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High-Efficiency Synergistic Conversion of CO\textsubscript{2} to Methanol Using Fe\textsubscript{2}O\textsubscript{3} Nanotubes Modified with Double-Layer Cu\textsubscript{2}O Spheres

Peiqiang Li\textsuperscript{1}, Hua Jing, Jinfeng Xu, Chenxiao Wu, Hui Peng, Jing Lu, Fusui Lu\textsuperscript{*}

Cuprous oxide/hematite nanotubes (Cu\textsubscript{2}O/Fe\textsubscript{2}O\textsubscript{3}NTs) were prepared by the potentiostatic electrodeposited method in which different structured Cu\textsubscript{2}O materials were modified onto Fe\textsubscript{2}O\textsubscript{3} NTs surface. Among them, the material with double-layer Cu\textsubscript{2}O spheres (Cu\textsubscript{2}O/Fe\textsubscript{2}O\textsubscript{3}NTs-30) showed excellent photoelectrocatalytic (PEC) properties with a suitable energy band gap (1.96 eV) and smaller overpotential (0.18 V). Furthermore, Cu\textsubscript{2}O/Fe\textsubscript{2}O\textsubscript{3} NTs-30 showed two types of synergy in the PEC reduction of CO\textsubscript{2}: (i) between electrocatalysis and photocatalysis and (ii) between Cu\textsubscript{2}O and Fe\textsubscript{2}O\textsubscript{3}NTs. The faradaic efficiency and methanol yield reached 93% and 4.94 mmol L\textsuperscript{-1} cm\textsuperscript{-2} after 6 h, respectively.

Introduction

Carbon dioxide (CO\textsubscript{2}) released by burning fossil fuels is a primary cause of global warming; therefore, the capture and efficient use of CO\textsubscript{2} have become an important issue. Among all the possible solutions, the catalytic conversion CO\textsubscript{2} to hydrocarbon fuels is a crucial goal that may positively influence the global carbon balance. Recently, attempts have been made to utilize CO\textsubscript{2} as a natural resource, i.e., as a feedstock rather than a waste product requiring costly disposal, such as high temperature and high pressure\textsuperscript{3,2}. The photocatalytic (PC) reduction CO\textsubscript{2} proceeds under ambient temperature and pressure driven by solar energy, which is inexhaustible in supply and always available for use\textsuperscript{3,5}. However, the PC conversion efficiency of CO\textsubscript{2} to methanol (CH\textsubscript{3}OH) and other energy-rich compounds is generally low. One of the reasons is the low utilization of visible light caused by the width of the energy band gap of the semiconductor material unsuitable for this purpose.

Moreover, electrocatalytic (EC) function has also received extensive attention in the field of CO\textsubscript{2} reduction because of the possibility of applying renewable electrical energy as the driving force. Furthermore, EC function is also conducted under ambient temperature and pressure which can dramatically simplify and lower the cost of CO\textsubscript{2} conversion to fuel\textsuperscript{6-10}. An efficient catalyst should mediate the transfer of multiple electrons and protons to CO\textsubscript{2} at low overpotential, reduce CO\textsubscript{2} in the presence of H\textsubscript{2}O, and selectively afford one product. However, the EC reduction CO\textsubscript{2} suffers from one or more of the following problems: low energetic efficiency (i.e., large overpotential requirement), rapid loss of CO\textsubscript{2} reduction activity in favor of H\textsubscript{2}O reduction, and poor selectivity\textsuperscript{11,12}. To achieve a more efficient catalytic process, photoelectrocatalytic (PEC) processes have been studied using visible light-sensitive materials to convert CO\textsubscript{2} to small-molecule organic fuels\textsuperscript{13-17}. The first use of a photocatalyst, as a photocathode, for the PEC reduction CO\textsubscript{2} was reported over 30 years ago\textsuperscript{13}. Most of the researches about the PEC reduction of CO\textsubscript{2} involve electrically assisted photocatalysis\textsuperscript{14-16}. A small bias is added to the catalyst materials based on the PC reduction to effectively separate the photo-generated holes and electrons and achieved higher photoelectric conversion efficiency; however, the applied bias is too small to conduct the EC reduction independently. Previously, we reported photo-enhanced electrolysis\textsuperscript{17}, with efficient reduction efficiency. However, the light itself could not provide the desired PC function independently. Therefore, we combined EC and PC functions to achieve a synergistic function between them on the same catalytic surface.

To achieve a synergistic function between PC and EC, the selection of a catalyst is the key point, which requires that the catalyst not only matches the energy band for the PC reduction, but also matches the small overpotential for the EC reduction simultaneously. Among the available materials, hematite (Fe\textsubscript{2}O\textsubscript{3}) is an excellent semiconductor photocatalyst and has been widely investigated because it is environmentally benign, very abundant,
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Figure 1. (a), (b) Scanning electron microscope (SEM) images of CuO/Fe2O3 NTs at a deposition time of 30 min and Fe2O3 NTs. (inset of b: high-magnification SEM image of Figure 1b).

The Cu2O/Fe2O3 NTs were prepared by the simple and practical
topotentiostatic electrodeposition method. Figure 1a shows the SEM
image of the Cu2O/Fe2O3 NTs at a deposition time of 30 min; three
layers are clearly observed. The bottom layer is Fe2O3 NTs; the
amplified Fe2O3 NTs grew in situ as volcano shape (Figure 1b),
which distributed evenly on the surface. The inset of Figure 1b
demonstrates the changes in the morphology with the progress in
electrodeposition. Herein, Cu2O/Fe2O3 NTs-15, Cu2O/Fe2O3 NTs-
30, and Cu2O/Fe2O3 NTs-45 represent the Cu2O /Fe2O3 NTs with
the electrodeposition times of 15 min, 30 min, and 45 min, respectively.
First, it was a piece of iron, as shown in Scheme 1a.
During the electrochemical anodic oxidation treatment, Fe2O3 NTs
in situ grew on the iron plate (Scheme 1b), as shown in Figure 1b.
Then, using Fe2O3 NTs as the working electrode, potentiostatic
electrodeposition was conducted for 15 min, as shown in Scheme
1c. The Cu2O nanosphere layer was evenly distributed on the
surface of the Fe2O3 NTs. The scanning electron microscope (SEM)
image shows the existence of the Cu2O nanosphere layer (Figure
S1). When the deposition time reached 30 min, as shown in
Scheme 1d, bigger Cu2O spheres appeared and formed another
Cu2O layer, which was sparse and extremely regular. A significant
portion of the middle layer was exposed owing to the sparse upper
layer (Figure 1a). When the deposition time reached 45 min, the
Cu2O microspheres were significantly produced and distributed in
one layer (Scheme 1e), which was thicker than the middle Cu2O
layer and totally covered the other two (Figure S2). Among the
three different types of structures, Cu2O/Fe2O3 NTs-30 perhaps
showed the largest specific surface that had more active sites for
the catalytic reaction.

The best activity of Cu2O/Fe2O3 NTs-30 was proved by the
maximum absorption intensity for visible light (MAI-vis), energy
band gap ($E_g$), electrochemical impedance spectroscopy (EIS), and
the overpotential of EC reduction of CO2. As shown in Table 1, in

Results and Discussion

Scheme 1 shows the growth mechanism of the Cu2O/Fe2O3 NTs,
demonstrating the changes in the morphology with the progress in
electrodeposition. Herein, Cu2O/Fe2O3 NTs-15, Cu2O/Fe2O3 NTs-
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and inexpensive18-20. Different hematite-based hierarchical
nanoarchitectures have been developed, such as nanowires,
flowerlike, urchinlike, nanobelts, nanotubes, nanorods, elliptic
superstructures, and dendritic-micropipes21. Among them, Fe2O3
nanotubes (NTs) are extensively used as photocatalyst because of
its large surface area, efficient charge transferring capacity, high
active sites, and the low recombination of electron-hole pairs22.

The most important characteristic is that Fe2O3 has a narrow band
gap (2.2 eV) that can absorb light of wavelength shorter than 600
nm. However, the reduction of Fe2O3 is very weak for the positive
conduction band (0.28 eV)23.

To achieve suitable conduction and valence bands for the
catalytic reduction of CO2, cuprous oxide (Cu2O) was selected to
couple with Fe2O3 NTs. Cu2O is a widely used p-type metal-oxide
semiconductor, and its conduction band is located at -1.3 eV (vs.
normal hydrogen electrode (NHE)) more negative than that of
Fe2O3, resulting in a strong reductive efficiency. In theory, the
coupling of Cu2O to Fe2O3 may lead to excellent PC reduction
efficiency for CO2 owing to the matched energy band gap.
Moreover, Cu2O is an outstanding electrocatalyst because of its
great selectivity to CH3OH and excellent conductive ability24,25.

Therefore, it is expected that the combination of the two materials
may exhibit a great PEC performance.

In this study, several Cu2O/Fe2O3 NTs with different
morphologies were prepared by the potentiostatic electrodeposition
method in which Cu2O films were deposited onto the surface of
Fe2O3 NTs at different electrodeposition times. The as-prepared
materials were investigated by a series of photochemical and
electrochemical measurements, indicating that the Cu2O/Fe2O3
NTs at a deposition time of 30 min showed more excellent PEC
properties than the materials obtained at other deposition times.

Compared to Cu2O/Fe or Fe2O3 NTs, the Cu2O/Fe2O3NTs showed
superior PEC reduction performance for the efficient conversion of
CO2 to CH3OH. The faradaic efficiency and CH3OH yield reached
93% and 4.94 mmol L-1 cm2 after 6 h, respectively. The Cu2O/Fe2O3NTs material showed two types of synergistic function:
(i) between the two materials (Cu2O and Fe2O3) and (ii) between
the PC and EC functions. The research provided a new
methodology for the material design for the PEC reduction of CO2;
the PEC synergistic conversion of CO2 has a great environmental
and social significance.

Results and Discussion

Scheme 1 shows the growth mechanism of the Cu2O/Fe2O3 NTs,
demonstrating the changes in the morphology with the progress in
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the overpotential of EC reduction of CO2. As shown in Table 1, in
In terms of the photochemical properties, the $E_g$ was obtained after a series of calculations from the UV-visible absorption spectrum.  The Cu$_2$O/Fe$_2$O$_3$ NTs-15, Cu$_2$O/Fe$_2$O$_3$ NTs-30, Cu$_2$O/Fe$_2$O$_3$ NTs-45 were found to have similar $E_g$ value ($\sim$1.96 eV), indicating that the Cu$_2$O-loading had no obvious effect on $E_g$. However, Cu$_2$O/Fe$_2$O$_3$ NTs-30 with the highest value of MAI-vis indicated that the material possessed the highest utilization efficiency for visible light and may possess better PC properties than the others.

In terms of electrochemical properties, Cu$_2$O/Fe$_2$O$_3$ NTs-30 had the smallest EIS, indicating that this type of structure possessed the highest electron transfer efficiency, and it may favor the catalytic reduction of CO$_2$. Furthermore, the lowest overpotential (0.26 V) of Cu$_2$O/Fe$_2$O$_3$ NTs-30 indeed proved that the target material showed the best EC reduction performance for CO$_2$. In the PEC process, Cu$_2$O/Fe$_2$O$_3$ NTs-30 has the largest CH$_3$OH yield than the other electrodeposited time. In summary, Cu$_2$O/Fe$_2$O$_3$ NTs-30 exhibited not only the best photochemical performance, but also the best electrochemical performance than the other materials obtained at different deposition times. Therefore, we further studied Cu$_2$O/Fe$_2$O$_3$ NTs-30.

### Table 1. Optical and Electrical properties of Cu$_2$O/Fe$_2$O$_3$ NTs prepared at different electrodeposition times.

<table>
<thead>
<tr>
<th>Photochemical properties</th>
<th>Electrochemical properties</th>
<th>PEC 6 h</th>
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<tbody>
<tr>
<td>MAI-vis (a.u.)</td>
<td>$E_g$ (eV)</td>
<td>EIS (ohm)</td>
</tr>
<tr>
<td>0 min</td>
<td>1.246</td>
<td>2.03</td>
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<tr>
<td>15 min</td>
<td>0.935</td>
<td>1.97</td>
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<tr>
<td>30 min</td>
<td>1.262</td>
<td>1.96</td>
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<tr>
<td>45 min</td>
<td>1.028</td>
<td>1.96</td>
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First, the crystal structures of the as-prepared materials were analyzed by X-ray diffraction (XRD). As shown in the XRD spectra (Figure 2a), the diffraction peaks are strong and sharp, indicating good crystallization. The major strong characteristic peaks of Fe$_2$O$_3$ NTs appeared at 20 of 24.19°, 30.27°, 33.31°, 35.61°, 43.5°, 49.44°, 54.25°, 57.1°, 62.64°, and 65.2°, corresponding to the crystal faces of (012), (206), (104), (110), (113), (024), (116), (112), (214), and (300), respectively. Its lattice parameters of $a = 5.0491$ Å and $c = 13.6577$ Å, matched well with JCPDS, No. 33-0664 of standard α-Fe$_2$O$_3$ sample, indicating that the sample was indeed α-Fe$_2$O$_3$. The major strong characteristic peaks of Cu$_2$O/Fe$_2$O$_3$ NTs-30 and Cu$_2$O/Fe appeared at 20 of 36.72°, 43.41°, 61.75°, and 74.33°, corresponding to the crystal faces of (111), (200), (220), and (311), respectively. Its lattice parameters, $a = b = c = 4.260$ Å, matched well with JCPDS card (No. 65-3288) of Cu$_2$O. After Cu$_2$O was loaded on Fe$_2$O$_3$ NTs, the peaks of Fe$_2$O$_3$ NTs weakened or even disappeared as a result of almost complete coverage of the Cu$_2$O on the surface of Fe$_2$O$_3$ NTs, which also agreed well with the SEM image (Figure 1a).
spectroscopy (XPS) spectrum of Cu$_2$O/Fe$_2$O$_3$ NTs-30 and the corresponding high-resolution XPS spectra of Cu$_{2p}$ (c), Fe$_{2p}$ (d). NTs = nanotubes.

Figure 2b shows the X-ray photoelectron spectroscopy (XPS) spectrum of Cu$_2$O/Fe$_2$O$_3$ NTs-30, and the data has been revised by C1s (284.6 eV). The wide-scan XPS spectrum showed the predominant presence of C, O, Fe, and Cu elements. Among those elements, O, Cu, and Fe elements were from the as-prepared composites, and the C element was from the XPS instrument itself.

Based on the corresponding high-resolution XPS spectra of Cu$_{2p_{3/2}}$ and Cu$_{2p_{1/2}}$, the comparison of the standard XPS spectrum showed that the valence states of the elements prepared were Cu$^{1+}$ (Figure 2c). The photoelectron peaks of Fe$_{2p_{3/2}}$ and Fe$_{2p_{1/2}}$ appeared ~711.1 eV and 724.8 eV, respectively (Figure 2d), which agreed well with the literature values$^{10}$ and indicated the existence of α-Fe$_2$O$_3$. Thus, the material was proved to be Cu$_2$O/Fe$_2$O$_3$.

![Figure 3](image-url)  
**Figure 3.** (a) Valence-band photoemission spectrum of Cu$_2$O/Fe$_2$O$_3$ NTs-30, 210(b) current-time (i-t) curve of Cu$_2$O/Fe$_2$O$_3$ NTs-30, Cu$_2$O/Fe$_2$O$_3$ NTs. The experiment was measured at the open circuit potential in 0.1 mol L$^{-1}$ KHCO$_3$ solution with CO$_2$ purged and light-on or light-off at every 25 s interval.

Figure 3a shows further analysis of the XPS spectrum. It is the valence-band photoemission spectrum and Gaussian fit graph of Cu$_2$O/Fe$_2$O$_3$ NTs-30 based on the XPS spectrum (Figure 2b). The valence-band maximum (VBM) of the material was directly determined from the electron-emission spectrum by the linear extrapolation of the onset of the valence-band emission$^{11}$. As shown in Figure 3a, the VBM is 1.09 eV. Table 1 showed that the energy band gap of Cu$_2$O/Fe$_2$O$_3$ NTs-30 was narrowed from 2.03 eV to 1.96 eV after modifying Fe$_2$O$_3$ NTs with Cu$_2$O, indicating that Cu$_2$O/Fe$_2$O$_3$ NTs-30 could absorb visible light shorter than 733 nm, and the absorption range for visible light was significantly broadened. Thus, the conduction-band minimum (CBM) could be obtained by the D-value of the VBM and $E_p$, which was -0.87 eV. This value was more negative than the CO$_2$/CH$_3$OH potential (-0.38 V vs. NHE), indicating Cu$_2$O/Fe$_2$O$_3$ NTs-30 with excellent PC reduction ability. Above all, the modification of Fe$_2$O$_3$ NTs with Cu$_2$O greatly improved the material’s PC reduction performance in theory because of the narrowed $E_p$ and more negative CBM.

Furthermore, current-time (i-t) experiment was used to test the PC performance in practice. The i-t curves were measured at the open circuit potential in 0.1 mol L$^{-1}$ KHCO$_3$ solution with CO$_2$ purged under light on or off conditions. The current density D-value of Cu$_2$O/Fe$_2$O$_3$ NTs-30 between illumination and dark was ~15 µA cm$^{-2}$, which was obviously larger than those of Cu$_2$O/Fe$_2$NTs (0.051 µA cm$^{-2}$) and Fe$_2$O$_3$ NTs (0.033 µA cm$^{-2}$). Further, the current density D-value of Cu$_2$O/Fe$_2$O$_3$ NTs-30 was 300 and 450 times those of Cu$_2$O/Fe$_2$O$_3$ NTs, respectively. Thus, it proved that the coupling of Cu$_2$O with Fe$_2$O$_3$ NTs greatly enhanced the PC reduction of CO$_2$. In addition, the current density of Fe$_2$O$_3$ NTs decreased slightly with time, indicating the occurrence of light corrosion. The current density of Cu$_2$O/Fe$_2$O$_3$ NTs almost had no change, indicating that the Cu$_2$O had good photochemical stability.

Excitingly, after coupling Cu$_2$O to Fe$_2$O$_3$ NTs, the light corrosion stopped. We assumed that Cu$_2$O protected Fe$_2$O$_3$ NTs against the light corrosion and strengthened the PC reduction ability. It was greatly consistent with the former theory.

![Figure 4](image-url)  
**Figure 4.** Current-potential ($I$-$V$) curves of the three materials under irradiation or dark (the black arrows point to the onset potential of the reduction of CO$_2$).

The linear-sweep voltammetry (LSV) results of Cu$_2$O/Fe$_2$O$_3$ NTs-30, Cu$_2$O/Fe$_2$O$_3$ NTs measured under the dark or visible-light irradiation, with N$_2$ or CO$_2$ bubbling are shown in Figure 4. The net current density ($I'$) was calculated by subtracting the current density of hydrogen evolution (the current density purged N$_2$) from the total current density (the current density purged CO$_2$). The overpotential of the EC reduction CO$_2$ on Fe$_2$O$_3$ NTs was ~550 mV; however, that of Cu$_2$O/Fe$_2$O$_3$ was only 270 mV. After coupling Cu$_2$O to Fe$_2$O$_3$ NTs, the overpotential of the EC reduction CO$_2$ further decreased to 220 mV. Thus, the Cu$_2$O modification decreased the overpotential of the EC reduction of CO$_2$, decreasing the energy consumption in the EC reduction of CO$_2$. Moreover, the overpotential of Cu$_2$O/Fe$_2$O$_3$ NTs-30 under the irradiation
The -1.3 V (vs. saturated calomel electrode (SCE)) potential was taken as an example, as determined from the following product analysis, for further analysis. It was found that \( I_{\text{Cu}_2O/\text{Fe}_2O_3\text{NTs-30-dark}} \) was about two times larger than \( I_{\text{Cu}_2O/\text{Fe}_{30}\text{NTs-dark}} \) and about ten times larger than \( I_{\text{Fe}_{30}\text{NTs-dark}} \). This result clearly shows that the EC reduction performance of the target material could be greatly enhanced by the light irradiation. This may lead to the synergistic function between the PC and EC reductions.

![Graph](image)

The main product of the PEC reduction CO\(_2\) on Cu\(_2\)O/Fe\(_2\)O\(_3\) NTs-30 was CH\(_3\)OH, as tested by GC, and no other products were detected. Further, when the parallel blank experiment (in 0.1 mol L\(^{-1}\) KHCO\(_3\) solution without CO\(_2\) purging) was conducted, CH\(_3\)OH could not be obtained, indicating that the carbon in CH\(_3\)OH originated from the injected CO\(_2\). Figure 5a shows that from -1.0 V to -1.3 V (vs. SCE), the CH\(_3\)OH yield increased, and from -1.3 V to -1.4 V (vs. SCE) it decreased. The results can be explained as follows: in the range 0-1.3 V, as the potential became more negative, the production quantity of CH\(_3\)OH increased gradually because the CO\(_2\) reduction was the main reaction that occurred. When the potential was more negative than -1.3 V, hydrogen evolution becomes the main reaction, and the production quantity of CH\(_3\)OH decreased. Further, the highest CH\(_3\)OH yield was 4.94 mmol L\(^{-1}\) cm\(^{2}\) after 6 h on Cu\(_2\)O/Fe\(_2\)O\(_3\) NTs-30.

