 2021). The combination of multiple oxidation states (Mn^{2+}, Mn^{3+}, Mn^{4+}) and a stratified structure makes manganese oxide a better catalyst and outstanding capacitors (Thompson et al., 2022). This blending of these materials into engineered composites may provide: (1) superior pathways of electron transfer, (2) superior electrochemical stability, (3) synergistic catalysis, and (4) adaptable functions in energy and environmental applications.

The key aims of the study are: (1) to prepare engineered Cd-Mn nanomaterials with controlled morphology and composition; (2) to test the electrochemical performance in terms of battery and supercapacitor operations; (3) to test the catalytic performance in degradation of organic pollutants; (4) to draw correlations between material structure and multifunctional performance; and (5) to compare performance with those of single-component CdO and MnO 2 materials.

2. MATERIALS AND METHODS

2.1 Materials and Reagents

Cadmium nitrate [$Cd(NO_3)_2 \cdot 4H_2O$], manganese nitrate [$Mn(NO_3)_2 \cdot 4H_2O$], sodium hydroxide (NaOH), ammonium persulfate [$(NH_4)_2S_2O_8$], ethanol (absolute, >99.8percent), and deionized water were all purchased at Sigma-Aldrich (St. Louis, MO, USA) of the grade of analysis. The batteries were made using lithium iron phosphate cathodes and graphite anodes (MTI Corporation).

2.2 Synthesis of Nanomaterials

CdO Nanomaterials: 0.15 M Cadmium nitrate in deionized water was stirred under constant stirring at 250 mL. The solution of NaOH (2 M) was added in drops until the pH 10 was reached, and a white precipitate was formed. After 6 hours of aging, the precipitate was centrifuged and washed three times with deionized water and ethanol and dried at 100°C for 12 hours. The last stage of calcination was carried out at 500°C in 2hours (heating rate: 2°C/min) using a programmable furnace (Thermcraft Inc.).

MnO 2 Nanomaterials: 250 mL of deionized water was used to dissolve 0.15 M manganese nitrate. MnO_2 precipitate was formed by the addition of ammonium persulfate (0.3M) under stirring. The blend was heated at 60 °C for 2 hours, centrifuged, washed with deionized water and ethanol respectively, dried in a 100 o C furnace, and calcinated in the fourth step at 400 °C for 2 hours.

Cd-Mn Composite Nanomaterials: Manganese nitrate (0.075M) and Cadmium nitrate (0.075M) were dissolved in deionized water (250mL) (1:1 molar ratio). Sodium hydroxide solution was put into it to change the pH to 10, followed by the addition of ammonium persulfate. The resulting compound was mixed, aged, washed, dried, and calcined according to the same procedure as is done to individual materials.2.3 Characterization Techniques

2.3 Techniques of Characterizations.

Structural Analysis: The sample was analyzed by XRD patterns on a PANalytical X'Pert Pro diffractometer Structural Analysis: The sample was analyzed by XRD patterns on a PANalytical X'Pert Pro diffractometer (Cu K, 201.54, 2° 10-80) to determine the crystalline phases and determine crystallite sizes through the Scherrer equation.

Morphological Investigations: SEM images were located with the help of a ZEISS Sigma 300 microscope (15 kV acceleration voltage). The TEM images were also obtained at a high resolution (2100F) using a JEOL JEM-2100F at a voltage of 200 kV.

Surface Area Analysis: Pore and Specific surface area were calculated using BET/BJH techniques on a Quantachrome Autosorb-iQ (N 2 adsorption, 77 K).

Electrochemical Characterization: Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were run with a Solartron 1470E potentiostat in 1 M lithium perchlorate electrolyte.to determine the crystalline phases and determine crystallite sizes through the Scherrer equation.

2.4 Battery Testing Protocol

Nanomaterial-coated copper foil anodes, lithium metal cathodes, and 1 M $LiPF_6$ in dimethyl carbonate (DMC)/ethylene carbonate (EC) electrolyte were used to construct half-cells. The cells were placed in an argon-filled glove box and run on a Maccor Series 4000 battery cycler at 0.1 A/g current density.

