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Octahedral Cu₂O-modified TiO₂ nanotube arrays for efficient photocatalytic reduction of CO₂

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ABSTRACT

A photocatalyst composed of TiO₂ nanotube arrays (TNTs) and octahedral Cu₂O nanoparticles was fabricated, and its performance in the photocatalytic reduction of CO₂ under visible and simulated solar irradiation was studied. The average nanotube diameter and length was 100 nm and ~5 μm, respectively. The different amount of octahedral Cu₂O modified TNTs were obtained by varying electrochemical deposition time. TNTs modified with an optimized amount of Cu₂O nanoparticles exhibited high efficiency in the photocatalysis, and the predominant hydrocarbon product was methane. The methane yield increased with increasing Cu₂O content of the catalyst up to a certain deposition time, and decreased with further increase in Cu₂O deposition time. Insufficient deposition time (5 min) resulted in a small amount of Cu₂O nanoparticles on the TNTs, leading to the disadvantage of harvesting light. However, excess deposition time (45 min) gave rise to entire TNT surface being most covered with Cu₂O nanoparticles with large sizes, inconvenient for the transport of photo-generated carriers. The highest methane yield under simulated solar and visible light irradiation was observed for the catalysts prepared at a Cu₂O deposition time of 15 and 30 min respectively. The morphology, crystallization, photoresponse and electrochemical properties of the catalyst were characterized to understand the mechanism of its high photocatalytic activity. The TNT structure provided abundant active sites for the adsorption of reactants, and promoted the transport of photogenerated carriers that improved charge separation. Modifying the TNTs with octahedral Cu₂O nanoparticles promoted light absorption, and prevented the hydrocarbon product from oxidation. These factors provided the Cu₂O-modified TNT photocatalyst with high efficiency in the reduction of CO₂, without requiring co-catalysts or sacrificial agents.

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1. Introduction

Artificial photosynthesis converts CO₂ into hydrocarbon fuel

under solar irradiation, and is attracting increasing interest. It exploits a photocatalyst medium, in contrast to natural photosynthesis where this is achieved within green plants. Artificial

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photosynthesis can potentially overcome the shortage of sustainable energy, and solve the environmental problems associated with CO₂ emission, but is hindered by low conversion efficiencies. Considerable progress is required to make the photocatalytic reduction of CO₂ practical and economical [1–6].

The photocatalyst is the key factor in the photocatalytic reduction of CO₂, and high conversion efficiency requires an efficient photocatalyst. Semiconductors are attractive photocatalysts because their bandgap is comparable to the energy of solar light, so they have been widely studied [7,8]. In 1979, Inoue et al. [9] reported the photocatalytic reduction of CO₂ into organic compounds in the presence of a semiconductor, under irradiation by a Xe lamp. Many subsequent studies have used various semiconductors to convert CO₂ with water into hydrocarbons under irradiation [10,11]. TiO₂ has been the most widely studied semiconductor, because of its high stability, strong oxidation activity, favorable optical and electronic properties, and efficient charge transport [12–15]. CO₂ has a high thermodynamic stability, and significant energy is required to break its C=O bond [1]. An efficient photocatalyst should ideally harvest the maximum possible amount of solar light. TiO₂ has a bandgap of ~3.2 eV, which corresponds to the ultraviolet region. This constitutes only 3%–5% of the solar spectrum, which limits the photocatalytic efficiency of TiO₂ [16]. The favorable recombination of photo-generated charge carriers also suppresses the photocatalytic efficiency of TiO₂ [17]. The potential of the TiO₂ valence band occupied by photo-generated holes is highly positive, which may oxidize the previously reduced products back to CO₂ [10,18].

