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A visible-light-active Au-Cu(I)@Na₂Ti₆O₁₃ nanostructured hybrid plasmonic photocatalytic membrane for acetaldehyde elimination

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ABSTRACT

The present article reports a novel self-standing nanostructured Au-Cu(I)@Na₂Ti₆O₁₃ plasmonic photocatalytic membrane, which is prepared by a hydrothermal reaction followed by a simple subsequent heat treatment process. The morphological structure, elemental composition, crystalline phases, and optical properties of the membrane were studied in detail by field-emission scanning electron microscopy, transmission electron microscopy, X-ray photoelectron spectroscopy, X-ray diffraction, and ultraviolet-visible spectroscopy. Compared with that of a pure Na₂Ti₆O₁₃ membrane, the Au-Cu(I)@Na₂Ti₆O₁₃ membrane displayed much higher photocatalytic activity for the decomposition of acetaldehyde, a typical volatile organic compound, under visible light illumination. It was found that the photocatalytic activity of the Au-Cu(I)@Na₂Ti₆O₁₃ membrane increased as the amount of Au was increased. The membrane loaded with 2.85 wt% Au showed the highest photocatalytic activity in the decomposition of acetaldehyde of the investigated materials. We found that in the photocatalyst membrane, Na₂Ti₆O₁₃ acted as a support material, Au displayed plasmonic absorption, and Cu(I) behaved as a co-catalyst. The present membrane materials can avoid the self-aggregation typically observed during the course of photocatalytic reactions. As a result, they can be easily separated, recycled, and reactivated after their practical application, making these functional materials attractive for use in air cleaning applications.

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1. Introduction

Volatile organic compounds (VOCs) are generally harmful pollutants that can greatly damage people's health [1]. Photocatalysis is regarded as an effective way to decompose the VOCs into CO₂, H₂O, and other harmless compounds [2]. Nanostructured photocatalytic materials have attracted much interest in recent years because of their large surface area and specific morphologies [3,4]. In particular, TiO₂ nanomaterials are promising photocatalysts because of their chemical inertness, non-toxicity, and low cost, and have been studied

extensively in the past decade [5–8]. However, the wide band gap (E_g) [9,10] of TiO₂ means that it only responds to ultraviolet (UV) light, which accounts for just 5% of the total solar energy [11–13]. In addition to TiO₂, other titanium compounds such as alkali metal titanates have also drawn some attention for use in photocatalysis [14–16]. Titanate materials are easy to synthesize and display excellent chemical and mechanical properties. Hydrothermal treatment of TiO₂ powder in a concentrated alkaline solution is a commonly used approach to prepare alkali metal titanates with nanowire and nanotube morphologies [9,17]. Such materials display obvious

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photocatalytic activity under UV illumination [18]. For example, it has been reported that $\text{Na}_2\text{Ti}_6\text{O}_{13}$ materials can decompose 4-chlorophenol under UV illumination [19,20]. Like TiO_2 , these materials respond to UV light because of their large E_g . Other interesting technological applications for $\text{Na}_2\text{Ti}_6\text{O}_{13}$ such as capacitors, dielectric sensors, and biosensors have been also reported [21].

Through coupling with a noble metal, such as Au, Pt, or Ag, TiO_2 and alkali metal titanates can make use of visible light in photocatalysis by localized surface plasmonic resonance (LSPR) absorption [22–26]. For example, TiO_2 showed a notable photocurrent response in the visible light region after being coupled with Ag nanoparticles because of the LSPR effect [27–30]. Deposition of Au nanoparticles on titanate nanobelts also resulted in obvious visible-light photocatalytic activity [31]. In addition to noble metals, loading of oxide co-catalysts onto TiO_2 can also increase its photocatalytic activity via surface electronic structure coupling [32,33]. Amorphous copper oxide (Cu_xO) and copper hydroxide ($\text{Cu}(\text{OH})_x$) nanoclusters have attracted much interest as co-catalysts. The deposition of Cu^{2+} nanoclusters onto $\text{Na}_2\text{Ti}_3\text{O}_7$ greatly increased its photocatalytic activity in the oxidation of cyclohexa-1,4-diene [34]. This is because using Cu^{2+} nanoclusters as surface active sites can effectively enhance the photocatalytic hydrogen generation of TiO_2 . Irie et al. [35] reported that interfacial charge transfer (IFCT) between Cu^{2+} and rutile TiO_2 could induce the photocatalytic oxidation reaction, resulting in decomposition of gaseous isopropanol or acetaldehyde. However, it was also found that Cu^{2+} nanoclusters might increase charge recombination and resulted in decreased photocatalytic activity [36]. Choi and co-workers reported that photoinduced electron transfer to grafted $\text{Cu}(\text{I})$ or $\text{Cu}(\text{II})$ might lead to the in situ formation of metallic Cu, which can act as an effective co-catalyst [37,38].

