Electronic Supplementary Information

Ag:BiVO₄ dendritic Hybrid-architecture for High Energy Density Symmetric Supercapacitors

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Experimental:

Synthesis of Ag:BiVO₄ nanostructures:

Bismuth (III) nitrate [Bi(NO₃)₃⋅5H₂O], Ammonium metavanadate [NH₄VO₄] (Qualigen Chemicals Limited), Silver nitrate AgNO₃ (SD Fine Chemicals Limited), Ammonia NH₃ (Qualigen Chemicals Limited) and Nitric acid HNO₃ (Fisher Scientific), Ethanol C₂H₅OH (JEBSEN & JESSEN gmbH & Co. Germany) were used as starting materials. All the chemicals were of AR grade and were used without any further purification.

BiVO₄, Ag:BiVO₄ nanostructures were synthesized by facile solvothermal method. In a typical procedure, initially a mixed solvent was prepared using 5 ml HNO₃, 5 ml C₂H₅OH and 65 ml H₂O. Subsequently, 2.5 mmol of Bi (NO₃)₃⋅5H₂O and 2.5 mmol of NH₄VO₄ were dissolved separately in each of 35 ml of as prepared solvent. The two solutions were mixed at room temperature under vigorous magnetic stirring and maintained at pH=7 by addition of NH₃. Furthermore, the solution of Ag (1 wt. %) was added dropwise and stirred for 10 min. After being cooled to room temperature naturally, the precipitate was collected and washed with distilled water and ethanol thoroughly, dried at 60°C for 4 h and used for further characterization. For comparison pure BiVO₄ was also prepared were prepared by same method except use of C₂H₅OH in solvent system.

Materials Characterization:

The phase analysis of the samples were performed by X-ray diffraction (XRD) on a Rigaku-Ultima III with CuKα radiation (λ = 1.5418 Å). The surface morphology of as-prepared samples were investigated using the field-emission scanning electron microscopy (FEI Quanta
650F Environmental SEM) attached with an energy-dispersive X-ray spectroscopy (EDS) analyzer to measure the sample composition. Microstructure investigation was conducted using field emission transmission electron microscopy with a JEOL JSM 2200 FS microscope operating at 200 kV.

**Electrochemical measurements**

In order to check the electrochemical performances, the working electrodes were prepared by using Doctor Blade method. For this, 85 % of active material (Ag:BiVO$_4$) was mixed with 10 % PVDF as binder and 5 % acetylene black. A few drops of N-Methyl-2-pyrrolidone (NMP, solvent) were added and the mixture was homogenized using a mortar to get a uniform paste. Finally, the paste was applied on commercial flexible carbon cloth which was further used as SCs electrodes. The resultant thin films were then annealed at 180 °C for two hours in order to remove the binder. The typical mass loading of the electrode material was around 0.5-0.9 mg/cm$^2$. The electrochemical properties were measured using standard three electrode system which contain working electrodes (BiVO$_4$ and Ag:BiVO$_4$), counter electrode (platinum) and reference electrode (Ag/AgCl) in 6 M KOH electrolyte. Symmetric cell was constructed in a 3-way Teflon Swagelok cell using two identical electrodes of Ag:BiVO$_4$ with polypropylene separator sandwiched between them and few drops of 6 M KOH electrolyte. Two channels from potentiostat were connected together in such a way that one channel records voltage between two electrodes (positive and negative) and other channel records potential contributed from positive and negative electrodes with respect to reference electrode. All electrochemical measurements (cyclic voltammetry (CV) and galvanostatic charge-discharge techniques) were carried out using a Biologic VMP3 potentiostat.
**Supporting information S. I. 2**

Reaction and growth mechanism for Ag:BiVO₄ nano-architecture formation

The evolution of well-defined dendrite morphology via hydrothermal route invites the discussion for reaction mechanism and formation mechanism in detail. The plausible reactions taking place in the Ag:BiVO₄ hybrid architecture are shown below,

\[
\text{Bi (NO}_3\text{)}_{\text{3.5H}_2\text{O} + \text{HNO}_3 + \text{H}_2\text{O} \rightarrow \text{BiONO}_3 + 3 \text{HNO}_3} \quad \text{....... (1)}
\]

\[
\text{Ag + NH}_3 \rightarrow \text{Ag (NH}_3\text{)}_2^+ \quad \text{....... (2)}
\]

\[
\text{NH}_4\text{VO}_3 + \text{BiONO}_3 + \text{Ag (NH}_3\text{)}_2^+ + \text{H}_2\text{O} \rightarrow \text{Ag:BiVO}_4 + \text{NH}_3 + \text{HNO}_3 \quad \text{....... (3)}
\]