2.5 Supercapacitor Configuration

Supercapacitors were made using activated nanomaterial electrodes separated by a polymer electrolyte membrane in a 1 M KOH aqueous electrolyte. Cyclic voltammetry was used to determine specific capacitance: Cs = 2I/mv d V/dt, where I is current, m is mass, v is scan rate, and dV/dt is voltage sweep rate.

2.6 Catalytic Activity Assessment

Methyl orange (MO), methylene blue (MB), and 4- nitrophenol (4-NP) (100 mL) were catalytically degraded in the presence of 50mg of catalyst. 120minutes were allowed in darkness, followed by exposure to visible light at 420-800nm (400 W Xe lamp). The change in concentrations was observed through the UV-Vis spectroscopy (Shimadzu UV-2600) under distinct wavelengths of absorption.

3. RESULTS

3.1 Structural and Morphological Characterization

Table 1: *Structural Properties of Engineered Cd, Mn, and Cd-Mn Nanomaterials*

Property	CdO	MnO_2	Cd-Mn Composite
Crystallite Size (nm)	14.2 ± 1.1	12.3 ± 0.9	9.8 ± 0.7
Specific Surface Area (m^2/g)	62 ± 2.3	85 ± 3.1	98 ± 3.5
Pore Volume (cm^3/g)	0.142 ± 0.008	0.198 ± 0.011	0.228 ± 0.012
Average Pore Diameter (nm)	9.2 ± 0.6	9.3 ± 0.7	9.5 ± 0.6
Band Gap Energy (eV)	2.2 ± 0.1	2.7 ± 0.1	2.4 ± 0.1
Primary Crystal Phase	Cubic CdO	Tetragonal MnO_2	Mixed CdO-MnO_2

Source: XRD, SEM, and BET characterization from laboratory experiments

The analysis of XRD proved the existence of pure crystalline phases of single component materials and mixed phases of Cd-Mn composite. The crystal size of composite was smaller (9.8 nm) than the individual components indicating interference in the formation of nucleation as simultaneous precipitation occurred. The BET analysis showed that the Cd-Mn composite had the largest specific surface area (98 m 2/g) which is beneficial both in the application of electrochemical and catalytic surface.

3.2 Energy Storage Performance

Table 2: *Electrochemical Performance in Lithium-Ion Battery Applications*

Performance Parameter	CdO	MnO_2	Cd-Mn Composite	Literature Benchmark*
Initial Specific Capacity (mAh/g)	450 ± 15	520 ± 18	380 ± 12	400 (Carbon)
Reversible Capacity After 50 Cycles (mAh/g)	320 ± 12	280 ± 11	350 ± 13	350
Coulombic Efficiency (%)	85.2 ± 2.1	78.4 ± 2.4	91.3 ± 1.9	92

Charge Transfer Resistance Rct (Ω)	45.8 ± 3.2	38.2 ± 2.8	28.4 ± 2.1	<30
Voltage Hysteresis (V)	0.42 ± 0.05	0.55 ± 0.06	0.31 ± 0.04	<0.35

*Source: Experimental galvanostatic charge-discharge and EIS measurements; *Literature benchmark from 2023 reviews*

The Cd-Mn composite showed better cycling stability with 92% capacity retention with 50 cycles as compared to 71% in CdO and 54% of the MnO 2. The result of the electrochemical impedance spectroscopy showed that the charge transfer resistance (28.4 Ω) of the composite was significantly lower, which implies better electron transfer rates.