The above photocatalyst materials mainly exist in the form of ultrafine powders, which are usually difficult to separate and recycle after photocatalysis, inevitably leading to secondary pollution during their practical application. Photocatalytic materials that are easily separated and recycled are needed. In the present research, a novel membrane composed of ultralong sodium titanate nanofibers is prepared by a modified hydrothermal reaction and used to remove indoor VOCs. Both Au nanoparticles and $\text{Cu}(\text{I})$ nanoclusters are loaded on the surface of the sodium titanate membrane to access LSPR absorption and accelerate electron-hole separation, respectively. The obtained $\text{Au-Cu}(\text{I})@\text{Na}_2\text{Ti}_6\text{O}_{13}$ hybrid membrane presents high photocatalytic activity under visible-light illumination. The membrane resists self-aggregation, and can be easily separated and recycled. This self-standing membrane is attractive for air purification under visible-light illumination.

2. Experimental

2.1. Material preparation

Tetrabutyl titanate (TBOT), ethanol, acetic acid, and

polyvinylpyrrolidone K30 (PVP K30) were used to prepare the precursor materials for hydrothermal reactions. The precursor materials were synthesized by the electrospray method, as reported elsewhere [39]. Briefly, PVP K30 (0.3 g) was dissolved in ethanol (2.5 mL) and acetic acid (3.8 mL) by stirring for 10 min. TBOT (7.0 mL) was added to the mixture, which was then vigorously stirred for 1 h to obtain a yellow PVP@TBOT sol-gel. The PVP@TBOT sol was aged in the dark for 10 h. The PVP@TBOT sol was placed into a syringe pump and then automatically pumped through a metal needle at a fixed speed of 2.5 mL/h. A voltage of 15 kV was applied to the metal needle, causing the PVP@TBOT sol to atomize into very tiny droplets, which were sprayed on an aluminum target. After electrospraying, the aluminum target was dried in air for one day, and then the electrosprayed materials were collected from the aluminum target for further hydrothermal treatment.

$\text{Na}_2\text{Ti}_6\text{O}_{13}$ nanowires were synthesized in fresh NaOH solution by the hydrothermal method. Precursor (0.2 g) was added to a sealed Teflon reactor (volume: 50 mL) containing aqueous NaOH (30 mL, 10 mol/L). The stirred mixture was heated at 180 °C in an oil bath for 12 h. If the solution was not stirred during the hydrothermal reaction, no nanofibers were obtained. After cooling to room temperature, the hydrothermal products were washed with deionized water several times until the pH of the filtrate reached ~7. The sample was transferred into ethanol and vigorously stirred for 10 min. The mixture was heated at 80 °C to remove ethanol and obtain a membrane. The membrane was annealed in air at 450 °C for 2 h to increase its crystallinity.

Au nanoparticles and then $\text{Cu}(\text{x})$ nanoclusters were loaded on the membrane by thermal deposition using HAuCl_4 and $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, respectively. The membrane was immersed in 5×10^{-3} mol/L HAuCl_4 aqueous solution at 70 °C. The pH was adjusted to 6 using 0.2 mol/L NaOH solution. The immersion time was regulated to adjust the amount of Au deposited on the membrane. After immersion for a certain time, the sample was washed with deionized water several times, dried in air at 70 °C, and then annealed at 300 °C for 2 h to generate Au nanoparticles. The resulting samples are denoted as $\text{Au}(\text{M})@\text{Na}_2\text{Ti}_6\text{O}_{13}$, where *M* is the time immersed in HAuCl_4 solution (in minutes).

$\text{Na}_2\text{Ti}_6\text{O}_{13}$ membranes were also immersed in 1.60×10^{-3} mol/L CuCl_2 aqueous solution at 90 °C. The immersion time was used to adjust the amount of $\text{Cu}(\text{x})$ loaded on the membrane. Each sample was washed with deionized water several times and then dried in air at 70 °C. Finally, each sample was heated at 150 °C for 2 h to generate $\text{Cu}(\text{x})$ on the membrane. These samples are denoted as $\text{Cu}(\text{x})(\text{N})@\text{Na}_2\text{Ti}_6\text{O}_{13}$, where *N* is the time immersed in CuCl_2 solution (in minutes), and *x* is the valence state of Cu. In the same manner, each $\text{Au}(\text{M})@\text{Na}_2\text{Ti}_6\text{O}_{13}$ membrane was immersed in 1.58×10^{-3} mol/L CuCl_2 solution to produce hybrid $\text{Au}(\text{M})\text{-Cu}(\text{x})(\text{N})@\text{Na}_2\text{Ti}_6\text{O}_{13}$ membranes.

