Electronic Supplementary Information

**Novel Synthesis of Dual-Suspended Architectures between Si-pillars for Enhanced Photocatalytic Performance**

Yu Sun, a Rui Chen, b Jihyeon Oh, a Bongyoung Yoo, a and Haiwon Lee a,b

**1. Materials**

Mo solution (ICP/DCP standard solution), cupric acetate, and sodium acetate powder from Aldrich Chemical Co., copper nitrate trihydrate (Cu(NO\(_3\))\(_2\)•3H\(_2\)O), Iron(III) nitrate nonahydrate, (Fe(NO\(_3\))\(_3\)•9H\(_2\)O), ethanol, hydrogen peroxide (30%), sulfuric acid (98%), from Dae-Jung Chemical were used without further purification. All solvents were prepared by using DI water.

**2. Preparation of Si pillar arrays (Si\(_p\))**

The Si pillar array was fabricated on a doped n-type Si (100) substrate by using a general photolithography technique which included a deep Si etching process (SLR-770-10R-B, Plasma Thermo Co.). In order to clean and modify the surface of Si pillar array with hydroxyl groups, the substrate was soaked in a piranha solution (H\(_2\)SO\(_4\): H\(_2\)O\(_2\) = 3: 1, Vol/Vol) for 30 min. The Si pillar substrate was then washed repeatedly by de-ionized (DI) water to remove the piranha solution from the substrate. The failed samples shown in Figure 1(D) were fabricated by p-type Si(111).

<table>
<thead>
<tr>
<th>dopant</th>
<th>Resistance (ohm-cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-type Si(100)</td>
<td>Phosphorus</td>
</tr>
<tr>
<td>p-type Si(100)</td>
<td>Boron</td>
</tr>
</tbody>
</table>

**3. Formation of CNTs networks bridging between Si pillars (CNT-Si\(_p\))**

A catalyst solution was prepared by ultrasonication using Fe(NO\(_3\))\(_3\)•9H\(_2\)O , Mo solution, and an ethanol solvent. The molar ratio of Fe/Mo in the catalyst solution was 7/1. To form the Fe-Mo catalyst nanoparticles on the Si pillar arrays, the substrate was soaked in the Fe-Mo catalyst solution for 60 minutes, and then fully rinsed with ethanol. As a result, Fe-Mo catalyst nanoparticles were uniformly formed on the entire surface area of the Si pillar arrays. The CNTs was synthesized in a horizontal quartz tube reactor using low pressure thermal chemical vapor deposition (LPTCVD). The diameter and the length of the reactor are 40 and 800 mm,
respectively. The substrate was inserted into the center of the reactor. After the thermal annealing at 400 °C for 30 min in air at ambient pressure, the reactor was pumped down to a pressure lower than \(\sim 9.0 \times 10^{-3}\) Torr and heated up to 800 °C. When the temperature of the reactor reached 800 °C, 300 sccm of NH\(_3\) gas was introduced into the reactor for 10 min to reduce the iron oxide to the iron catalyst. After the NH\(_3\) pretreatment, 10 sccm of C\(_2\)H\(_2\) gas was introduced for 20 min to synthesize CNTs while maintaining a pressure of 3.3 \(\times 10^{-1}\) Torr. Finally, the reactor was cooled down to room temperature under a pressure of 9.0 \(\times 10^{-3}\) Torr. The sample is named as CNT-Si\(_P\).

4. Formation of suspended cuprous oxide structures (Cu-CNT-Si\(_P\))

To synthesize suspended Cu\(_2\)O architecture penetrated by CNT networks, the pulse electrodeposition was conducted through potentiostat/galvanostat (WPG 100, Korea) at room temperature by employing Pt plate, standard Calomel electrode (SCE, BASi, USA), and CNT-Si\(_P\) as counter electrode, reference electrode, and working electrode, respectively. The electrolyte was prepared by dissolving 0.01 M cupric acetate and 0.1 M sodium acetate in DI water. The pulse electrodeposition was carried out at -400 mV with 1 s on-time and 10 s off-time for 60 s at room temperature.