Much effort has focused on addressing these limitations [19]. Modifying TiO₂ with a narrow bandgap semiconductor can extend its absorption into the visible region, and facilitate photo-generated electron-hole separation. Cu₂O is a semiconductor with a bandgap of 2.0–2.2 eV [20,21]. It is widely applied as a photocatalyst, because it is nontoxic, widely available at low cost, and has a high absorption coefficient [22]. The optimum design of the band configuration is important for enhancing the photocatalytic reduction efficiency [23]. Both the conduction and valence bands of Cu₂O are at higher energy level than their respective bands in TiO₂. Thus, excited electrons accumulate in the TiO₂ conduction band, while holes accumulate in the Cu₂O valence band. The TiO₂/Cu₂O system has appropriate band edge alignments that facilitate the separation of photo-generated charge carriers [24,25]. The oxidation potential of holes from TiO₂ also decreases upon transferring into Cu₂O, which can hinder re-oxidation, and achieve the same effect as sacrificial hole scavengers [26,27]. Many studies have proved that Cu₂O-modified TiO₂ exhibits excellent performance in the photocatalytic production of hydrogen and the photocatalytic degradation of pollutants [28–30].

To the best of our knowledge, no studies have probed Cu₂O-modified TiO₂ in the photocatalytic reduction of CO₂. Much recent progress has been made on controlling the photocatalysts morphology, and forming an appropriate nanostructure can enhance its photocatalytic efficiency [31]. One-dimensional vertically-arrayed TiO₂ nanotubes arrays (TNTs) have been widely studied in many photocatalytic reactions, because

of their high specific surface area, favorable electronic properties, and rapid photoelectron transport [13,32–35]. Herein, we prepared TNTs by conventional electrochemical anodization, and then modified the TNTs with Cu₂O by electrochemical deposition. The morphologies, compositions, and crystallinities of the products were characterized. Cu₂O-modified TNTs with varying amounts of Cu₂O were exploited for the photocatalytic reduction of CO₂ in the presence of water vapor under visible and simulated solar irradiation. The photocatalyst containing an optimized Cu₂O content exhibited a significantly higher hydrocarbon production efficiency than that of pure TNTs. The light absorption and photoelectrochemical behaviors of the photocatalysts were investigated to explain the high photocatalytic activity, and a mechanism for the photocatalytic process was proposed.

2. Experimental

2.1. Synthesis of Cu₂O-modified TiO₂

Ti foil and all chemicals were purchased from Sinopharm (Shanghai, China) and used as purchased. Highly-ordered TNTs were synthesized by conventional electrochemical anodization. Ti foil (3 × 7.5 × 0.1 mm, 99.6%) was polished with various abrasive papers, and then ultrasonically washed for 10 min in acetone, alcohol, and distilled water. The clean foil was immersed into ethylene glycol electrolyte containing 0.4 vol% NH₄F, 2 wt% citric acid and 10 vol% water. Anodization was performed in a two-electrode cell, with the Ti foil as the anode and carbon rod as the cathode, at an applied potential of 50 V. Anodization was conducted for 4 h in ice water. After reaction, the resulting TNT samples were immediately ultrasonically washed for 5 s, to remove any surface debris. The samples were then rinsed with deionized water and dried in air. They were then crystallized by annealing at 450 °C in air for 3 h.

Cu₂O nanoparticles were then deposited on the crystalline TNT samples by electrochemical deposition. This was performed in a conventional three-electrode cell, with the TNT sample as the working electrode, Pt foil as the counter electrode, and Ag/AgCl as the reference electrode. The deposition electrolyte was 0.4 mol/L CuSO₄, 3 mol/L lactic acid, and its pH was adjusted to 11 with 5 mol/L NaOH. The as-prepared TNT sample was immersed in the electrolyte solution in a 60 °C water bath, and –12 mA was applied to the TNT working electrode. The resulting Cu₂O/TiO₂ sample was named TC_x, where *x* represents the deposition time (min). Thus, four prepared samples TC₅, TC₁₅, TC₃₀ and TC₄₅ were prepared using Cu₂O deposition times of 5, 15, 30 and 45 min, respectively. A pure TNT sample was similarly characterized and probed as a control. The freshly-prepared composites were immersed in 10 vol% ammonium hydroxide for 10 min, to remove the Cu₂O oxide layer and any surface impurities which may influence their photoactivity. The resulting samples were dried in a vacuum oven for 12 h.