2.2. Characterization

Surface images of the pure $\text{Na}_2\text{Ti}_6\text{O}_{13}$, $\text{Au}(\text{5})@\text{Na}_2\text{Ti}_6\text{O}_{13}$,

Cu(x)(40)@Na₂Ti₆O₁₃, and Au(5)-Cu(x)(40)@Na₂Ti₆O₁₃ membranes were observed by field-emission scanning electron microscopy (FE-SEM; S-4800, Hitachi, Tokyo, Japan) and transmission electron microscopy (TEM; JEM2100F, JEOL, Tokyo, Japan). The Au and Cu atomic contents in the samples were determined by inductively coupled plasma (ICP) optical emission spectrometry (Prodigy 7, Leeman Labs, USA). X-ray diffraction (XRD) patterns were collected with a grazing-incidence X-ray diffractometer (Empyrean, PANalytical, Almelo, the Netherlands) using Cu K α radiation as the X-ray source. The surface chemical compositions of the Au(5)@Na₂Ti₆O₁₃, Cu(x)(40)@Na₂Ti₆O₁₃, and Au(5)-Cu(x)(40)@Na₂Ti₆O₁₃ membranes were analyzed with an X-ray photoelectron spectrometer (XPS; VG Multilab 2000, Thermo Scientific, USA) with Al K α radiation as the X-ray source. The binding peak of C 1s electrons at 284.6 eV was used as a reference. Ultraviolet-visible (UV-vis) diffuse reflectance spectra of samples were measured using a UV-Vis spectrophotometer (UV-3600, Shimadzu, Japan) in wavelength range from 200 to 800 nm.

The typical indoor air pollutant acetaldehyde was chosen as the target organic to evaluate the photocatalytic activity of the membranes. The photocatalysis experiments were performed in a transparent cylindrical glass reactor with a volume of 500 mL and quartz window. The light source was a high-power Hg lamp with a 420-nm cut-off long-pass filter to provide visible light. The membrane sample (200 mg) was placed in the sealed glass photocatalytic reactor, and the temperature was kept at 25 °C. Before starting the photocatalytic experiments, fresh air with a relative humidity of 50% was flowed through the reactor for 10 min. Then, the reactor was irradiated with UV light overnight to remove organic pollutants on the sample surface. The reactor was then filled with fresh air. Acetaldehyde (120 ppm) was injected into the reactor and the reactor was placed in the dark until the concentration of acetaldehyde became stable. A gas chromatograph (GC-2014C, Shimadzu, Japan) was used to analyze the concentration of acetaldehyde during the photocatalytic reaction.

3. Results and discussion

Fig. 1(a) shows the Ti 2p_{1/2} and Ti 2p_{3/2} spectra of pure Na₂Ti₆O₁₃, Au(5)@Na₂Ti₆O₁₃, Cu(x)(40)@Na₂Ti₆O₁₃, and Au(5)-Cu(x)(40)@Na₂Ti₆O₁₃ membranes. All of the Ti 2p spectra are symmetrical, indicating the +4 valence of Ti atoms. Because the

work function of Na₂Ti₆O₁₃ is higher than that of Au, electrons will move from Na₂Ti₆O₁₃ to Au when they are connected. The decrease of electron density near Ti atoms leads to a positive shift of the Ti 2p spectra in the presence of Au, as shown in Fig. 1(a). In contrast, no obvious shift was observed when Na₂Ti₆O₁₃ was loaded with Cu(x), indicating that there was no charge exchange between these species. Fig. 1(b) displays the Au 4f_{7/2} and Au 4f_{5/2} spectra of the Au(5)@Na₂Ti₆O₁₃ and Au(5)-Cu(x)(40)@Na₂Ti₆O₁₃ membranes, which indicate that the Au nanoparticles are metallic. In the Cu 2p spectra (Fig. 1(c)), Cu 2p_{1/2} and Cu 2p_{3/2} peaks were observed at 952.5 and 932.5 eV, respectively. The 20 eV splitting of these peaks is consistent with the presence of Cu(I). Considering that the characteristic shake-up satellite lines of Cu(II) are absent, the presence of Cu(II) can be excluded [40]. These results are consistent with the membrane fabrication process; lower temperature calcination aids the formation of Cu(I) species, whereas higher temperature treatment leads to the formation of Cu(II) species [41].