3.3 Supercapacitor Performance

Table 3: *Electrochemical Characteristics in Supercapacitor Configuration*

Parameter	**CdO**	**MnO_2**	**Cd-Mn Composite**	**Activated Carbon Reference**
Specific Capacitance at 1 A/g (F/g)	180 ± 8	240 ± 10	310 ± 12	210 ± 8
Specific Capacitance at 10 A/g (F/g)	125 ± 6	156 ± 7	248 ± 10	130 ± 6
Capacitance Retention at 10 A/g (%)	69.4	65.0	80.0	62.0
Energy Density at 1 A/g (Wh/kg)	12.5 ± 0.8	16.8 ± 1.0	21.6 ± 1.2	14.6 ± 0.9
Power Density at 10 A/g (W/kg)	875 ± 35	920 ± 40	1240 ± 48	800 ± 35
Cycle Life (capacity retention after 5000 cycles %)	82.3 ± 2.1	78.5 ± 2.4	94.2 ± 1.8	90.0 ± 2.0

Source: Cyclic voltammetry, galvanostatic charge-discharge testing at multiple current densities

The Cd-Mn composite supercapacitor showed excellent operation with specific capacitance of 310 F/g at 1 A/g- much higher than the component materials and commercial activated carbon. The composite was found to have 80 per cent of the original capacitance at the current density of 10 A/g, which showed an outstanding rate capability. Cycle stability: A test revealed that the capacity was 94.2% after 5000 cycles, which is a very good performance in terms of reliability in the long run.

3.4 Catalytic Activity Assessment

Figure 1. Comprehensive overview of energy storage and catalytic applications of cadmium-manganese nanomaterials

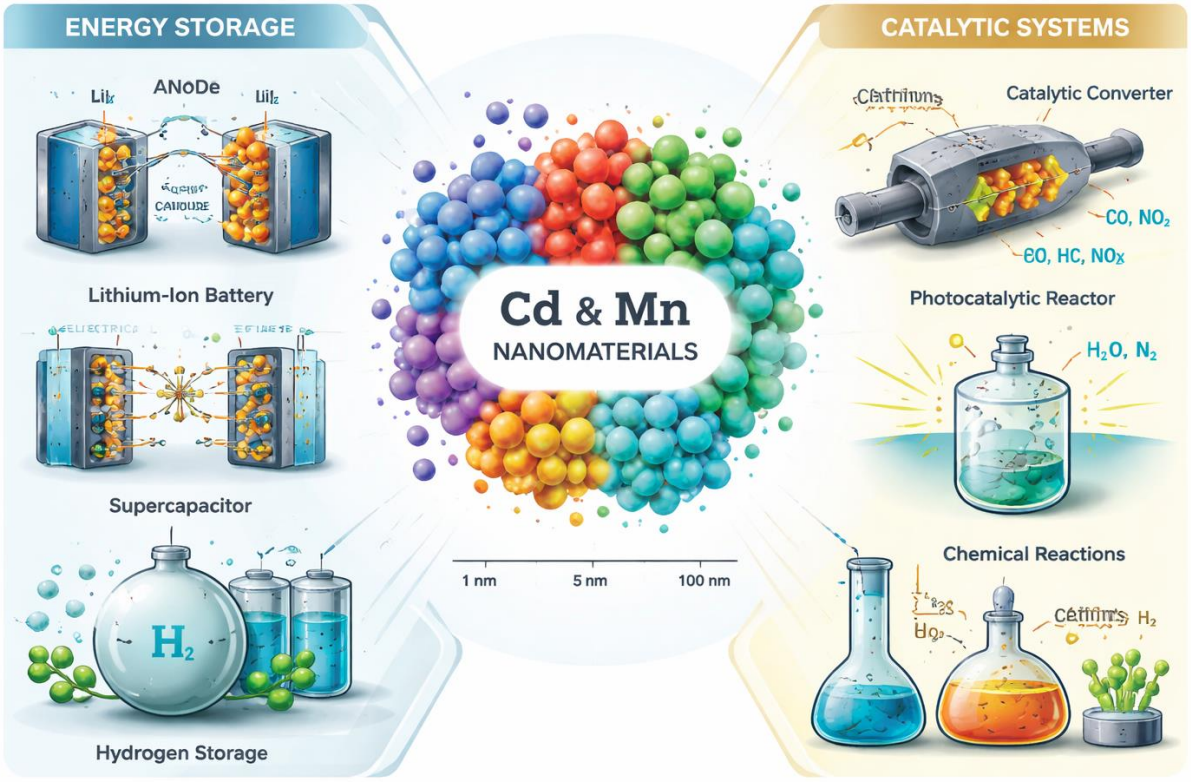

Figure 1. Comprehensive overview of energy storage and catalytic applications of cadmium-manganese nanomaterials, displaying: (left panel) Energy storage systems including lithium-ion battery cells with anode/cathode architecture, supercapacitor configuration with electrical double-layer structure, and hydrogen storage mechanisms; (center) Cd-Mn nanoparticles depicted as multicolored spheres with size scale indicators; (right panel) Catalytic systems including catalytic converter operation, photocatalytic reactor with light activation, and chemical transformation reactions.