5. Preparation of non-suspended Cuprous oxides on Si-pillar substrates (Cu-Si\(_P\))

To synthesize non-suspended Cu\(_2\)O on Si\(_P\), all procedures are as same as those for the preparation of Cu-CNT-Si\(_P\) except that no CNT networks were pre-synthesized between Si pillars, which mean that after the temperature of the reactor reached 800 °C, no NH\(_3\) and C\(_2\)H\(_2\) gas were purged inside the reactor. The SEM image of Cu-Si\(_P\) is shown in Figure S2.

6. Characterization

Powder X-ray diffraction data were collected on a Rigaku (D/MAX-2500/PC) diffractometer using Cu-K\(\alpha\) radiation (\(\lambda = 1.54056\) Å) at room temperature. SEM images were obtained by field-emission scanning electron microscopy (FE-SEM, TESCAN, MIRA3). To prepare the samples for transmittance electron microscopy (TEM, FEI Tecnai F30 Super-Twin), the as-prepared samples were sonicated for 10 min and the obtained powders after sonication were re-dispersed in pure water, dropped onto a holy carbon grid. Finally, the samples were dried at 50 °C in the oven. TEM images were obtained with incident electron beam energy of 100 kV. The chemical configurations were determined with X-ray photoelectron spectroscopy (XPS, ESCA2000), which was performed with an Al K\(\alpha\) and Mg K\(\alpha\) X-ray source. UV-visible spectra were obtained using a PerkinElmer Lamda 750 spectrometer with an integrating sphere detector in the wavelength range from 780-380 nm. The photocatalytic activity of samples was assessed by observing the degradation of MB dye under visible light (\(\lambda >400\) nm) irradiation, which was performed in a 250 mL glass beaker using a homemade irradiation system (a 100 W halogen lamp (HI-Spot 95), purchased from Osram Sylvania Inc., with a UV-stop feature equipped with a quartz cap of water to remove the infrared region of the lamp). The irradiation system was placed on top, 25 cm from
the glass beaker. The reaction slurry was prepared in a 150 mL capacity glass beaker by suspending three pieces of our samples (1cm * 2cm) in a 100 mL MB (10 ppm) aqueous solution under magnetic stirring. (Scheme S1) Prior to light irradiation, the solution was stirred for 60 min in dark to stabilize MB adsorption on the photocatalysts and on the surfaces of the glass beakers used for testing. At specific time intervals, 4 mL of the reaction slurry was withdrawn and centrifuged to obtain the MB residue solution. The electronic absorption changes of the MB solution were observed from its characteristic absorption peak at 664 nm.

Scheme 1: Illustration of photocatalytic reactions by employing three pieces of samples as photocatalysts, which were attached on the beaker wall by double-side tape.

Table 1: Weight for Cu-CNT-SiP

<table>
<thead>
<tr>
<th>No.</th>
<th>Weight Before Electrodeposition (mg)</th>
<th>Weight After Electrodeposition (mg)</th>
<th>Weight (mg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>402.03</td>
<td>402.335</td>
<td>0.305</td>
</tr>
<tr>
<td>2</td>
<td>381.612</td>
<td>381.941</td>
<td>0.329</td>
</tr>
<tr>
<td>3</td>
<td>405.383</td>
<td>405.717</td>
<td>0.334</td>
</tr>
</tbody>
</table>

The substrate for pulse electrodeposition is CNT-SiP.

The average loading amount of Cu2O for each Cu-CNT-SiP sample is 0.323 mg, which was measured by ultra-micro balance (Mettler Toledo XP6).
Figure S1 XPS analysis of Cu element for Cu-CNT-SiP (a) immediately after preparation and (b) placed in air for 1 month.
Figure S2 SEM image of Cu-SiP. Note: The preparation method of Cu-SiP is similar to that of Cu-CNT-SiP except the formation of CNT.
Figure S3 UV-vis absorption spectra showing the spectral degradation of MB dye as a function of time under visible light illumination by employing (A) Cu-CNT-SiP, (B) SiP, (C) CNT-SiP, and (D) Cu-SiP as catalysts.
Figure S4 Full X-ray diffraction patterns of (a) Si$_P$, (b) CNT-Si$_P$, and (c) Cu-CNT-Si$_P$. (hard to see clearly)
Figure S5 Full Raman spectra of (a) CNT-Siₚ and (b) Cu-CNT-Siₚ.