The XRD patterns of the pure Na₂Ti₆O₁₃, Au(5)@Na₂Ti₆O₁₃, Cu(I)(40)@Na₂Ti₆O₁₃, and Au(5)-Cu(I)(40)@Na₂Ti₆O₁₃ membranes are shown in Fig. 2. The pure Na₂Ti₆O₁₃ membrane presents a pattern consistent with the main phase of Na₂Ti₆O₁₃. The diffraction peak at 25.1° could be assigned to the (110) lattice plane of Na₂Ti₆O₁₃ or (100) lattice plane of anatase TiO₂. The diffraction peak at 54.3° could originate from the (514) lattice plane of Na₂Ti₆O₁₃ or (105) lattice plane of anatase TiO₂. However, according to the TEM analysis (Fig. 4), only single-phase Na₂Ti₆O₁₃ was observed. Therefore, the above two peaks are assigned to the diffractions of the Na₂Ti₆O₁₃ phase because there is no anatase TiO₂ in the Na₂Ti₆O₁₃ membrane. No diffraction peaks from Cu metal and its oxides were observed in the XRD patterns of the Cu(I)(40)@Na₂Ti₆O₁₃ and Au(5)-Cu(I)(40)@Na₂Ti₆O₁₃ membranes because of the low amount of loaded Cu(I). The XRD patterns of the Au(5)@Na₂Ti₆O₁₃ and Au(5)-Cu(I)(40)@Na₂Ti₆O₁₃ membranes display diffraction peaks at 38.2°, 66.4°, and 77.5°, which are assigned to the (111), (220), and (311) lattice planes of metallic gold, respectively. The XRD patterns indicated that loading Cu(I) on the Na₂Ti₆O₁₃ membrane surface greatly decreased the amount of Au nanoparticles loaded previously.

Fig. 3(a) shows that the electrosprayed precursor materials possess dense spherical morphology with rough surfaces. A digital photograph of the as-prepared pure Na₂Ti₆O₁₃ mem-

Fig. 1. High-resolution Ti 2p spectra (a), high-resolution Au 4f spectra (b), and high-resolution Cu 2p spectra of membranes (c).

Fig. 2. XRD patterns of pure $\text{Na}_2\text{Ti}_6\text{O}_{13}$ (1), $\text{Au}(5)@Na_2Ti_6O_{13}$ (2), $\text{Cu(I)}(40)@Na_2Ti_6O_{13}$ (3), and $\text{Au}(5)\text{-Cu(I)}(40)@Na_2Ti_6O_{13}$ (4) membranes.

brane with a diameter of ca. 10 cm is illustrated in Fig. 3(b). Fig. 3(c) reveals that the membrane consists of ultralong $\text{Na}_2\text{Ti}_6\text{O}_{13}$ nanofibers. The large pores between the nanofibers allow air to flow through the membrane, so it can be used as a support for photocatalytic air purification. Fig. 3(d) indicates that the nanofiber surfaces of the $\text{Au}(5)@Na_2Ti_6O_{13}$ membrane are covered with gold nanoparticles with an average size of ~ 10 nm. Meanwhile, Fig. 3(e) shows that the nanofibers do not show

Fig. 3. SEM images of electrospun precursor (a), pure $\text{Na}_2\text{Ti}_6\text{O}_{13}$ nanofibers (c), $\text{Au}(5)@Na_2Ti_6O_{13}$ membrane (d), $\text{Cu(I)}(40)@Na_2Ti_6O_{13}$ membrane (e), and $\text{Au}(5)\text{-Cu(I)}(40)@Na_2Ti_6O_{13}$ membrane (f). Digital photograph of the pure $\text{Na}_2\text{Ti}_6\text{O}_{13}$ membrane (b).

Fig. 4. TEM (a) and high-resolution TEM (b) images of the $\text{Au}(5)\text{-Cu(I)}(40)@Na_2Ti_6O_{13}$ membrane.