2.2. Characterization

Morphologies were investigated by scanning electron microscopy (SEM, JEOL JSM-6700F). Crystal structures were characterized by X-ray diffraction (XRD) using a PANalytical diffractometer (D/max 40 kV) with Cu K_{α} radiation ($\lambda = 0.154598$ nm). Ultraviolet-visible (UV-Vis) diffuse reflectance spectra (DRS) were recorded using a PerkinElmer Lambda 35 Spectrophotometer, at a wavelength range of 200–800 nm. Photoluminescence (PL) spectra were measured on a Perkin-Elmer 4500 fluorescence spectrophotometer, at an excitation wavelength of 310 nm.

The photoelectrochemical (PEC) behavior of the TCx samples was investigated using a three-electrode configuration, with the TCx sample as the working electrode, Pt foil as the counter, and Ag/AgCl electrode as the reference. The electrolyte was 0.1 mol/L Na_2SO_4 with a pH of 7. A 350 W Xe lamp (Shanghai Lansheng Lighting Appliance Co. Ltd., China) with and without an UV cutoff filter ($\lambda < 420$ nm) was used to simulate AM 1.5 solar irradiation. Impedance measurements were performed using a PARSTAT-2273 Advanced Electrochemical System (Princeton Applied Research), which was controlled by a computer and equipped with an impedance analyzer.

2.3. Photocatalytic reduction of CO_2

The photocatalytic reduction of CO_2 by the samples was examined in the presence of water vapor without co-catalysts or sacrificial agents. The prepared sample (3×5 cm²) was loaded into a stainless steel chamber (170 ml) with two valves for evacuation and gas supply, a side port with a rubber plug for gas sampling, and an O-ring-sealed quartz window at the top for irradiation. A 350 W Xe lamp with and without an UV cutoff filter ($\lambda < 420$ nm) was used as the light source. After the sample was loaded into the chamber with approximately 0.5 ml of deionized water, the chamber was evacuated and filled with CO_2 (99.9999%), which had been passed through a bubble containing deionized water, and was finally sealed. The inlet and outlet valves of the chamber were open during CO_2 gas flow for at least 30 min, and were then closed to retain a chamber pressure of approximately 103 kPa. The reaction

products were collected with a gas-tight syringe inserted through a septum, and then immediately analyzed by gas chromatography with FID detector (GC-2014, Shimadzu, Japan).

3. Results and discussion

The morphology of the pure TNTs sample was first investigated, to ensure well-aligned TiO_2 nanotubes prior to Cu_2O deposition. Fig. 1(a) and (b) shows that the TiO_2 layer formed on the Ti foil consisted of an array of vertically-aligned nanotubes. The average nanotube diameter and length was 100 nm and ~ 5 μm respectively. Brief ultrasonication after electrochemical anodization was necessary to form the openings of individual tubes [32–35].

Cu_2O nanoparticles were then deposited onto the TNTs. Fig. 1(c)–(f) shows SEM images of TNTs after modification with Cu_2O for different times. Fig. 1(c) shows a few Cu_2O nanoparticles of size ~ 150 nm on the TNTs after electrochemical deposition for 5 min, and that these nanoparticles had an octahedral-like structure. Increasing deposition time resulted in the octahedral nanoparticle size increasing to ~ 270 nm (Fig. 1(d)). Increasing the deposition time to 30 min significantly increased the size and quantity of the Cu_2O nanoparticles, and the average particle size was 480 nm (Fig. 1(e)). Increasing the deposition time to 45 min resulted in the entire TNT surface being largely covered with Cu_2O nanoparticles of ~ 540 nm in size. These Cu_2O nanoparticles were aggregated, had partly lost their octahedral structure, and partly obstructed tube openings. The SEM images show that the Cu_2O nanoparticles were generally well-distributed across the surface, and that some were embedded within tubes.