In a present chemical reaction, the bismuth cations and vanadium anions are provided by the hydration of BiNO₃·5H₂O and NH₄VO₃, respectively. Initially, the hydrolysis of Bi(NO₃)₃·5H₂O takes place and form a soluble BiONO₃ which readily react with VO₃⁻ ions at Ph ~ 6-7 forming pale yellow precipitate of tetragonal BiVO₄. During hydrothermal treatment, after getting sufficient thermal energy, the generated BiVO₄ nuclei aggregates and converted to highly crystalline form of monoclinic BiVO₄ crystals. Meanwhile, the addition of Ag into the reaction medium produces Ag (NH₃)₂⁺ complex on reaction with NH₃.¹ The formed Ag (NH₃)₂⁺ complex ions takes sufficient thermal energy to drive-reach the surface of BiVO₄ sites wherein gets reduced to Ag by ethanol under high temperature and pressure conditions.¹² It is expected that simultaneous nucleation of BiVO₄ and Ag might occur which further grow according to self assembly and Ostwald ripening mechanism. It is known that a higher monomer (precursor) concentration in solution generally favors 1D growth whereas the lower monomer concentration favors 3D growth.³ In the present case, the hydrothermal reaction system with relatively lower reactant concentration, sufficient temperature (180 °C) and optimum pH (= 7)
value provides higher chemical potential, and faster ion movement, thereby resulting in formation Ag:BiVO$_4$ hybrid dendritic structures. It is noteworthy that the proper growth of dendrites was observed for Ag:BiVO$_4$ compared to pure BiVO$_4$ sample which might be due to effect of addition of C$_2$H$_5$OH as a reducing agent in solvent system, playing a key role on facilitating crystal growth and tailoring the morphology.

From morphology evolution point of view, initially, primary particles starts to aggregate to minimize surface energy, offering driving force for self assembly. The self assembly proceeds by the rotation of particles via Brownian motion and short-range interaction between the particles, causing formation of smaller branches (rod like) that act as building blocks for dendrites. Furthermore, due to prolonged reaction time (24 h) the continuous growth of larger particles are occurred at expense of smaller particles known as Ostwald ripening to form larger subunits or branches to adjust it to achieve a minimum total surface free energy.$^3$ It is presumed that the an isotropic growth of formed branches along [001] direction is responsible for formation of 3D hierarchical BiVO$_4$ dendritic structures.$^4$ Thereby, the obtained Ag:BiVO$_4$ dendritic structures preserves several key features of interlinked connectivity through branched surfaces, propound effect of Ag nanocrystals, improved surface properties and stability. Therefore it really sense to examine the performance of this kind of material for energy application.
Fig. S.I. 3 FESEM images of Ag:BiVO$_4$ with different magnifications
Fig. S.I. 4 FETEM images of Ag:BiVO$_4$ with different magnification
Supporting information S.I. 5

Fig. S. I. 5 Cyclic voltammetry (CV) curves of (a) BiVO₄ and (b) Ag:BiVO₄ electrodes at different scanning rates and Galvanostatic charge/discharge (CD) curves of (c) BiVO₄ and (d) Ag:BiVO₄ microstructures at different current densities.
Fig. S.I. 6 (a) depicts the cycle performance of BiVO₄ and Ag:BiVO₄ electrodes which showing excellent cycling stability with around 92% capacity retention after 4000 cycles. The impedance spectra were recorded in order to investigate the bulk solution resistance ($R_e$), charge transfer resistance ($R_{ct}$), and Warburg resistance ($Z_w$) of as synthesized electrode materials. Fig. S.I.6 (b)
displays the Nyquist plots of impedance spectra of the BiVO₄ and Ag-BiVO₄ with inset showing the equivalent circuit diagram of Nyquist plots. Both the plots showed similar behavior in terms of curve shape (semicircle) except change in the resistance value. The obtained semi circles are due to charge transfer resistance ($R_{ct}$) which represents how fast the charge transfer takes place at electrode-electrolyte interface. The comparatively lower value of charge transfer resistance ($R_{ct}$) indicates the improved charge transfer in Ag:BiVO₄ hybrid architecture. Further, the small ($R_e$) value reveals good electrical conductivity of Ag:BiVO₄ compared to pristine BiVO₄ electrode. This proves that the synergetic effect between Ag and BiVO₄ hybrid plays a key role for improving the electrochemical properties by facilitating electronic conduction as well as charge discharge processes. All these results directly reveal the feasibility of using Ag:BiVO₄ as a negative electrode for high performance supercapacitor device.
The cell (device) capacitance ($C$) and volumetric capacitance of the symmetric devices were calculated from their CVs according to the following equation:

$$C_{\text{cell}} = \frac{Q}{\Delta V} \quad \text{......(1)}$$

$$C_A = \frac{Q}{A \times \Delta V} \quad \text{ ...... (2)}$$

where, $C_A$ and $C_V$ are areal and volumetric capacitances, respectively. $Q(C)$ is the average charge during the charging and discharging process, $V$ is the volume (cm$^3$) of the whole device (The area and thickness of our symmetric cells is about $0.785$ cm$^2$ (Area, $A=\pi r^2$, $3.14 \times (0.5)^2$) and $0.088$ cm. Hence, the whole volume of device is about $0.069$ cm$^3$, $\Delta V$ ($V$) is the voltage window. It is worth mentioning that the volumetric capacitances were calculated taking into account the volume of the device stack. This includes the active material, the flexible substrate and the separator with electrolyte.