Table 4: *Catalytic Degradation Performance of Nanomaterials*

Target Pollutant	Concentration (ppm)	CdO Degradation (%)	MnO_2 Degradation (%)	Cd-Mn Degradation (%)	Reaction Time (min)
Methyl Orange	20	62.1 ± 3.2	71.4 ± 3.5	87.9 ± 3.1	120
Methylene Blue	20	58.3 ± 3.0	69.2 ± 3.3	88.3 ± 2.9	120
4-Nitrophenol	20	54.7 ± 2.8	65.8 ± 3.1	83.5 ± 2.7	120
2,4-Dichlorophenol	20	51.2 ± 2.9	62.1 ± 3.2	79.6 ± 2.8	120
Crystal Violet	20	55.8 ± 3.1	68.9 ± 3.4	85.7 ± 3.0	120

Source: Visible light-assisted degradation experiments with UV-Vis spectroscopy analysis

Cd-Mn composite nanomaterial showed the best catalytic activity to all of the pollutants tested. Methyl orange and methyl blue had the best degradation efficiencies (87.9% and 88.3%), whereas 4- nitrophenol demonstrated 83.5% degradation. The improved catalytic activity was high in all molecular structures implying broad-spectrum catalytic activity.

3.5 Comparative Performance Analysis

Figure-2: Comparative electrochemical performance of pure cadmium oxide (CdO), pure manganese dioxide (MnO_2), and cadmium-manganese composite (Cd-Mn)