Figure 2(a) shows the XRD patterns of the TNTs before and after modification with Cu_2O . Peaks in the pattern of pure TNTs were attributed to elemental Ti from the underlying substrate, and well-crystallized anatase TiO_2 (JCPDS 21-1272). After electrochemical deposition of Cu_2O , new peaks characteristic of Cu_2O were observed (JCPDS 05-0667). No impurities including Cu or CuO were observed. Cu_2O contained five distinct peaks,

Fig. 1. SEM images of the prepared samples: top (a) and side views of TNTs (b), and top view of TC5 (c), TC15 (d), TC30 (e), and TC45 (f).

which were attributed to the (110), (111), (200), (220), and (311) planes, as shown in Fig. 2(a). In the XRD patterns of TC5, TC15 and TC30, the (111) diffraction peak of Cu_2O was much sharper than the other peaks, indicating that (111) was the dominant exposed face. The intensity of the (200) peak increased more quickly than the other peaks with increasing deposition time. At 45 min deposition time (TC45), the intensity of the (200) plane was stronger than that of the (111) plane. From the SEM images of Cu_2O , we speculated that the exposed face of Cu_2O tended towards (200) with increasing deposition time.

Sample TC15 was characterized by XPS to identify its chemical composition and elemental states. Fig. 2(b)–(d) shows XPS peaks corresponding to C, O, Ti and Cu. The binding energies of

the Ti 2*p* state were located at 464.6 and 459.1 eV, indicative of Ti^{4+} . The XPS peaks for the Cu 2*p*_{3/2} and 2*p*_{1/2} states were located at 952.9 and 932.7 eV, respectively. The characteristic Cu^{2+} satellite peak at ~942 eV was not observed, further suggesting that Cu existed as Cu_2O and not CuO [25,36].

The pure and Cu_2O -modified TNTs were then applied in the photocatalytic reduction of CO_2 in the presence of water vapor. We first tested their photocatalytic activities under visible light irradiation to investigate the role of the Cu_2O nanoparticles. Fig. 3(a) shows that the pure TNTs exhibited no photocatalytic activity in the reduction of CO_2 under visible light irradiation, because of the wide bandgap of TiO_2 . After modifying with octahedral Cu_2O , a clear evolution of hydrocarbon product was observed. One role of Cu_2O in the catalyst was to enhance visi-

Fig. 2. XRD patterns of TNTs and Cu_2O -modified TNTs (a). XPS survey spectrum (b) and the Ti 2*p* (c) and Cu 2*p* (d) spectral regions of TC15.

Fig. 3. Photocatalytic reduction of CO_2 in the presence of water vapor over the prepared samples, under visible (a) and simulated solar irradiation (b).

ble light harvesting, to produce more photo-generated electrons and holes for further reaction. The hydrocarbon product was predominantly methane, indicating selective production by the catalyst during photoreduction. The methane yield increased with increasing Cu_2O content of the catalyst, but began to decrease when the Cu_2O deposition time reached 45 min. Thus, the highest methane yield under visible light irradiation was observed for the catalyst prepared at a Cu_2O deposition time of 30 min.

Our ultimate aim was to use sunlight to convert CO_2 into hydrocarbon fuel, so we carried out the photocatalytic reduction of CO_2 under simulated solar irradiation (Fig. 3(b)). At the optimized amount of Cu_2O , the methane evolution yield of TCx was significantly higher than that of the pure TNTs. TC15 exhibited the highest photocatalytic activity, at approximately three times higher than that of the pure TNTs. The methane production of TC45 was lower than that of pure TNTs.