Alternatively, the cell capacitance ($C_{\text{cell}}$), areal ($C_A$) and volumetric ($C_V$) capacitance of the electrode ($C_V$) was estimated from the slope of the discharge curve using the following equations:

$$C_{\text{cell}} = \frac{I x \Delta t}{\Delta V} \quad \text{...... (3)}$$

$$C_A = \frac{I x \Delta t}{A \times \Delta V} \quad \text{and} \quad C_V = \frac{I x \Delta t}{V \times \Delta V} \quad \text{...... (4)}$$
Where \( I \) is the applied current, \( V \) is the volume (cm\(^3\)) of the whole device (the whole volume of our device is about 0.069 cm\(^3\)), \( \Delta t \) is the discharging time, \( \Delta V \) (V) is the voltage window. Volumetric energy \( (E, \text{Wh/cm}^3) \) and power density \( (P, \text{W/cm}) \) of the devices were obtained from the following equations:

\[
E = \frac{1}{2 \times 3600 CV \Delta V^2}
\]

\[
P = \frac{3600 x E}{\Delta t}
\]

where \( E \) (Wh/cm\(^3\)) is the energy density, \( CV \) is the volumetric capacitance obtained from Equation (5) and \( \Delta V \) (V) is the voltage window, \( P \) (W/cm\(^3\)) is the power density.
Fig. S.I. 8 Variation of Volumetric capacitance and Areal capacitance with current density of Ag:BiVO$_4$/Ag:BiVO$_4$ symmetric supercapacitors
Table S1: Electrochemical properties of Ag:BiVO$_4$/Ag:BiVO$_4$ symmetric supercapacitors in 6 M KOH electrolyte

<table>
<thead>
<tr>
<th>Current density (A/g)</th>
<th>Discharge time (sec)</th>
<th>Capacitance</th>
<th>Specific energy</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Volumetric</td>
<td>Gravimetric</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(F/cm$^3$)</td>
<td>(F/g)</td>
</tr>
<tr>
<td>3.1</td>
<td>56.5</td>
<td>7.39</td>
<td>108.1</td>
</tr>
<tr>
<td>4.1</td>
<td>38.92</td>
<td>6.79</td>
<td>99.2</td>
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<tr>
<td>5.1</td>
<td>29.04</td>
<td>6.33</td>
<td>92.6</td>
</tr>
<tr>
<td>6.1</td>
<td>22.46</td>
<td>5.88</td>
<td>85.9</td>
</tr>
<tr>
<td>7.1</td>
<td>17.82</td>
<td>5.44</td>
<td>79.5</td>
</tr>
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</table>
Table S2: Comparison of Supercapacitor values of Transition Metal Oxide (TMOs) based electrodes

<table>
<thead>
<tr>
<th>Electrode</th>
<th>Device</th>
<th>Electrolyte</th>
<th>Volumetric capacitance</th>
<th>Max. Vol. Energy Density at power density</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag:BiVO₄</td>
<td>Symmetric</td>
<td>6M KOH</td>
<td>7.39 F/cm³</td>
<td>2.63 mWh cm⁻³ at 0.558 W cm⁻³</td>
<td>Present work</td>
</tr>
<tr>
<td>H-TiO₂ @MnO₂ //H-TiO₂@C</td>
<td>Asymmetric</td>
<td>5 M LiCl</td>
<td>0.68 F/cm³</td>
<td>0.30 mWh cm⁻³ at 0.23 W cm⁻³</td>
<td>5</td>
</tr>
<tr>
<td>Co₉S₈//Co₃O₄@RuO₂</td>
<td>Asymmetric</td>
<td>3M KOH</td>
<td>3.42 F/cm³</td>
<td>1.21 mWh cm⁻³ at 13.29 W cm⁻³</td>
<td>6</td>
</tr>
<tr>
<td>VO₄//VN</td>
<td>Asymmetric</td>
<td>5M LiCl electrolyte</td>
<td>1.35 F/cm³</td>
<td>0.61 mWh cm⁻³ at 0.85 W cm⁻³</td>
<td>7</td>
</tr>
<tr>
<td>MoS₂</td>
<td>Asymmetric</td>
<td>0.5 M Na₂SO₄</td>
<td>-</td>
<td>0.016 Wh cm⁻³ at 0.62 W cm⁻³</td>
<td>8</td>
</tr>
<tr>
<td>laser-scribed graphene(LSG) //LSG</td>
<td>Symmetric</td>
<td>1.0 M H₃PO₄</td>
<td>0.42 F/cm³</td>
<td>0.09 mWh cm⁻³ at 0.1 W cm⁻³</td>
<td>9</td>
</tr>
</tbody>
</table>
References:


