A Green and Facile Synthesis of Carbon-Incorporated Co$_3$O$_4$ Nanoparticles and Their Photocatalytic Activity for Hydrogen Evolution

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Carbon-incorporated Co$_3$O$_4$ nanoparticles with an average diameter of 50 nm were prepared via a facile and environmentally friendly one-pot carbon-assisted method using degreasing cotton as a template as well as a reactant. The elemental analysis indicates the incorporation of carbon species into the Co$_3$O$_4$ nanoparticles and the XPS measurements demonstrate the presence of carbon species which comes from the incomplete combustion of the degreasing cotton. Interestingly, the resultant sample was able to split pure water into hydrogen under visible light irradiation without any cocatalyst, which is mainly due to the enhanced light absorption behavior confirmed by the UV-Vis absorption spectra. This facile method provided a potential strategy for applying narrow bandgap semiconductors in pure water splitting.

1. Introduction

In recent years, photocatalytic production of hydrogen from water splitting has been regarded as an ideal solution to deal with the energy problem, due to its clean, nonprecious, and environmentally friendly process via utilizing solar energy [1, 2]. In this field, a large amount of semiconducting materials have been explored to choose the ideal material which is capable of splitting water into hydrogen efficiently.

Co$_3$O$_4$ with a bandgap of 2.1 eV has been widely explored for photocatalytic production of O$_2$ from water splitting, owning to its excellent oxidation ability and low energy gap [3]. However, due to the lower conduction band minimum (CBM) compared to the H$^+$ reduction potential, much less reports on photocatalytic production of hydrogen have been reported. Although Zhang et al. reported that the Co$_3$O$_4$ quantum dots prepared by a reverse micelle method using a microwave-assisted solvothermal reaction had an excellent photocatalytic performance on splitting water into hydrogen because of the CBM upshift [4], this method required difficult procedures. Boumaza et al. reported that Co$_3$O$_4$, a multifunctional spinel-type p-type, was capable of promoting hydrogen photoproduction in the presence of methanol as sacrificial agent. This material, however, suffered rapid deactivation [5]. Therefore much research should go deep into the Co$_3$O$_4$ as a photocatalyst for hydrogen production.

It has been reported recently that carbon species can serve as sensitizers [6, 7]. Zhang et al. reported that the carbon species incorporated TiO$_2$ had a high hydrogen production rate, which is 1.8 times larger than that of P25, owing to the sensitization effect of carbon [8]. Kado et al. also synthesized TiO$_2$ with an enhanced photoresponse, which was modified by a thin carbon [9]. Nevertheless, Co$_3$O$_4$ modified with the carbon species as a photocatalyst for water splitting into hydrogen has not been reported.
In this work, a facile and environmentally friendly one-pot carbon-assisted method using degreasing cotton as a template as well as a reactant was used to synthesize the carbon-incorporated Co$_3$O$_4$ and its hydrogen production from photocatalytic splitting of water has been studied. To the best of our knowledge, this is the first time that the carbon-incorporated Co$_3$O$_4$ prepared as a photocatalyst was used to split water into hydrogen and the sample prepared interestingly even has photocatalytic activity under visible light irradiation.

2. Materials and Methods

*Synthesis.* Typically, 17.46 g Co(NO$_3$)$_2$·6H$_2$O was added to 20 mL deionized water followed by vigorous stirring for 10 min, producing a stable pink solution. Subsequently, 1.5 g degreasing cotton was immersed into the obtained pink solution and kept in an ultrasonic bath for 10 min in order to have a good dispersion of Co$^{2+}$ on the surface of degreasing cotton. Then the treated degreasing cotton was collected and transferred into a quartz petri dish in the tube furnace (OTF-1200X-III, Hefei, China) and kept at 600°C for 2 h in air. The resultant sample designated as Co$_3$O$_4$-DC was obtained without any postprocedures. For comparison, the product labeled as Co$_3$O$_4$-WA was fabricated directly calcining Co(NO$_3$)$_2$ solution at 600°C for 2 h without any additive. The formation procedure is shown as Scheme 1.

*Characterization.* The crystal structure of the sample was performed through X-ray diffraction (XRD, a Bruker D8, $\lambda = 1.5406$ Å) in the 2$\theta$ of 10–80° with scan rate of 10°/min and Cu Kα radiation, 40 KV. Scanning electron microscopy (SEM) images were obtained on a Hitachi S-4800 scanning electron microscope. The particle shapes and sizes were characterized by TEM measurement (JEOL JEM-1200EX) with a working voltage being 120 kv. Chemical composition analysis was carried out using energy dispersive X-ray (EDX) spectroscopy and X-ray photoelectron spectroscopy (XPS) which was collected using an ESCALAB 250Xi spectrometer with a standard Al Kα radiation with the binding energies calibrated based on the contaminant carbon (C1s = 284.6 eV). The Raman spectrum was measured using a Renishaw inVia-Reflex Raman spectrometer. Specific surface areas and pore size distributions were computed from the results of N$_2$ adsorption-desorption isotherms.
physiosorption at 77 K (Micromeritics ASAP 2020) by using the BET (Brunauer-Emmett-Teller) and BJH (Barrett-Joyner-Halenda). A Cary 300 Scan UV-Vis spectrophotometer was employed to record the UV-Vis diffuse reflectance spectra (DRS) in a region of 200 to 800 nm.

**Photocatalysis.** The photocatalytic activity for hydrogen production generated from water was estimated under simulated solar light condition. Typically, 0.02 g photocatalyst was added into the solution (~200 mL) containing 100 mL water and 100 mL ethanol as the sacrificial reagent, as it is more sustainable and renewable than methanol. The mixture was put in an ultrasonic stirring for 20 min, purged by Ar gas for 20 min, and then irradiated under simulated solar light with magnetic stirring. A 300 W Xe arc lamp (LSH-A500, Kaifeng Hxsei Science Instrument Co., Ltd., China) with UV cut-off filters (420 nm) was used as the light source. The hydrogen produced was analyzed by a gas chromatography (GC-9890B, Shanghai Linghua Instrument Co., Ltd., China) equipped with a thermal conductivity detector and a stainless steel column packed with molecular sieve (5Å). Ar gas (99.999%) was used as the carrier gas.

### 3. Results and Discussions

#### 3.1. Characterization

The XRD patterns of the Co$_3$O$_4$-DC are shown in Figure 1. No impurity peaks are found in the XRD patterns and all peaks have a good agreement with the standard spinel cubic Co$_3$O$_4$ spectrum (JCPDS number 42-1467; space group Fd-3m; lattice constant $a = 8.084$ Å), suggesting that the sample is well-crystallized Co$_3$O$_4$ with high purity. The crystalline sizes of Co$_3$O$_4$-DC and Co$_3$O$_4$-WA are estimated to be 51.64 nm and ~100 nm according to Scherrer’s formula, $D = 0.89 \lambda / (B \cos \theta)$, where $\lambda$ is the X-ray wavelength, $\theta$ is the Bragg angle, and $B$ is the Full Width at Half-Maximum (FWHM) of a peak at half-height, thus confirming that the crystal size of Co$_3$O$_4$-DC is much smaller than that of Co$_3$O$_4$-WA.

To further observe the morphologies of Co$_3$O$_4$-DC and Co$_3$O$_4$-WA, SEM and TEM were performed. It is clear from the panoramic view that the Co$_3$O$_4$-DC interestingly contains uniform and weak agglomerated Co$_3$O$_4$ nanospheres with 50 nm in diameter, while Co$_3$O$_4$-WA, which is in accordance with the value calculated from XRD. In addition, disordered hole-like arrangement of pores also can be seen in inset (a), making a promising favor to facilitate the water splitting due to the large specific surface area. The BET surface area and BJH pore size distributions of the as-prepared Co$_3$O$_4$-DC are shown in Figure S2 and the BET surface area is calculated to be 17.46 m$^2$ g$^{-1}$ and the average pore size is 23.67 nm while the Co$_3$O$_4$-WA is only 5.8 m$^2$ g$^{-1}$.

The insets of Figure 2 show the elemental analysis on the surface (a) and the cross section (b) of the Co$_3$O$_4$-DC. The inset bottom red bars indicate the standard reflections from Co$_3$O$_4$ (JCPDS number 42-1467). The insets sof Figure 2 show the elemental analysis on the surface (a) and the cross section (b) of the Co$_3$O$_4$-DC. The inset bottom red bars indicate the standard reflections from Co$_3$O$_4$ (JCPDS number 42-1467). The inset bottom red bars indicate the standard reflections from Co$_3$O$_4$ (JCPDS number 42-1467).
respectively. These results indicate the incorporation of carbon species into the Co$_3$O$_4$ nanoparticles, as a result of incomplete decomposition of degreasing cotton.

Figure 3 presents the X-ray photoemission spectroscopy (XPS) of Co$_3$O$_4$-DC to estimate the chemical composition of the sample. Peaks corresponding to cobalt, carbon, and oxygen are detected in the spectrum, indicating that only Co, O, and C elements can be found in the Co$_3$O$_4$-DC. The strong peak of C 1S centers at 284.6 eV can be assigned to elemental carbon which has given rise to the incomplete burning of degreasing cotton [12]. The other two weak peaks showed at 286.5 and 288.1 eV, respectively, which, as expected, are ascribed to the C–O bonds from insufficient combustion residual degreasing cotton [13, 14]. Additionally, no Co–C bond at 282.5 eV has been clearly found [15], revealing that nearly no carbon is doped into the lattice of Co$_3$O$_4$. As a consequence, it is proved that the carbon species incorporated in Co$_3$O$_4$ matrix are almost present as elemental state, which is in line with the results obtained in Teng’s work [12].

The inset of Figure 3(a) shows the O 1S spectrum of the evaluated sample. The asymmetric O 1S spectra are fitted using two component peaks centered at 530 and 531.3 eV, which are ascribed to the surface lattice oxygen species and the surface adsorbed oxygen species (O$^-$ or O$^2-$), respectively [16]. The peak at 532.5 can be assigned to C–O [8], which is caused by the incomplete decomposition of degreasing cotton. Figure 3(b) gives the Co 2p$_{3/2}$ high resolution XPS spectrum of the as-synthesized Co$_3$O$_4$-DC. The peaks at 780.1 and 781.8 eV correspond to Co$^{2+}$ and Co$^{3+}$, respectively [17, 18]. The ratio of Co$^{3+}$/Co$^{2+}$ on the surface of Co$_3$O$_4$-DC estimated by quantitative analysis is 2.84 instead of 2 in the chemical form of Co$_{3/2}$(Co$^{3+}$)$_{3/2}$O$_4$ while it is 1.89 in that of the Co$_3$O$_4$-WA (Figure S4), and the probable reason is the presence of abundant surface oxygen vacancies on the Co$_3$O$_4$-WA with much less defects on Co$_3$O$_4$-DC [16]. Importantly, it has been confirmed that less defects give rise to higher photocatalytic activity, as the recombination between photogenerated electrons and holes is decreased at the defect [19], thus indicating that our prepared sample may have a better performance on splitting water into hydrogen.

The optical absorption properties of the Co$_3$O$_4$-DC were investigated at room temperature by UV-Vis spectroscopy (Figure 4(a)). It is obvious that more intense and broad background absorption in the visible light region is observed for Co$_3$O$_4$-DC, and the absorption edges shift to longer wavelength compared with that of Co$_3$O$_4$-WA. The carbon residuals on the Co$_3$O$_4$-DC may be responsible for this phenomenon. In addition, the bandgap $E_g$ value calculated according to the UV-Vis spectroscopy of Co$_3$O$_4$-DC is 2.0 eV (Figure 4(b)) which is greater than that of Co$_3$O$_4$-WA ($E_g = 1.9$ eV, inset of Figure 4(c)). The increase in the bandgap of the Co$_3$O$_4$-DC may be ascribed to the quantum confinement effects of nanomaterials [20]. Importantly, inset of Figure 4(a) shows the valence band maximum of Co$_3$O$_4$-DC and Co$_3$O$_4$-WA, clearly indicating that they have almost the same position of valence-band XPS spectra, thus demonstrating that bandgap widening of Co$_3$O$_4$-DC was mainly attributed to the conduction band minimum upshift, which would provide higher potential for H$^+$ reduction beneficial for photocatalytic hydrogen production.

Control experiments demonstrated that no hydrogen was evolved when the reaction proceeded without a photocatalyst or in the dark under stirring conditions while other conditions remained unchanged.

Figure 5(a) shows the photocatalytic hydrogen production on Co$_3$O$_4$-DC and Co$_3$O$_4$-WA at water/sacrificial agent (1:1) under simulated solar light. Higher photocatalytic splitting of water is observed for the Co$_3$O$_4$-DC (0.85 umol
 Figure 4: (a) UV-Vis spectrum of Co$_3$O$_4$-DC and Co$_3$O$_4$-WA, (b) $(A\nu)^2-\hbar\nu$ curve of Co$_3$O$_4$-DC, and (c) $(A\nu)^2-\hbar\nu$ curve of Co$_3$O$_4$-WA. Inset of (a): valence-band XPS spectra of Co$_3$O$_4$-DC and Co$_3$O$_4$-WA.

The improvement of activity of Co$_3$O$_4$-DC could be ascribed to the small particle size and a high surface area resulted from the disordered hole-like arrangement of pores produced by the decomposition of degreasing cotton as a hard template, an abundance of oxygen vacancies, and a much more intense and broad background absorption in the visible light region which were caused by the sensitization of carbon residuals. Figure 5(b) displays the photocatalytic hydrogen production on Co$_3$O$_4$-DC and Co$_3$O$_4$-WA at pure water under simulated solar light; the hydrogen product decreases to 0.13 umol h$^{-1}$ for Co$_3$O$_4$-DC, indicating that the sacrificial agent has a significant effect on the photocatalytic hydrogen production. It is evidently seen that Co$_3$O$_4$-DC showed photocatalytic activity for hydrogen evolution while Co$_3$O$_4$-WA did not have a photocatalytic performance in pure water under visible light (Figure 5(c)). Zhang et al. [8] and Lettmann et al. [21] have proved that the carbon residuals in semiconducting metal oxide are prone to carrying out a charge transfer process and are responsible for the photosensitization of semiconducting metal oxide. Thus, the enhanced photocatalytic activity of the sample can be ascribed to the sensitization effect of carbon and the conduction band minimum upshift. Proposed mechanism for photocatalytic hydrogen production for Co$_3$O$_4$-DC is shown in Figure 5(d). After an electron is excited from the carbon residual by light irradiation, the electron is injected to the conduction band of Co$_3$O$_4$; meanwhile, the electron excited in Co$_3$O$_4$ also takes part in the hydrogen production and then hydrogen evolves on the surface of Co$_3$O$_4$ [22]. These results confirm that the carbon-incorporated Co$_3$O$_4$
synthesized via carbon-assisted method using degreasing cotton has a good performance in hydrogen production and even has photocatalytic ability under visible light for hydrogen evolution.

4. Conclusions

In summary, carbon-incorporated Co₃O₄ was successfully prepared by a facile and environmentally friendly carbon-assisted method using degreasing cotton and further applied as a photocatalyst in photocatalytic water splitting for hydrogen evolution. The carbon-incorporated Co₃O₄ was able to split pure water into hydrogen under visible light condition without any cocatalyst, which is mainly due to the sensitization effect of carbon. In addition, it provided a potential strategy for applying narrow bandgap semiconductors in pure water splitting.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.
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