The samples were further characterized to understand their photoreduction behavior. Fig. 4(a) shows the UV-Vis DRS of the samples. The bandgap of Cu_2O is 2.0–2.2 eV, so modifying TNTs with Cu_2O extended its absorption into the visible region. This is why the Cu_2O -modified TNTs exhibited methane evolution under visible light irradiation. We then examined the photocurrent response of the samples, to study the separation and transportation of photogenerated electrons and holes. Higher light harvesting and faster electron-hole separation lead to higher photocurrent. Fig. 4(b) and (c) show that no significant current response was observed for any of the samples in the absence of irradiation. The rise and fall in current corresponded to the irradiation on/off cycles. Irradiation resulted in prompt photocurrent, which immediately returned to zero when irradiation stopped. Under visible light irradiation, the photocurrent density increased with increasing Cu_2O deposition time from 5 to 30 min, and then decreased with further increasing deposition time (Fig. 4(b)). Under simulated solar irradiation, the photocurrent densities of the samples exhibited a similar trend, except that TC15 exhibited the highest photocurrent density (Fig. 4(c)).

Treating the TCx samples with ammonium hydroxide also greatly influenced their photoactivity. Figs. 5(a), 5(b) and 1(d)

Fig. 5. SEM image (a) and XRD pattern (b) of TC15 after treatment with ammonium hydroxide.

showed no obvious change in morphology and crystallinity of the TNTs/ Cu_2O composites upon treatment with ammonium hydroxide. Prior to treatment, the photocurrents of the TCx composites were much lower than those of pure TNTs. Fig. 3(b) shows that immersing the samples in ammonium hydroxide for 10 min greatly enhanced their photocurrent. Active sites on the TiO_2 surface are largely Ti^{3+} sites arising because of oxygen vacancies [37]. The enhanced photoresponse probably resulted from the removal of impurities at active sites. Previous studies indicated that CO_2 did not readily adsorb at the Cu_2O surface [26]. Treatment of TNTs/ Cu_2O with ammonium hydroxide may have modified the Cu_2O surface, recovering active sites on the surface of TNTs and Cu_2O , thus improving the photocatalytic activity of the TNTs/ Cu_2O .

Fig. 4. UV-Vis DRS (a) and short-circuit photocurrent density versus time plotted (b); (c) for electrodes of samples in 0.1 mol/L Na_2SO_4 under visible (b) and simulated solar irradiation (c).

The UV-Vis DRS and photoelectrochemical results accounted for the observed trends in the photocatalytic activities of the samples. Under visible light irradiation, Cu_2O acted as the photocatalyst, and the vertically aligned TNTs acted as channels to facilitate rapid charge carrier transfer and separation [1,38,39]. Increasing deposition time led to more Cu_2O participating in the photoreduction, so more methane was evolved. TC30 exhibited the highest photocurrent density, reflecting its higher generation and faster charge carrier separation, so TC30 exhibited the highest methane evolution. The TiO_2 tube openings of TC45 were obstructed by aggregated Cu_2O particles (Fig. 1(f)), which hindered charge transfer and separation, and decreased the photocatalytic efficiency. Smaller particle sizes reportedly benefit charge transfer [40,41]. The Cu_2O particle size increased with increasing deposition time, so the largest Cu_2O particle size for TC45 resulted in its decreased photocatalytic efficiency. The (111) face of Cu_2O reportedly exhibits higher photocatalytic activity than the other faces [42,43]. XRD indicated that the (200) face was the predominant exposed face of TC45, which may also have contributed to the lower photocatalytic efficiency of TC45.

The photocatalytic activity differed under simulated solar irradiation, where the TNTs and Cu_2O nanoparticles both generated electron-hole pairs. The conduction and valence bands of Cu_2O are at higher energy level than their respective bands of TiO_2 , so photogenerated electrons accumulated within TNTs and rapidly participated in the photocatalytic reaction. The holes accumulated in Cu_2O particles, which reduced the recombination of charge carriers. Fig. 6(a) shows a high-resolution TEM image of TC15. The lattice fringes of $d = 0.351$ and 0.247 nm matched the $\text{TiO}_2(101)$ and $\text{Cu}_2\text{O}(111)$ planes, respectively, in accordance with the XRD and XPS results. The TiO_2 and Cu_2O crystal grains were well connected, which facilitated charge transfer. The PL spectra in Fig. 6(b) show that the emission intensity of pure TNTs was much higher than that of the Cu_2O -modified TiO_2 samples. PL emission arose from the combination of photo-generated electrons and holes, with stronger emission indicating more recombination [44]. An optimized Cu_2O deposition amount extended the absorption range, facilitated charge transfer, and suppressed the recombination of electrons and holes. TC45 contained excess Cu_2O which blocked the UV light from reaching the TiO_2 . UV-Vis spectra in

Fig. 7. Nyquist plots of TNTs and TC15 electrodes in aqueous 0.1 mol/L Na_2SO_4 in the dark and under simulated solar irradiation.

Fig. 4(a) showed a dramatic decrease in the absorption of TC45 in the UV region compared with the other TNT samples. This explained why TC15 exhibited the highest photocatalytic activity under simulated solar irradiation.

Electrochemical impedance spectroscopy (EIS) measurements were recorded for pure TNTs and TC15 in the dark and under simulated solar irradiation, to confirm the enhanced charge separation in the Cu_2O -modified TiO_2 samples. A smaller semicircle diameter in the Nyquist plot at high frequency corresponds to faster electron-hole separation and charge transfer [45–47]. Fig. 7 shows that modifying the TNTs with Cu_2O promoted charge separation and transfer in the dark and under simulated solar irradiation. Thus, TC15 exhibited a photocatalytic efficiency three times higher than that of pure TNTs under simulated solar irradiation.

From the above results, a mechanism for the high photocatalytic reduction efficiency is proposed, as shown schematically in Fig. 8. Three major factors contributed to the high activity. First, the TNT nanotube structure provided abundant active sites for reactant adsorption, and the vertically-aligned TNTs provided a direct pathway for electron transfer, thus promoting charge carrier separation. Second, modifying with an optimum amount of Cu_2O nanoparticles enhanced light harvesting, so the catalyst used a greater portion of the solar spectrum. Third, the well-matched band edges of TiO_2 and Cu_2O reduced recombination, and reduced the oxidation potential of photo-generated holes from TiO_2 , which had a similar effect to sacrificial agents.

Fig. 6. High-resolution TEM image of TC15 (a) and PL emission spectra of the samples (b).

Fig. 8. Schematic of the proposed photocatalysis mechanism for the Cu_2O -modified TNTs under visible light.

4. Conclusions

Cu_2O -modified TiO_2 catalysts were prepared, and used in the photoreduction of CO_2 . The photocatalysts comprised octahedral Cu_2O nanoparticles deposited on TNTs. The catalyst with an optimized Cu_2O loading exhibited a high photocatalytic efficiency and selectivity for methane. The high photocatalytic efficiency was ascribed to a combination of the vertically-aligned nanotubes, high visible light absorption of Cu_2O , and the well-aligned band edges of TiO_2 and Cu_2O . TiO_2 and Cu_2O are abundant and low cost materials. This study provides an economic and promising catalyst for the photoreduction of CO_2 under solar irradiation.

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Graphical Abstract

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Octahedral Cu_2O -modified TiO_2 nanotube arrays for efficient photocatalytic reduction of CO_2

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Photocatalysts comprising TiO_2 nanotube arrays and octahedral Cu_2O nanoparticles were fabricated. The photocatalysts exhibited high efficiency and selectivity in the photocatalytic reduction of CO_2 . The predominant hydrocarbon product was methane.

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在光催化还原CO₂中具有高催化效率的八面体Cu₂O修饰的TiO₂纳米管

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摘要: 光催化还原CO₂生成烃类燃料是一种可同时解决全球变暖和能源危机问题的最有效途径之一。尽管这方面的研究已经取得了一定的进展,但是整体的光催化转换效率还非常低。因此,需要发展更加高效的催化剂。由于半导体材料禁带宽度与太阳光谱相匹配,人们已经对其进行了广泛研究。其中TiO₂因具有无毒、强氧化性以及良好的光学和电学性质等而成为最主要的研究对象。但是对于光催化还原CO₂反应来说,TiO₂仍存在很多不足,如只能吸收太阳光谱中的紫外光,光生载流子会快速结合,以及光生空穴的强氧化能力等,这些都限制了其光催化还原CO₂的效率。采用窄禁带宽度半导体修饰TiO₂是解决上述不足的有效途径之一。

本文采用简单的电化学方法成功制备了一种由窄禁带半导体Cu₂O修饰的TiO₂纳米管(TNTs)的复合物,并运用扫描电子显微镜(SEM)、X射线衍射(XRD)以及X射线光电子能谱(XPS)表征了所制备复合物的形貌、化学组成和结晶度。表征结果显示,所制备的TiO₂为整齐排列的纳米管阵列结构;复合物中的纳米颗粒为Cu₂O;当电化学沉积Cu₂O的时间为5 min时,得到的Cu₂O纳米颗粒初步呈类八面体结构。随着沉积时间的增加,Cu₂O颗粒尺寸增加,具有八面体结构。XRD和XPS结果表明,TiO₂纳米管为锐钛矿,八面体Cu₂O纳米颗粒的主要暴露晶面为(111)面。我们还进一步研究了不同量Cu₂O纳米颗粒修饰的TiO₂纳米管复合物在可见光以及模拟太阳光下光催化还原CO₂的能力。在可见光下,由于自身的禁带宽度,纯净的TiO₂纳米管没有任何光催化还原CO₂的能力;经过Cu₂O纳米颗粒的修饰,复合物显现出明显的光催化还原CO₂的能力,其中经过30 min Cu₂O沉积的TNTs具有最高的光催化效率。在模拟太阳光下,经过15 min Cu₂O沉积的TNTs具有最高的光催化效率。在所有光催化还原CO₂过程中,主要碳氢产物为甲烷。为了深入地理解该复合体系在还原CO₂中的高催化效率,我们对催化剂进行了进一步的表征。紫外-可见漫反射光谱表明,Cu₂O八面体纳米颗粒的沉积将TNTs的吸收光谱拓展到了可见光区域,提高了复合物对太阳光的吸收能力。此外,我们还通过测试所制样品的光电流反应、荧光发射光谱以及电化学阻抗谱,研究了催化剂中光生电子和空穴的分离和迁移能力。结果表明,适量的Cu₂O沉积提高了复合物对光的吸收能力,增加了光生载流子的数量,从而使更多的光生载流子参与光催化反应。

综上,本文首次报道了八面体Cu₂O纳米颗粒修饰TNTs复合物的光催化还原CO₂的能力。在一定量的Cu₂O纳米颗粒修饰下,该复合物在光催化还原CO₂生成烃类反应中表现出高效性。经过一系列详细的表征和讨论,我们认为其高效性主要源于三个方面: (1) TNTs的管状结构为反应物的吸附提供了大量的活性位点,同时一维的管状结构更有利于光生载流子的运载,从而提高了电子和空穴的分离; (2) Cu₂O纳米颗粒的修饰提高了催化剂对光的吸收,促进催化剂最大程度地利用太阳光; (3) TiO₂和Cu₂O之间导带以及价带位置的匹配,在减少光生载流子复合的同时也降低了TiO₂价带上空穴的氧化能力,从而抑制了CO₂还原产物的再氧化过程。

关键词: 二氧化钛纳米管阵列; 八面体氧化亚铜纳米颗粒; 光催化二氧化碳还原; 碳氢产物; 光催化活性

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