Next, the PEC, PC, and EC reductions of CO\(_2\) on Cu\(_2\)O/Fe\(_2\)O\(_3\) NTs-30 were compared (Figure 5b); the CH\(_3\)OH content reached 4.94, 0.90, and 1.39 mmol L\(^{-1}\) cm\(^{2}\), respectively. From the CH\(_3\)OH yield point of view, the EC property of the composite catalyst was better than the PC performance. However, when PC was coupled to EC, a higher yield was obtained, and this value was even higher than that of the simple sum of the EC and PC (2.29 mmol L\(^{-1}\) cm\(^{2}\)) processes. Therefore, in terms of the product yield, the synergistic effect of the PC and EC reductions of CO\(_2\) on Cu\(_2\)O/Fe\(_2\)O\(_3\) NTs-30 was thoroughly proved.
In addition, to verify the importance of material design, the PEC reduction of CO₂ on Cu₂O/Fe₂O₃ NTs-30, Cu₂O/Fe, and Fe₂O₃ NTs were carried out. The results showed that the CH₃OH yield on Cu₂O/Fe₂O₃ NTs-30 after 6 h was larger than those on Cu₂O/Fe (0.55 mmol L⁻¹ cm⁻²), Fe₂O₃ NTs (1.29 mmol L⁻¹ cm⁻²), and the addition of both the processes (1.84 mmol L⁻¹ cm⁻²). Therefore, another synergistic effect existed, i.e., the synergistic function between Cu₂O and Fe₂O₃ NTs.

Finally, the faradaic efficiency well explained the synergistic function. As shown in Figure 5d, the faradaic efficiencies of Fe₂O₃ NTs and Cu₂O/Fe for the conversion of CO₂ to CH₃OH were only ~35% and 40%, respectively. However, the faradaic efficiency of Cu₂O/Fe₂O₃ NTs-30 reached 93%. This is probably because the existence of two synergistic functions leaded to such a high faradaic efficiency.

Scheme 2. Mechanism of the photoelectrocatalytic reduction of CO₂ on Cu₂O/Fe₂O₃-30 nanotubes.

According to the above analysis and discussion, the mechanism of the PEC reduction of CO₂ on Cu₂O/Fe₂O₃ NTs-30 was deduced. As shown in Scheme 2, two reactions occurred on the electrode surface under irradiation: (i) water was oxidized by the photogenerated holes to protons and oxygen because of the valence band oxidation. (ii) CO₂ could be reduced to CH₃OH. On the one hand, the suitable conduction band of the as-prepared material was -0.87 eV, which was more negative than the reduction potential of CH₃OH/Cu₂O (-0.38 V vs. NHE). This indicated that the catalyst possessed enough PC reductive ability to reduce CO₂ to CH₃OH. On the other hand, the external potential could not only enhance the separation of electrons and holes to improve the PC reduction of CO₂, but also supplied sufficient electrons to sustain the EC reduction of CO₂. Thus, the high efficiency of the PEC synergistic reduction of CO₂ on the Cu₂O/Fe₂O₃ NTs-30 could be reasonably explained.

Experimental Section

Preparation of Catalysts

Cu₂O/Fe₂O₃ NTs were prepared by the potentiostatic electrodeposition method by depositing a Cu₂O film on the surface of Fe₂O₃ NTs. Further, the Fe₂O₃ NTs were obtained by the potentiostatic anodization method according to a previous report published by our group²⁰. The electrodeposition experiments were performed under 0.5 V for 30 min (20 °C). The Fe₂O₃ NTs were the working electrode, and the titanium foil was the counter electrode. The electrolytes comprised 0.4 mol L⁻¹ CuSO₄ and 3 mol L⁻¹ lactic acid. After washing with water and ethanol and drying, the Cu₂O/Fe₂O₃ NTs were obtained. The Cu₂O/Fe was prepared by a similar potentiostatic electrodeposition method in which the working electrode was pure Fe plate, not Fe₂O₃ NTs.

Characterization

The surface morphologies of the as-prepared samples were characterized by scanning electron microscopy (SEM, Philips XL30 FEG) using an accelerated voltage of 20 kV. The particle size was tested by the nano measurer software, and the result was the mean value, the standard deviation is less than 4.66%. The crystals were characterized by XRD (Rigaku D/MAX-RA, Japan) using a diffractometer with Cu Kα radiation, λ = 1.54184 Å in the range 2θ = 20-80° and a scan rate of 4° min⁻¹. The surface compositions were detected by XPS, ESCALAB 250, using a monochromatic X-ray source (Al Kα hν = 1486.6 eV). The photochemical properties were determined by measuring the UV-visible absorbance spectra using IS19-1 combined with a single reflection internal accessory (Beijing Purkinje General Instrument Co., Ltd). The electrochemical properties were measured by CHI660D electrochemical workstation (Shanghai Chenhua Instrument Co., Ltd.).

The PEC properties were measured using a CHI660D electrochemical workstation. A SCE was used as the reference electrode; a platinum wire was used as the counter electrode; and the as-prepared materials were used as the working electrode. A 500 W xenon lamp (Solar-500, NBET Group Corp.) with a filter (λ ≥ 420 nm, 100 mW cm⁻²) served as the visible light source. LSV and Amperometric i-t curves were measured in 0.1 mol L⁻¹ KHCO₃ with the scan rate 50 mV s⁻¹. N₂ or CO₂ was bubbled into the KHCO₃ solution at the rate of 40 sccm for 20 min before the experiment started. Overpotential of CO₂ reduction is equal to the D-value between the actual reduction potential and the theoretical reduction potential (CO₂/CH₃OH=−0.38 V vs. NHE).

The PEC reduction of CO₂ experiments were conducted in a double cell reactor with circulating water at the constant temperature of 25 °C. Cu₂O/Fe₂O₃ NTs, platinum slice, and SCE were used as the working electrode, counter electrode, and reference electrode, respectively. The electrode area was 2 × 2 cm², electrode interval was 1.0 cm, flow rate of CO₂ was 40 sccm during the entire experiment. A 500 W xenon lamp (λ ≥ 420 nm, 100 mW cm⁻²) served as the source of visible light. The intermediates and products were detected by gas chromatography (6890-N, Agilent) using a column (2 m, inner diameter 3 mm, Parapok Q, 80-100) and flame ionization detector. The column temperature was maintained at 100 °C, while the detector temperature was maintained at 150 °C. High purity N₂ was used as the carrier gas with a flow rate of 30 sccm. All the experimental data were taken from the average of three parallel experiments.

Preparation of Catalysts

Experimental Section

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Conclusions

In this study, Cu₂O/Fe₂O₃ NTs were prepared by the potentiostatic electrodeposition method in which Cu₂O film was deposited onto the surface of Fe₂O₃ NTs. The growth mechanism of Cu₂O/Fe₂O₃ NTs was studied in detail; the Cu₂O film showed various structures with the progress in the electrodeposition. Moreover, diverse photoelectric properties were determined for the materials with different morphologies. Among them, the material with double-layer Cu₂O spheres (Cu₂O/Fe₂O₃NTs-30) showed excellent PEC properties with a suitable energy band gap (1.96 eV) and smallest overpotential (180 mV). The morphology and composition of Cu₂O/Fe₂O₃NTs-30 were determined by the XRD and XPS analyses. Furthermore, Cu₂O/Fe₂O₃NTs-30 showed two types of synergism in the PEC reduction of CO₂: (i) between electrocatalysis and photocatalysis and (ii) between Cu₂O and Fe₂O₃NTs. The faradic efficiency and methanol yield reached 93% and 4.94 mmol L⁻¹ cm⁻² after 6 h, respectively. The outstanding performance of Cu₂O/Fe₂O₃NTs-30 for the PEC reduction of CO₂ was well confirmed. Finally, the mechanism for the reduction CO₂ by Cu₂O/Fe₂O₃NTs-30 was elucidated in detail.

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Notes and references

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