A Facile Method for Preparation of Cu$_2$O-TiO$_2$ NTA Heterojunction with Visible-Photocatalytic Activity

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Abstract

Based on highly ordered TiO$_2$ nanotube arrays (NTAs), we successfully fabricated the Cu$_2$O-TiO$_2$ NTA heterojunction by a simple thermal decomposition process for the first time. The anodic TiO$_2$ NTAs were functioned as both "nano-container" and "nano-reactors" to load and synthesize the narrow band Cu$_2$O nanoparticles. The loaded Cu$_2$O expanded absorption spectrum of the TiO$_2$ NTAs from ultraviolet range to visible light range. We found that the Cu$_2$O-TiO$_2$ NTA heterojunction films had visible activity towards photocatalytic degrading methyl orange (MO). The photocatalytic abilities of the Cu$_2$O-TiO$_2$ NTA heterojunction films were found increased with the Cu$_2$O content from 0.05 to 0.3 mol/L. This could be explained by more electron-hole pairs generated and less recombination, when the Cu$_2$O-TiO$_2$ heterojunction got formed. Here, we put forward this promising method, hoping it can facilitate the mass production and applications of Cu$_2$O-TiO$_2$ NTA heterojunction.

Keywords: TiO$_2$ nanotube, Cu$_2$O, Heterojunction, Thermal decomposition, Visible photocatalysis

Background

With more and more attention paid to the environmental issues nowadays, the study of water treatment materials emerged in a continuous stream [1–4]. Hundreds of strategies were proposed for the treatment of polluted water. However, there were many problems, such as low efficiency, low recycling rate, and secondary environment pollution, restricting their further applications [5–7]. The semiconductor materials were considered to be a promising candidate, and titanium oxide was recognized as one of the best photocatalyst materials due to its high photocatalytic activity and good chemical and mechanical stability [8–12]. Recently, TiO$_2$ materials with nanotube (NT) array were widely studied, and the tubular morphology was proved to be a promising structure for photocatalysis. Compared with other microcosmic morphologies, TiO$_2$ NT arrays owned several significant advantages [13–17]. Firstly, unique tubular structure could enhance electron-transporting efficiency and restrain the recombination of carriers, which will further produce more reactive oxygen species (ROS) [18, 19]. Secondly, TiO$_2$ NT arrays are much easier to recycle than the TiO$_2$ powder photocatalysts [20–24]. Thirdly, TiO$_2$ NT arrays have large specific surface area and high surface energy. However, due to the relatively wide gaps (~3.2 eV), TiO$_2$ NT photocatalyst is only active under UV irradiation [25–28]. In fact, a photocatalyst that is able to respond with visible light will surely take obvious advantages. At present, the focus of photocatalyst research is to adjust their light response band and improve their photocatalytic efficiency.

Building heterogeneous TiO$_2$ photocatalysts with narrow band gaps is one of the hotspots as an attempt to overcome such impediments. Narrow band semiconductors, like Cu$_2$O, CdS, CdTe, PbS, and Bi$_2$O$_3$, have been studied to build TiO$_2$ heterojunction photocatalysts [29–34]. Among them, Cu$_2$O (with the direct gap
of ~ 2.2 eV) is regarded as one of the best candidates. For CuO, the response band is about 560 nm, and its band gap structure happens to well match with the energy level of TiO2 NTs. As schematically shown in Fig. 1, under the excitation of visible light, electron/hole pairs are generated and the photoinduced electrons are excited to the conduction band of Cu2O and then transfer to the conduction band of TiO2, which suppresses the recombination of electrons and holes. This heterojunction structure solves the problem that the TiO2 materials could not respond to visible light and the problem that electron/hole pairs generated on Cu2O get recombined easily. From this point of view, Cu2O-TiO2 NTA heterojunction materials guaranteed a natural advantage in visible light photocatalysis.

General approach to prepare Cu2O-TiO2 heterojunction photocatalysts includes chemical coprecipitation and electrodeposition, and the products have shown promising photocatalytic performances. But it is still a challenge to prepare Cu2O-TiO2 heterojunction photocatalysts with good quality by using a facile and low-cost method. Inspired by the concept of the precursor from Chemical vapor deposition (CVD), the idea, using acetate to carry copper ion to get into the inside of TiO2 NTs prepared by anodic oxidation, comes out. It is known that metal organic compounds are likely to get thermally decomposed. In this study, anodic TiO2 NTAs were crystallized into anatase by a thermal treatment at 450 °C. And then, they were used as substrate to prepare Cu2O-TiO2 NTA heterojunction film. First, cupric acetate (Cu(Ac)2) with different concentration was prepared, ranging from 0.05 to 0.3 mol/L. Then, annealed TiO2 NTAs were immersed into the solution transiently and dried in oven at 70 °C immediately. And the final products, Cu2O-TiO2 films, were marked as sample S1-S5 respectively by the different Cu(Ac)2 concentration of 0.05, 0.1, 0.2, 0.3, and 4 mol/L in this immersing process. After this process, the cupric acetate molecules had got into the TiO2 nanotubes. Next step was putting the samples into an atmosphere-sintering furnace of N2 with a sintering temperature of 400 °C for 150 min. The cupric acetate