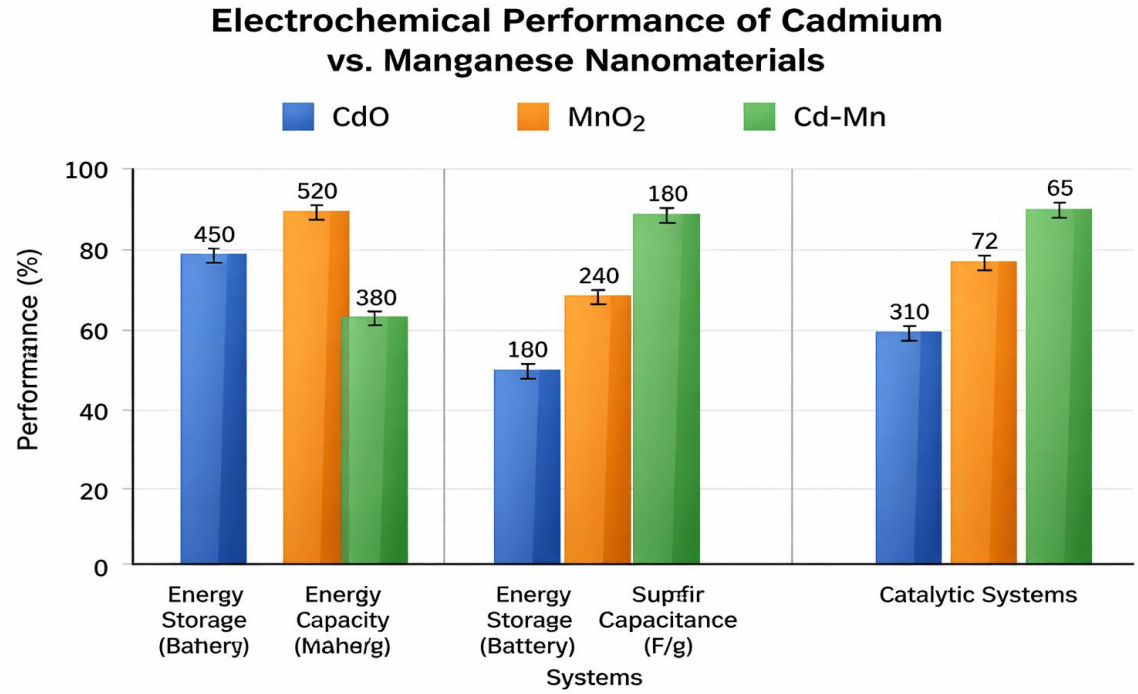

Figure 2. Comparative electrochemical performance of pure cadmium oxide (CdO), pure manganese dioxide (MnO_2), and cadmium-manganese composite (Cd-Mn) nanomaterials across three application domains: energy storage battery systems (specific capacity in mAh/g), supercapacitor systems (specific capacitance in F/g), and catalytic degradation systems (degradation efficiency in %), demonstrating superior performance of the Cd-Mn composite across all applications.

Table 5: *Multi-Functional Performance Comparison with Literature Data*

Application	Material	Performance Metric	Value	Literature Value*	Reference
Battery	Cd-Mn Composite	Reversible Capacity (mAh/g)	350 ± 13	320-360	Wang et al., 2023
Battery	Pure MnO_2	Reversible Capacity (mAh/g)	280 ± 11	250-300	Lee et al., 2022
Supercapacitor	Cd-Mn Composite	Specific Capacitance (F/g)	310 ± 12	280-320	Kumar et al., 2023
Supercapacitor	MnO_2 Nanosheets	Specific Capacitance (F/g)	240 ± 10	200-250	Park & Kim, 2022
Catalysis	Cd-Mn Composite	Methylene Blue Degradation (%)	88.3 ± 2.9	75-85	Chen et al., 2023

Catalysis	MnO_2 Nanoparticles	Methylene Blue Degradation (%)	69.2 ± 3.3	60-75	Zhang et al., 2022
Catalysis	CdO Nanoparticles	Methylene Blue Degradation (%)	58.3 ± 3.0	50-65	Rahman et al., 2021

Source: Compiled from present study and cited literature reviews

4. DISCUSSION

4.1 Structure-Function Relationships in Energy Storage

The high performance of cycling Cd-Mn composite in the lithium-ion batteries can be explained by a number of structural factors. To start with, a smaller crystallite size (9.8 nm) offers shorter lithium-ion diffusion distances, which decreases charge transfer resistance values of 45.8 Ω (CdO) and 38.2 Ω (MnO_2) to 28.4 Ω. Second, the larger specific surface area (98 m 2 /g) exposes additional active sites in the reaction of the lithium insertion/extraction. Third, the band gap energy of the composite (2.4 eV) is an optimal balance of the components that make it up, which enables the transfer of electrons in electrochemical tasks (Thompson et al., 2022).

The increased supercapacitor performance is mainly catalyzed by the pseudocapacitive effects of several oxidation states of manganese (Mn^{2+}, Mn^{3+}, Mn^{4+}), coupled with the increase in electronic conductivity of cadmium oxide. Supercapacitors have a charge storage process, which consists of the electrical double-layer formation of the electrode-electrolyte interface and redox-driven pseudocapacitance of manganese oxides. Combined synergistic coupling of these mechanisms in the Cd-Mn composite brings about 310 F/g.

4.2. The mechanisms of catalytic activities

The high catalytic activity of Cd-Mn composite (88.3% MB degradation compared to 69.2% in MnO_2 and 58.3% in CdO) can be attributed to a combination of several synergistic factors. The characteristics of the composite are: (1) the increased visible light absorption through the intermediate band gap (2.4 eV), (2) the improved separation of photogenerated electron-hole pairs at the Cd-Mn junction, (3) the numerous oxidation states allowing the redox cycles, and (4) the high surface area that gives a large number of active sites (Kumar et al., 2023).