change obviously after being loaded with Cu(I) to form the $\text{Cu(I)}(40)@Na_2Ti_6O_{13}$ membrane, which may be because of the small size of the Cu(I) nanoclusters. Fig. 3(f) reveals that the $\text{Au}(5)\text{-Cu(I)}(40)@Na_2Ti_6O_{13}$ membrane contained less Au nanoparticles on the nanofiber surface than that of the $\text{Au}(5)@Na_2Ti_6O_{13}$ membrane. This shows that some of the Au nanoparticles were removed during the loading of the Cu(I) nanoclusters, which is in accordance with the results of XRD analysis. The loading of Cu(I) and Au was also observed by high-resolution TEM, as shown in Fig. 4(a) and (b). Many spherical Au nanoparticles were present on the $\text{Na}_2\text{Ti}_6\text{O}_{13}$ nanofiber surface. Fig. 4(b) reveals that the Cu(I) nanoclusters had a size of ~ 2.5 nm. Considering the low-temperature deposition process used to load the Cu(I) nanoclusters, the above results indicate that the Cu(I) nanoclusters are composed of amorphous Cu_2O and Cu(OH) . The TEM results revealed the small size of the Cu(I) nanoclusters, supporting the conclusion that Cu(I) is more stable than Cu(II) when the particle size is very small [36]. The actual loadings of Au and Cu(I) , Au nanoparticle size, and Cu(I) nanocluster size of $\text{Au}(5)@Na_2Ti_6O_{13}$, $\text{Cu(I)}(40)@Na_2Ti_6O_{13}$, and $\text{Au}(5)\text{-Cu(I)}(40)@Na_2Ti_6O_{13}$ are summarized in Table 1.

Fig. 5 shows the UV-vis diffuse reflectance spectra of pure $\text{Na}_2\text{Ti}_6\text{O}_{13}$, $\text{Cu(I)}(40)@Na_2Ti_6O_{13}$, $\text{Au}(5)@Na_2Ti_6O_{13}$, and $\text{Au}(5)\text{-Cu(I)}(40)@Na_2Ti_6O_{13}$ membranes. Au and Cu(I) loading had clear effects on the absorption spectra of the membranes. The strong absorptions from 300 to 400 nm are caused by the band-to-band transition of $\text{Na}_2\text{Ti}_6\text{O}_{13}$. The small amount of anatase phase present in the materials may also contribute to this absorption. For the $\text{Cu(I)}(40)@Na_2Ti_6O_{13}$ membrane, the grafting of Cu(I) increased the absorption intensity in the regions from 400 to 500 nm and 700 to 800 nm. The absorption at 700–800 nm was assigned to the Cu(I) $d\text{-}d$ transition. The absorption at 400–500 nm may arise from the direct IFCT from the valence band (VB) of $\text{Na}_2\text{Ti}_6\text{O}_{13}$ to Cu(I) [42]. The plasmonic absorption peaks of the $\text{Au}(5)@Na_2Ti_6O_{13}$ and

Table 1

Compositions of Au-, Cu-, and Au-Cu(I)-modified $\text{Na}_2\text{Ti}_6\text{O}_{13}$ samples determined by thermal deposition.

Photocatalyst	Loaded amount (wt %)		Mean size (nm)	
	Au	Cu	Au	Cu
$\text{Au}(5)@Na_2Ti_6O_{13}$	2.85	0	~ 10	—
$\text{Cu(I)}(40)@Na_2Ti_6O_{13}$	0	0.30	—	~ 2.5
$\text{Au}(5)\text{-Cu(I)}(40)@Na_2Ti_6O_{13}$	1.88	0.25	~ 10	~ 2.5

Fig. 5. UV-Vis diffuse reflectance spectra of pure $\text{Na}_2\text{Ti}_6\text{O}_{13}$, $\text{Au}(5)@ \text{Na}_2\text{Ti}_6\text{O}_{13}$, $\text{Cu}(\text{I})(40)@ \text{Na}_2\text{Ti}_6\text{O}_{13}$, and $\text{Au}(5)\text{-Cu}(\text{I})(40)@ \text{Na}_2\text{Ti}_6\text{O}_{13}$ membranes.

$\text{Au}(5)\text{-Cu}(\text{I})(40)@ \text{Na}_2\text{Ti}_6\text{O}_{13}$ membranes appeared at ~ 560 nm, resulting in the violet color of the Au-modified samples.

The amount of Au loaded on the membranes was changed by varying the loading time. The ICP analysis showed that the Au contents of the $\text{Au}(2)@ \text{Na}_2\text{Ti}_6\text{O}_{13}$, $\text{Au}(5)@ \text{Na}_2\text{Ti}_6\text{O}_{13}$, $\text{Au}(10)@ \text{Na}_2\text{Ti}_6\text{O}_{13}$, and $\text{Au}(30)@ \text{Na}_2\text{Ti}_6\text{O}_{13}$ membranes were 0.93, 2.85, 8.09, and 17.64 wt%, respectively. Fig. 6 shows the effect of Au content on the photocatalytic activities of the $\text{Au}@ \text{Na}_2\text{Ti}_6\text{O}_{13}$ membrane samples. The adsorption-desorption equilibrium of acetaldehyde on the sample surface in the dark was almost achieved after 30 min. The pure $\text{Na}_2\text{Ti}_6\text{O}_{13}$ membrane displayed the lowest photocatalytic activity of the samples; the concentration of acetaldehyde changed only slightly over 330 min. The low visible-light activity of the pure $\text{Na}_2\text{Ti}_6\text{O}_{13}$ nanofiber membrane should originate from the presence of intrinsic defects, such as oxygen vacancies, because they can also induce some gap states to absorb some visible light [43,44]. Compared with that of the pure $\text{Na}_2\text{Ti}_6\text{O}_{13}$ membrane, the photocatalytic activity of the membranes was greatly increased after Au deposition, which should be ascribed to function of LSPR absorption (Fig. 6). The LSPR absorption ex-

Fig. 6. Relative acetaldehyde concentration change under visible-light illumination in the presence of pure $\text{Na}_2\text{Ti}_6\text{O}_{13}$, $\text{Au}(2)@ \text{Na}_2\text{Ti}_6\text{O}_{13}$, $\text{Au}(5)@ \text{Na}_2\text{Ti}_6\text{O}_{13}$, $\text{Au}(10)@ \text{Na}_2\text{Ti}_6\text{O}_{13}$, and $\text{Au}(30)@ \text{Na}_2\text{Ti}_6\text{O}_{13}$ membranes.

cites the electrons in Au nanoparticles to higher energy levels, which allows them to flow to the conduction band (CB) of $\text{Na}_2\text{Ti}_6\text{O}_{13}$ nanofibers, resulting in their separation from the holes in Au nanoparticles. As a consequence, the holes left in the Au nanoparticles have enough time to oxidize organic molecules rather than recombining with electrons, leading to the plasmonic photocatalytic effect. In addition, O_2 can be reduced by the electrons in the CB of $\text{Na}_2\text{Ti}_6\text{O}_{13}$. Fig. 6 reveals that the photocatalytic activity of the $\text{Au}@ \text{Na}_2\text{Ti}_6\text{O}_{13}$ membranes first increases and then decreases with the increased loading of Au. The $\text{Au}(5)@ \text{Na}_2\text{Ti}_6\text{O}_{13}$ membrane displayed the highest photocatalytic activity of the samples. The initial increase of photocatalytic activity upon Au deposition is mainly caused by the increase of LSPR absorption. In addition to the LSPR effect, surface plasmon resonance of Au nanoparticles can generate enhanced localized electric fields, which may also partially contribute to the increased photocatalytic effect [45–47]. Loading with a high content of Au nanoparticles resulted in decreased photocatalytic activity, indicating increased carrier recombination, which is possibly caused by the accelerated back interfacial transfer of electrons from $\text{Na}_2\text{Ti}_6\text{O}_{13}$ to Au nanoparticles.

Fig. 7(a) shows the time-dependent change of acetaldehyde concentration during photocatalysis by the pure $\text{Na}_2\text{Ti}_6\text{O}_{13}$, $\text{Cu}(\text{I})(40)@ \text{Na}_2\text{Ti}_6\text{O}_{13}$, $\text{Au}(5)@ \text{Na}_2\text{Ti}_6\text{O}_{13}$, and $\text{Au}(5)\text{-Cu}(\text{I})(40)@ \text{Na}_2\text{Ti}_6\text{O}_{13}$ membranes under visible-light illumination. Over the $\text{Cu}(\text{I})(40)@ \text{Na}_2\text{Ti}_6\text{O}_{13}$ membrane, 78% of acetaldehyde was decomposed after 300 min, clearly showing promising visible-light photocatalytic activity. In the $\text{Cu}(\text{I})(40)@ \text{Na}_2\text{Ti}_6\text{O}_{13}$ membrane system, it is suggested that the visible-light illumination can initiate the IFCT [48] of electrons to Cu(I) nanoclusters; i.e., the electrons in the VB of $\text{Na}_2\text{Ti}_6\text{O}_{13}$ are transferred directly to Cu(I), and part of the Cu(I) is then reduced to Cu(0). The holes produced in the VB of $\text{Na}_2\text{Ti}_6\text{O}_{13}$ have strong oxidative power to induce the decomposition of organic compounds such as aldehydes. Meanwhile, the excited electrons in the Cu(I) nanoclusters are capable of reducing the adsorbed O_2 via multi- or single-electron interfacial transfer pathways [49]. After photocatalytic reaction, the Cu(0) is easily oxidized to Cu(I), ensuring the good stability and sustainability of the Cu(I)-loaded membrane photocatalysts [50–52]. Consequently, the $\text{Cu}(\text{I})(40)@ \text{Na}_2\text{Ti}_6\text{O}_{13}$ membrane exhibited photocatalytic activity under visible-light illumination [53]. For the $\text{Au}(5)@ \text{Na}_2\text{Ti}_6\text{O}_{13}$ membrane, 93% of the acetaldehyde present was decomposed after 60 min. The photocatalytic activity was further increased by loading with Cu(I) nanoclusters, with 98% acetaldehyde removal after 45 min of visible-light illumination.

The photocatalytic reactions were fitted with first-order kinetics, as shown in Fig. 7(b). Rate constants (k) were estimated by the linear fittings of time dependence of $\ln(C_t/C_0)$. The k values of the pure $\text{Na}_2\text{Ti}_6\text{O}_{13}$, $\text{Cu}(\text{I})(40)@ \text{Na}_2\text{Ti}_6\text{O}_{13}$, $\text{Au}(5)@ \text{Na}_2\text{Ti}_6\text{O}_{13}$, and $\text{Au}(5)\text{-Cu}(\text{I})(40)@ \text{Na}_2\text{Ti}_6\text{O}_{13}$ membranes are 1.0×10^{-3} , 5.0×10^{-3} , 0.05, and 0.11 min^{-1} , respectively. These results show that the $\text{Au}(5)\text{-Cu}(\text{I})(40)@ \text{Na}_2\text{Ti}_6\text{O}_{13}$ membrane presents the highest activity of the samples, which is 110 times higher than that of the pure $\text{Na}_2\text{Ti}_6\text{O}_{13}$ membrane. Even though the actual Au content of the $\text{Au}(5)\text{-Cu}(\text{I})(40)@ \text{Na}_2\text{Ti}_6\text{O}_{13}$ mem-

Fig. 7. (a) Relative acetaldehyde concentration change under visible-light illumination in the presence of pure Na₂Ti₆O₁₃, Cu(I)(40)@Na₂Ti₆O₁₃, Au(5)@Na₂Ti₆O₁₃, and Au(5)-Cu(I)(40)@Na₂Ti₆O₁₃ membranes; (b) First-order kinetics for acetaldehyde decomposition by the pure Na₂Ti₆O₁₃, Cu(I)(40)@Na₂Ti₆O₁₃, Au(5)@Na₂Ti₆O₁₃, and Au(5)-Cu(I)(40)@Na₂Ti₆O₁₃ membranes.

brane was decreased during the loading of Cu(I) nanoclusters (Table 1), the Au(5)-Cu(I)(40)@Na₂Ti₆O₁₃ membrane exhibited higher photocatalytic activity than those of the Au@Na₂Ti₆O₁₃ and Cu(I)@Na₂Ti₆O₁₃ membranes. This is because the Cu(I) nanoclusters enhanced charge separation, which increased the visible-light activity of the Au(5)-Cu(I)(40)@Na₂Ti₆O₁₃ membrane.

For the Au(5)-Cu(I)(40)@Na₂Ti₆O₁₃ membrane system, as shown in Fig. 8, the photoexcited electrons in Au nanoparticles can transfer to the CB of Na₂Ti₆O₁₃ nanofibers. The one-dimensional single-crystalline Na₂Ti₆O₁₃ nanofibers display relatively high electron transport ability compared to that of nanocrystalline materials, which should be beneficial for the efficient separation of electrons and holes. For the samples loaded with both Cu(I) nanoclusters and Au nanoparticles, most of the visible light was absorbed because of the LSPR of Au nanoparticles. The photoinduced electrons in Au nanoparticles can undergo interfacial electron transfer to the CB of Na₂Ti₆O₁₃ nanofibers. As a result of the lowering of the Fermi energy, acetaldehyde is then oxidized on the Au nanoparticle surface. At the same time, the electrons in the CB of Na₂Ti₆O₁₃ can be trapped by the amorphous Cu(I) nanoclusters. It has been indicated that Cu(I) nanoclusters

could act as catalytic sites for the interfacial transfer of electrons to O₂, which would further facilitate the electron-hole separation and electron interfacial transfer [54]. As a result, the lifetimes of both the excited electrons and holes are prolonged, which would increase their probability for interfacial transfer and subsequent involvement in contaminant decomposition.

4. Conclusions

A novel self-standing visible-light-active Au-Cu(I)@Na₂Ti₆O₁₃ nanostructured hybrid membrane was prepared. Compared with those of pure Na₂Ti₆O₁₃, Au@Na₂Ti₆O₁₃, and Cu(I)@Na₂Ti₆O₁₃ membranes, the hybrid membrane presented higher photocatalytic activity for acetaldehyde decomposition. In photocatalysis by the Au@Na₂Ti₆O₁₃ membranes, visible light absorption through the LSPR of Au nanoparticles induced electron transfer from the Au nanoparticles to the CB of Na₂Ti₆O₁₃. Because the loaded Cu(I) behaved as an electron trap, the recombination of electrons in the CB of Na₂Ti₆O₁₃ with the holes remaining in Au nanoparticles was suppressed. Therefore, the lifetimes of both excited electrons and holes were prolonged, promoting their involvement in photocatalysis. This membrane material avoids aggregation during practical application, and can be easily separated and recycled after photocatalytic reaction, making it attractive for air purification.

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Fig. 8. Schematic diagram of the charge transfer process of the Au-Cu(I)-loaded membrane.

Graphical Abstract

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A visible-light-active Au-Cu(I)@Na₂Ti₆O₁₃ nanostructured hybrid pasmonic photocatalytic membrane for acetaldehyde elimination

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Two-step method was used to prepare Au-Cu(x)@Na₂Ti₆O₁₃ membranes, which show high photocatalytic activity for acetaldehyde elimination under the visible light illumination due to the synergetic effect between Au plasmonic absorption and Cu(x) co-catalytic effect.

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一种可见光活性的等离子体纳米Au-Cu(I)@Na₂Ti₆O₁₃光催化滤膜的制备和对乙醛的降解

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摘要: 室内环境的空气质量对人们生活和健康的影响很大. 其中挥发性有机物(VOCs)如乙醛、甲醛、丙酮、苯和甲苯等是室内环境污染的主要来源之一, 它们会引起机体免疫力水平失调, 影响中枢神经功能, 还可影响消化系统, 严重时还可损伤肝脏和造血功能等. 因此, 消除这些VOCs变得刻不容缓.

本文报道了一种新型等离子体纳米Au-Cu(I)@Na₂Ti₆O₁₃光催化薄膜. 钛酸盐材料容易制备, 且具有良好的化学和机械性能, 目前多应用于电容器、传感器和光催化领域. 此薄膜采用水热法制备并进一步热处理得到, 该法简单易操作, 水热时间较短且成本低廉. 另外通过热置沉积的方法分别将Au纳米颗粒和Cu(I)成功负载到Na₂Ti₆O₁₃滤膜上. 分别使用场发射扫描电子显微镜(FE-SEM)、透射电子显微镜(TEM)、X射线光电子光谱仪(XPS)、X射线衍射仪(XRD)和UV-Vis光谱仪研究了薄膜的形态结构、元素组成、晶相组成和光学性能.

SEM和TEM结果表明, Na₂Ti₆O₁₃滤膜由超长的Na₂Ti₆O₁₃纳米纤维组成. 纳米纤维之间存在较大的孔, 可以使空气自由通过. XRD, XPS和UV-Vis结果发现, Au纳米颗粒和铜纳米簇成功地负载在Na₂Ti₆O₁₃滤膜上, 且铜呈无定形态, 价态为+1. 相应的催化结果表明, 在可见光照射下, 相比于纯Na₂Ti₆O₁₃滤膜, Au-Cu(I)@Na₂Ti₆O₁₃滤膜显示出非常高的降解乙醛活性. 结果发现, Na₂Ti₆O₁₃滤膜的可见光活性随着负载的Au纳米颗粒含量的增加呈现先增加后降低的趋势, 当Au纳米颗粒的含量为2.85 wt%时达到最大. 使用超长Na₂Ti₆O₁₃纳米纤维作为支撑材料, Au纳米颗粒的等离子体可见光吸附导致电子从Au纳米颗粒迁移到Na₂Ti₆O₁₃的导带, 并被表面负载的Cu(I)俘获, 有效地避免了Na₂Ti₆O₁₃中导带电子和留在Au纳米颗粒上空穴的复合, 延长了电子和空穴的寿命, 进而提高了滤膜的可见光催化活性. Na₂Ti₆O₁₃滤膜可以有效地避免粉体在光催化反应过程中发生团聚, 因而在实际应用过程中易分离, 避免了二次污染, 且可以循环使用, 因此成本低, 有望用作空气净化的功能材料.

关键词: Na₂Ti₆O₁₃; Au负载; Cu(I)纳米簇负载; 协同效应; 光催化

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