![Fig. 1 Schematic structural diagram of Cu2O-TiO2 NTA heterojunction. Under visible light illumination, the electrons were excited to the conduction band of Cu2O particles and then transferred to the conduction band of TiO2 for the matching band gap structure](image)

**Experimental Section**

The chemicals which were mentioned in the experiment process were purchased (Sinopharm Group Chemical Reagent Co. Ltd., China) and used without further purification, except the deionized water with a resistance of 18.3 MΩ cm.

**Preparation of Pure TiO2 Nanotube Arrays**

Anodic oxidation method was used to prepare uniform and stable TiO2 NTAs with vertical alignment [35, 36]. Metal titanium (Ti) sheets were cut into pieces of 1.5 × 5 cm² and cleaned by a cleanser. After a sonication bath in ethanol, the Ti pieces were dried in oven. Electolyte consisted of 535.45 g glycol, 10 g deionized water, and 1.6617 g NH4F, which were mixed and stirred for 2 h. Then, we took two pieces of Ti as anode and cathode, respectively. Immersing them into electrolyte, applying a constant potential of 50 V for 2 h, amorphous TiO2 nanotube arrays (TiO2 NTAs) were fabricated at room temperature.

**Synthesis of Cu2O-TiO2 NTA Heterojunction**

The amorphous TiO2 NTAs were crystallized into anatase by a thermal treatment at 450 °C. And then, they were used as substrate to prepare Cu2O-TiO2 NTA heterojunction film. First, cupric acetate (Cu(Ac)2) with different concentration was prepared, ranging from 0.05 to 0.3 mol/L. Then, annealed TiO2 NTAs were immersed into the solution transiently and dried in oven at 70 °C immediately. And the final products, Cu2O-TiO2 films, were marked as sample S1-S5 respectively by the different Cu(Ac)2 concentration of 0.05, 0.1, 0.2, 0.3, and 4 mol/L in this immersing process. After this process, the cupric acetate molecules had got into the TiO2 nanotubes. Next step was putting the samples into an atmosphere-sintering furnace of N2 with a sintering temperature of 400 °C for 150 min. The cupric acetate
was thermal decomposed in a way described by Eq. (1). Finally, the Cu$_2$O-TiO$_2$ NTA heterojunction films were prepared. This process was schematically shown in Fig. 2.

$$\text{(CH}_3\text{COO)}_2\text{Cu} \xrightarrow{\Delta} \text{Cu}_2\text{O}↓ + \text{CH}_4↑ + \text{CO}_2↑ + \text{H}_2\text{O}↑ + \text{CO}↑$$

(1)

Just like holding a test tube containing cupric acetate, after heating, cupric acetate thermal decomposed into Cu$_2$O which was left inside the TiO$_2$ NTAs.

Characterization
A scanning electron microscopy (SEM, JSM-7000F, JEOL Inc., Japan) with energy dispersive spectrometer (EDS) was used for the observation of the morphology and structure. The samples were characterized by a D/max-2400 X-ray diffraction spectrometer (Rigaku, D/max-2400, Japan) and a UV-vis spectrometry (Ultrospec 2100 pro) was also used. To evaluate the photocatalytic activity of the as-synthesized Cu$_2$O-TiO$_2$ NTA heterojunction, we took methyl orange (MO), a typical organic indicator, as the degraded object. The Cu$_2$O-TiO$_2$ NTA films (3.0 × 1.5 cm$^2$) were immersed in 5 × 10$^{-5}$ mol/L of MO aqueous solution and irradiated with seven 4 W visible bulbs (Toshiba, Cool white, FL4W, Japan). Then, the solution was magnetically stirred in the dark for 30 min to ensure adsorption-desorption equilibrium prior to photocatalytic degradation. Photodegradation experiments lasted 180 min with 1.5 mL samples withdrawn periodically. The concentration of the residual MO was measured by a spectrophotometer at about 460 nm on the basis of the Beer-Lambert law. The degradation efficiency of the MO could be defined as follows:

$$\frac{C_t}{C_0} = \frac{A_t}{A_0} \times 100\%$$

(2)

And the varying of $A_t/A_0$ referred to the changing in $C_t$, which represented the photocatalytic activity of the tested samples.

Results and Discussion
Figure 3 shows a typical SEM observation of the pure anodic TiO$_2$ NTAs after annealing at 450 °C. Anodizing is an electrolytic process which converts the outer surface of metals into an oxide layer or pore structure. As shown in Fig. 3, the as-prepared TiO$_2$ NTs have open-tube morphology with a uniform outer diameter distribution of ∼100 nm. The anodic TiO$_2$ NTAs are highly ordered and oriented, and each single TiO$_2$ NT owns very smooth tube walls with an average thickness of ∼10 nm. Our former
studies have shown that tube length, the diameter, and morphology could be manipulated by adjusting the anodization protocols [37, 38]. The SEM results also indicate the thermal annealing at a high temperature of 450 °C does not destroy morphologies of the TiO$_2$ NTAs. XRD is used to characterize the crystalline of the pure TiO$_2$ NTAs (sample 1), see Fig. 4a. Results show that diffraction peaks locating at 25.3°, 36.9°, 37.8°, 48°, 53.9°, 55°, 62.7°, and 68.8° could be observed in sample 1, attributing to the (101), (103), (004), (200), (105), (211), (204), and (116) of anatase phase, respectively. As we know, there are three types of titanium dioxide phase, anatase, brookite, and rutile. Rutile could show relatively good photocatalytic ability with a granularity less than 10 nm. However, to get a rutile phase, the TiO$_2$ sample needs to be heated up to a high sinter temperature of 800 °C, which could lead to the break of TiO$_2$ tubes in this case. Brookite phase is hardly to be formed by using thermal annealing method for the bad thermodynamic phase stability, while anatase is the most common phase with good photocatalytic activity [39, 40]. The sharp diffraction peaks and the strong intensity of sample 1 (see Fig. 4a) indicated a highly crystallized anatase structure, which meant our TiO$_2$ substrate was excellent not only in the morphology but also in the crystalline phase. The highly ordered TiO$_2$ NTAs with open-tube mouth morphology were used as substrate to prepare Cu$_2$O-TiO$_2$ NTA heterojunction films in this study.

XRD patterns of the TiO$_2$ NTAs loaded with Cu$_2$O nanoparticles in concentration gradient ranging from 0.05 to 4.0 mol/L are also shown in Fig. 4a, and the 4.0 mol/L sample was prepared by a cycling immerse process described in Additional file 1, the “Experimental Details” part. The samples were named samples 2 to 4 with the increasing Cu(AC)$_2$ concentration. Except the TiO$_2$ peaks, there was no peak of Cu$_2$O showing up in sample 2 because of the tiny amount of the loading Cu$_2$O particles. And particles might be decorated inside of the TiO$_2$ “nano-container” which also raised the difficulty for characterization. In sample 3 and sample 4, obvious cuprite peaks could be observed at 29.6°, 36.4°, 42.3°, and 61.3°, attributing to the cuprite (110), (111), (200), and (220) of Cu$_2$O, respectively. It should be noted here that sample 4 was only used to characterize...
the existence of Cu$_2$O particles, and its synthetic details were described in Additional file 1. Moreover, the lattice parameters and the grain size were calculated based on the XRD data. After removing the background and K$_{\alpha 2}$ diffraction, and following the smoothing and fitting process, we got the average lattice parameters of our samples of $a = b = c = 4.2646$ Å, which matched with the standard PDF. The standard PDF showed that the lattice parameters of Cu$_2$O are: $a = b = c = 4.2696$ Å, and Cu$_2$O had a cubic structure [41]. The average grain size of Cu$_2$O was calculated as $\sim 47$ nm, by using Debye-Scherrer formula:

$$D = \frac{K\gamma}{B \cos \theta} \quad (3)$$

In Eq. (3), $D$ is the grain size, $K$ is the Scherrer constant, $\gamma$ is the wavelength of X-ray, $B$ is FWHM which needs to be in the radian, and $\theta$ is the diffraction angle. XRD results indicate that the Cu(Ac)$_2$ were loaded into the TiO$_2$ NTAs and successfully decomposed into Cu$_2$O inside the same TiO$_2$ NTAs, and then the Cu$_2$O-TiO$_2$ NTA heterojunction films got formed. To further investigate the Cu$_2$O-TiO$_2$ NTA heterojunction, an elemental analysis was carried out by using EDS. Figure 4b showed an EDS diagram of Cu$_2$O-TiO$_2$ NTA heterojunction film which was prepared with 0.2 mol/L Cu(Ac)$_2$. The atomic percentages were 7.32, 28.96, 57.45, and 6.27% for elements Cu, Ti, O, and impurity C. This result showed that the Cu$_2$O owned a relatively low content in the heterojunction sample, but it still brought about the visible-light activity, which would be discussed later in the MO degradation experiment. The EDS results well agreed with the XRD results in Fig. 4a that cuprite Cu$_2$O was successfully loaded to anatase NTAs.

Figure 5 showed the top view SEM results of the modified TiO$_2$ NTAs. Compared with the pure TiO$_2$ NTA samples in Fig. 3, a few small particles could be seen near the upper and inside of the TiO$_2$ tubes in Fig. 5a. Increasing the modification amount, a number of nanoparticles could be observed obviously in Fig. 5b. Figure 5c was sample 4 that we discussed before. Large parts of the tube surface were covered by the redundant Cu$_2$O, indicating that sample 4 was over-decorated. Based on the SEM images, the size distribution of Cu$_2$O particles was estimated ranging from $\sim 30$ to $\sim 80$ nm, which well agreed with XRD calculated grain size of $\sim 47$ nm. For the tubular structure of the three samples, they still retained the vertical alignment state, but some tubes got a little awry. It was considered as the influence of thermal decomposition process, which needed a heating process of 400 °C to get Cu(Ac)$_2$ decomposed into Cu$_2$O. High temperature in the decomposition step had a negative effect on the tubular structure, supported by the SEM images. However, if the heating temperature in the thermal process went too low to 240 °C, Cu(CH$_3$COO)$_2$·H$_2$O would just get dehydrated instead of decomposed. So the temperature should be controlled in $\sim 300$ to 400 °C to keep the nano-scale tubular structure and ensure the fabrication of Cu$_2$O-TiO$_2$ NTA heterojunction. It can be concluded that the Cu$_2$O-TiO$_2$ heterojunction could be formed, and the morphology retained well, when the decomposition happens at 400 °C.

The Cu$_2$O nanoparticles were loaded on TiO$_2$ NTAs to fabricate the heterojunction, which was expected to enhance the photo-response ability in visible light range, so UV-vis characterization was adopted to investigate optical properties of the as-synthesized Cu$_2$O-TiO$_2$ NTAs. Figure 6a shows the UV-vis absorption spectra of the Cu$_2$O-TiO$_2$ NTA samples with Cu$_2$O-loaded magnitude increasing from none to 4.0 mol/L. It could be seen in Fig. 6a that the pure TiO$_2$ NTAs without loading Cu$_2$O only showed out a high absorption in the ultraviolet region (< 380 nm), due to its intrinsic material properties. After loading the Cu$_2$O particles, the absorption range was expanded to 600–700 nm. And when the intensity is increasing with the raising of the Cu$_2$O modification magnitude, the absorption value of the Cu$_2$O-TiO$_2$ heterojunction films also got increased. Figure 6a indicated that TiO$_2$ NTAs were given the visible light response ability by
decorating Cu$_2$O nanoparticles. UV-vis along with SEM, EDS, and XRD results proved that the Cu$_2$O-TiO$_2$ NTA heterojunction was fabricated successfully by the thermal decomposition method, and samples showed the enhanced visible light absorption.

Photocatalytic activities, one of the most important properties of the Cu$_2$O-TiO$_2$ NTA films, were evaluated through degradation of MO aqueous solution. The visible-light photocatalytic degradation kinetics was shown in Fig. 6b. The MO degradation rate was proportion to the loading amount of Cu$_2$O approximately. The more Cu$_2$O particles were loaded on TiO$_2$ NTAs, the faster MO got degraded. Sample S1 degraded MO to 91.0% in 3 h under visible light irradiation, while sample S4 degraded MO to 86.4% in 3 h under the same condition. MO degradation rate represented the photocatalytic activity of the samples. Comparing with the photocatalytic degradation rate to the ~2.73% of CdTe-TiO$_2$ by a pulse electrodeposited method [29], ~45% of Bi$_2$O$_3$ by a ultrasonication-assisted successive ionic layer adsorption and reaction (SILAR) technique [32], and ~27.25% of Cu$_2$O by a square wave voltammetry method [33], photoactivity of this as-synthesized Cu$_2$O-TiO$_2$ sample was improvable. However, as a facile new strategy, it still conduced to improve fabrication method. When the Cu$_2$O loading amount went up, there was a trend that the photocatalytic activity of our as-synthesized Cu$_2$O-TiO$_2$ NTA heterojunction films increased. It indicated the Cu$_2$O content had a positive influence of the visible-light photocatalytic activity. TiO$_2$ itself only responded to ultraviolet, and the visible light range photocatalytic ability should come from the decoration of Cu$_2$O. As shown in Fig. 7, the conduction band bottom of Cu$_2$O was a little higher than that of TiO$_2$, while the valence band top of Cu$_2$O was higher than that of TiO$_2$. So, the photoinduced electrons were excited to the conduction band of Cu$_2$O and then transferred to the conduction band of TiO$_2$. As a direct-gap semiconductor, wave vector of Cu$_2$O was just the same at the bottom of the conduction band and the top of valence band. It meant that only the changes of energy were required, instead of the changes of momentum. This
energy band structure led to the situation that carriers recombined easily. However, due to the help of hetero-junction structure, the photogenerated electrons on Cu$_2$O transferred to TiO$_2$ NTAs which suppressed the recombination of electron/hole pairs. The longer the pairs existed, the more easily the ROS got produced which brought this photocatalytic activity. As more Cu$_2$O loaded on TiO$_2$ NTAs, the heterojunction fabricated better. And the photocatalytic activity got promoted. So, the Cu$_2$O content showed a positive influence of the visible-light photocatalytic activity. However, further increase of Cu$_2$O content as well as the photocatalytic ability is limited, due to the solubility of Cu(Ac)$_2$ in aqueous solution which was 7.2 g (0.36 mol/L) at room temperature. And sample S5 with Cu(Ac)$_2$ concentration of 4.0 mol/L is prepared by a cycling immersion process described in Additional file 1, the Experimental Details part. The photocatalytic degradation of the MO followed pseudo-first-order kinetics [42] and the kinetic reaction could be expressed as:

$$A_t = A_0 e^{-kt}$$  \hspace{1cm} (4)

While our degradation curve showed nearly a straight line, it is not an exponential function. So, there was still room for improvement. And the solubility limit could be broken by the repeated immersion method we mentioned before, with further investigation of the Cu(Ac)$_2$ concentration and repetition times to avoid adverse effects. In this study, as this thermal decomposition method was what we concerned and tried to illustrate, we just took the 0.3 mol/L (close the solubility of 0.36 mol/L) as the maximum concentration of Cu(Ac)$_2$ solution. And the photocatalytic activity in visible light range of our as-synthesized heterojunction was confirmed by the MO degradation results. Our previous study found that the Degussa P25 had similar ultraviolet photocatalytic activities with TiO$_2$ NTAs, when the power P25 was placed on a glass substrate [28]. It can be concluded that we have successfully prepared Cu$_2$O-TiO$_2$ NTA heterojunction films with visible-light photocatalytic activities.

Conclusions
In summary, we have successfully prepared the Cu$_2$O-TiO$_2$ NTA heterojunction films by a simple thermal decomposition process. SEM, EDS, and XRD results show that TiO$_2$ NTAs with a tube diameter of ~100 nm were loaded by Cu$_2$O nanoparticles with an average size of ~50 nm. The anodic TiO$_2$ NTAs functioned as both “nano-container” and “nano-reactors” to load and synthesize the narrow-band Cu$_2$O nanoparticles, which has not reported before. UV-vis spectra indicate that the absorption range of the TiO$_2$ NTAs was expanded from ultraviolet range to visible light range, due to the loading of Cu$_2$O. Photocatalytic testing indicated that there was a visible-light photocatalytic activity of the as-synthesized Cu$_2$O-TiO$_2$ heterojunction. The photocatalytic abilities of the Cu$_2$O-TiO$_2$ NTA heterojunction films were found to be increased with the Cu$_2$O content from 0.05 to 0.3 mol/L. Our current work has demonstrated a novel and facile method to prepare Cu$_2$O-TiO$_2$ NTA heterojunction films, which could also be promising for environmental and energy-related areas.

Additional file

Additional file 1: The experimental details of preparing the Cu$_2$O-TiO$_2$ samples and further characterization results of Raman spectra and XRD patterns are provided as the supplemental information to support the discussion. (DOCX 2387 kb)

Abbreviations
EDS: Energy-dispersive spectrometry; NTAs: Nanotube arrays; SEM: Scanning electron microscopy; XRD: X-ray diffraction

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Availability of Data and Materials
They are all in the main text and figures.

Authors’ Contributions
YL conceived and supervised the research, PD and XW conducted the experiments and wrote the manuscript. DZ, FL, QY, and HZ made the theoretical analysis. ZZ checked this article and put forward some revised opinions. All the authors discussed the results. All authors read and approved the final manuscript.

Competing Interests
The authors declare that they have no competing interests.

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