Supplementary Information

Low temperature pseudomorphic synthesis of nanocrystalline carbide aerogels for electrocatalysis

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Experimental details

Synthesis of carbide aerogels. The pseudomorphic transformation of polycrystalline TiC and NbC aerogels was carried out from carbon aerogels by a low-temperature carburization reaction. 200 mg of Ti powder (Sigma-Aldrich) was separated from 15 mg of carbon aerogel plates (1 mm thickness) and 40 mg of iodine, and placed in the two ends of a 4 inch-long quartz tube (0.5 inch diameter). The quartz tube was then evacuated to vacuum at ~0.67 Pa and flame sealed. The tube was then heated up to 800 °C and held at that temperature for 6 h, with the end of carbon aerogels at the center of a horizontal furnace. After cooling down, the quartz tube was cut open and products at carbon aerogels end were collected. The similar synthetic strategy for NbC aerogels was also taken.

Characterization. The morphology of samples was observed by a scanning electron microscopy (SEM, JSM6700F). TEM images were obtained on a transmission electron microscope (TEM, JEOL JEM-2010) operated at 200 kV. Samples were dispersed in ethanol and deposited onto copper grids coated with an amorphous carbon film. Powder X-ray diffraction (XRD) patterns were collected on a Rigaku D/Max-RB diffractometer with Cu Kα radiation (λ=1.5418 Å, 40 kV, 100 mA). Raman spectroscopy was performed with a micro-Raman system (Jobin Yvon LabRAM HR800) at room temperature, using an Ar+ laser (514.5 nm, 25 mW) for the excitation. Nitrogen sorption isotherms were obtained at 77 K (Quantachrome Autosorb-iQ analyzer) after vacuum degassing of samples at 150 °C for 24 h. Values of specific surface area were obtained using the Brunauer-Emmett-Teller (BET) method. The nonlocal density functional theory (NLDFT) was applied to obtain pore size distributions. The total pore volume was evaluated by the single-point method using the adsorbed amount of nitrogen at a relative pressure p/p0 of 0.99.
**Electrode fabrication.** In the preparation process of DSSCs, TiO$_2$ photoanodes with the effective area of 0.3×0.3 cm$^2$ were immersed overnight in 0.3 mM ethanolic solution of dye N-719 (Solaronix) at room temperature, then taken out and rinsed with ethanol to remove excess dye adsorbed, and dried in air at room temperature. The carbide aerogel CEs were prepared as follows: 10 mg of the carbides were ultrasonically dispersed in 1 mL of isopropanol for 30 min. The prepared pastes were sprayed onto FTO glass and sintered under argon atmosphere at 500 °C for 20 min. The carbide catalyst layer thickness was ~1μm and the active area of carbide electrodes was 0.5 cm$^2$. The sandwich-type solar cells were assembled by placing the CEs on the N-719 dye-sensitized photoelectrodes and clipped together as an open cell. The cell was then filled with a liquid electrolyte composed of 0.1 M anhydrous LiI, 0.12 M I$_2$, 1.0 M DMPII, and 0.5 M tert-butyapyridine in dehydrated acetonitrile by capillary force. In the HER experiments, a commercial Pt/C (20 wt %, E-TEK) and a saturated calomel electrode (SCE) were used as counter and reference electrodes, respectively. The working electrode was prepared on a glass carbon (GC) electrode. Typically, a mixture containing 5.0 mg carbide catalysts, 1 mL ethanol and 0.03 mL Nafion solution (0.05 wt%, Sigma-Aldrich) was ultrasonicated for 15 min to obtain a well-dispersed ink. Then 10μL of ink was dropped onto a glassy carbon electrode of 3 mm in diameter and dried at 100 °C in vacuum.

**Measurements.** Cyclic voltammetry (CV) and Tafel polarization measurements were carried out with an electrochemical workstation system (CHI630, Chenhua, Shanghai) in a three-electrode system in an argon-purged acetonitrile solution of 0.1 M LiClO$_4$, 10 mM LiI, and 1 mM I$_2$ at a scan rate of 10 mV/s. Platinum served as a counter electrode, and the Ag/Ag$^+$ couple was used as a reference electrode. Electrochemical impedance spectroscopy (EIS) was performed in the dark using an impedance measurement unit (ZAHNER-elektrik IM6) in the frequency range of 0.1-10$^5$ Hz with ac amplitude of 10 mV. The photocurrent-voltage (J-V) measurements were taken on a digital source meter (Keithley 2400, computer-controlled) with the device under simulated AM 1.5 illumination (Newport solar simulator, Oriel class A, SP91160A, USA). The light power density was calibrated against a Si-based reference cell (Hamamatsu S1133) to accurately simulate the full-sun intensity (100 mW/cm$^2$). In HER experiments, linear sweep voltammetry with scan rate of 5 mV/s was conducted in 0.5 M H$_2$SO$_4$, the electrolyte solutions were purged with argon for 20 min prior to the experiments in order to remove oxygen. The potentials of working electrodes were referenced to a reversible hydrogen electrode (RHE) by adding a value of (0.241+ 0.059) V.
Table S1 Photovoltaic and electrochemical parameters for DSSCs with various counter electrodes

<table>
<thead>
<tr>
<th>CE</th>
<th>$V_{oc}$(V)</th>
<th>$J_{sc}$(mA/cm$^2$)</th>
<th>FF</th>
<th>PCE(%)</th>
<th>$R_s$(Ω)</th>
<th>$R_{ct}$(Ω)</th>
<th>CPE(μF)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiC</td>
<td>0.71</td>
<td>14.02</td>
<td>0.60</td>
<td>6.10</td>
<td>45</td>
<td>34</td>
<td>212</td>
</tr>
<tr>
<td>NbC</td>
<td>0.72</td>
<td>12.89</td>
<td>0.44</td>
<td>4.10</td>
<td>48</td>
<td>206</td>
<td>25</td>
</tr>
<tr>
<td>C</td>
<td>0.70</td>
<td>7.81</td>
<td>0.26</td>
<td>1.42</td>
<td>51</td>
<td>1100</td>
<td>9</td>
</tr>
<tr>
<td>Pt</td>
<td>0.72</td>
<td>14.31</td>
<td>0.63</td>
<td>6.55</td>
<td>47</td>
<td>37</td>
<td>37</td>
</tr>
</tbody>
</table>

$J_{sc}$: short-circuit current density; $V_{oc}$: open-circuit voltage; FF: fill factor; PCE: power conversion efficiency; $R_s$: series resistance; $R_{ct}$: charge-transfer resistance at the CE/electrolyte interface; CPE: constant phase angle element.
**Fig. S1** XRD patterns of TiC aerogels after reaction from 600 °C to 900 °C for 6h.

**Fig. S2** TEM images(a), SAED patterns (inset in a) and XRD patterns (b) of TiC/C composite aerogels after reaction at 550 °C for 24h.
Fig. S3 Equivalent circuit diagram used in EIS measurements.

Fig. S4 Electrocatalytic properties of TiC and NbC aerogel catalysts for hydrogen evolution reaction (HER). (a) Polarization curves, (b) Tafel plots.