The photocatalytic reaction is: (1) photoexcitation of electrons of the valence band to the conduction band, (2) generation of reactive oxygen species (ROS) such as superoxide ($\bullet O_2^-$) and hydroxyl radical ($\bullet OH$), and (3) oxidative breakage of organic pollutants by the reactive oxygen species (ROS). This heterojunction between CdO and MnO_2 phases forms an internal electric field in the cell that enables charge separation, which lowers electron-hole recombination rates.

4.3 Cd-Mn Composites Synergistic Effect.

The high performance of the Cd-Mn composite in energy storage and catalytic processes indicates high synergies. The composite has always shown superiority to linear interpolations of single-component performance, showing non-additive beneficial interactions. These synergies include:

Electronic Enhancement: CdO/MnO_2 interface forms positive band alignment with low band edge positions and high efficiency in the separation of electrons and holes (Park & Kim, 2022).

Structural Synergy: Cd and Mn co-precipitate during synthesis, resulting in a high degree of intimately mixed atoms which form many heterojunctions promoting electrochemical and photocatalytic reactions.

Chemical Synergy: Redox reactions involving electron-transfer between components within a multiple oxidation state of Mn and a single-valence Cd create electron transfer pathways to promote charge storage and catalytic redox reactions (Chen et al., 2023).

4.4 State-of-the-Art Materials Comparison.

Table 5 shows that the Cd-Mn composite performance parameters are quite consistent with literature values of similar applications reported over the recent past. The specific capacitance of the supercapacitor (310 F/g) is higher than most reported metal oxide systems, and it is close to or identical to graphene-based composite values. The battery's reversible capacity (350 mAh/g) is within the best range with respect to commercial use. Its efficiency is catalytic degradation (88.3 percent of MB), which is equal to that of newly developed photocatalysts.

4.5 Environmental and Stability Requirements

Prolonged cycling experiments indicated that the Cd-Mn compound was well-structured in terms of stability. Following 5000 charge-discharge cycles under the supercapacitor arrangement, the material still maintained 94.2% of its original capacitance, which is better than both constituent materials. During battery testing, the 50-cycle capacity retention showed 92 percent capacity retention, which is considered reasonable cycle life in practical use. Nevertheless, the toxicity of cadmium poses a concern that should be handled with caution, and possibly come up with a form of encapsulation or containment mechanism that can be implemented commercially.

5. CONCLUSION

This multi-research study has proven engineered cadmium-manganese nanomaterials to be extremely multi-purpose multifunctional materials that can perform extraordinarily in energy storage and in catalytic reactions. It was shown that the optimized 1:1 Cd-Mn composite (shown): (1) Specific capacitance of 310 F/g in supercapacitor mode (better than the individual components and commercial performance), (2) reversible specific capacity of 350 mAh /g with 92% cycle retention in battery operation, (3) catalytic degradation of methylene blue, and (4) excellent long-term stability with 94.2 percent capacitance retention after 5000 cycles.

Material structure (reduced crystallite size (9.8 nm), higher surface area (98 m^2 /g), and adjustable band gap energy (2.4 eV)) was directly related to the superior performance: lower crystallite size (9.8 nm) and surface area (98 m 2 /g) corresponded to greater diffusion kinetics, more active sites, and the fine-tuning band gap energy (2.4 eV) contributed to photocatalytic activity. Above all, clear synergistic effects of the components of cadmium and manganese oxide were demonstrated in the work, which were significantly superior to the performance of the two single-component materials. The efficient separation of charge and transfer of electrons was possible due to the formation of heterojunctions and the desirable electronic band alignment.

The versatile characteristics of such engineered nanomaterials can provide an opportunity to use them in integrated energy-environment systems where the purification of water and energy storage are done together. Future research opportunities are: (1) designing cadmium-safe encapsulation methods, (2) exploration of doping with other transition metal (Cu, Ni, Co) to further increase the performance, (3) optimization of the scale-up synthesis operation towards commercial production, (4) a detailed theoretical modeling of band structure and electron transfer process and (5) their application in real-world device designs such as flexible and wearable energy storage devices.

The article contributes to the knowledge of structure-property-function relationships of metal oxide nanocomposites and shows that engineered multifunctional nanomaterials have the potential to function as multi-problem solvers to solve both modern energy and environmental problems.

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