Fabrication and Photocatalytic Activity of Cu₂O Nanobelts on Nanoporous Cu Substrate

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Abstract

In this paper, we report the fabrication of the photocatalysts composed of Cu₂O nanobelts and nanoporous Cu (NP Cu) substrate, which is obtained by soaking the NP Cu in dehydrated ethanol. The NP Cu substrate is achieved by dealloying of Ti_{40.6}Zr_{9.4}Cu_{40.6}Ni_{6.3}Sn_{3.1} amorphous ribbons in HF solutions. The dealloying process is considered to be a thermally activated process, obeying the Arrhenius law. The surface diffusivity increases with increasing dealloying temperature and concentration of HF solutions. The activation energy of the diffusion of Cu adatoms is estimated to be 76.4 kJ/mol. The Cu₂O nanobelts with the width of 10–15 nm and the length of about 1 μm are formed on the surface of NP Cu after immersion in dehydrated ethanol. The photocatalysts of Cu₂O on nanoporous Cu exhibit superior photocatalytic activity toward the degradation of methyl orange and methylene blue under the irradiation of the sunlight due to the coexistence of Cu₂O semiconductor nanobelts and large amount of heterojunctions as flowing path for photoelectrons.

Keywords Nanoporous Cu · Dealloying · Cu₂O · Photocatalytic activity

1 Introduction

With the rapid development of modern industry, environmental pollution and energy crisis have become the two major challenges for humans today. Photocatalytic technology with the advantages of low cost, environment friendliness and low energy consumption is developed to degrade organic pollutants by utilizing the solar energy. Recently, more and more researchers devote themselves to researching nanoporous metallic and nanosemiconductor

photocatalysts. Nanoporous metals exhibit excellent physical and chemical properties, such as low weight-to-volume density, high electrochemical stability and large surface-to-volume ratio due to bicontinuously open nanoporosity extending in three dimensions. Therefore, the nanoporous metals have great application prospects in the fields of separation, catalysis, energy and other fields [1–6]. Dealloying is an effective method for preparation of nanoporous metals, which is a process that the active elements are selectively dissolved into the dealloying solution, with the inert elements reserved and reassemble to form the porous structure [7]. The pore size and distribution of the pores are associated with the process parameters, hinting that the porosity and size of the nanopores are flexible and controllable [8, 9]. So far, some crystalline alloy systems have been demonstrated to be precursors to form nanoporous structures by dealloying process, such as Ag–Au [5, 10], Cu–Pt [11, 12], Al–Cu [13], Mn–Cu [14] and Cu–Au [15]. The amorphous alloys are also considered as proper precursors for dealloying due to their homogeneous structure, strong element capacity, the absence of the grain boundary, etc. [6, 11]. The homogeneous microstructure of the amorphous precursor is beneficial to the formation of nanoporous structure uniformly. Recently, different nanoporous metals such as NP Cu [16, 17], NP Pd [18] and NP

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Fe [19] have been fabricated from amorphous precursors. Additionally, more researchers have paid much attention to developing low-cost nanoporous metals [16, 17, 19], which are low cost, no toxicity, good stability and high catalytic performance. Particularly, NP Cu exhibits high applying propability since the copper resources are abundant in the earth.

On the other hand, Cu_2O is a p-type semiconductor with a narrow band gap of 2.0–2.2 eV, which can absorb most of the visible light ($\lambda < 600$ nm) [20]. Therefore, Cu_2O is a kind of photocatalytic material with high application potential. However, photogenerated electrons of the Cu_2O photocatalysts prefer to combine with the holes, reducing the photocatalytic activities [21]. The existence of the heterojunction of Cu and Cu_2O may enhance the photocatalytic property of Cu_2O photocatalysts, because the existence of Cu may transfer photoelectrons promptly, avoiding the recombination of electron–hole pairs [22, 23]. So far, different types of Cu_2O in nanostructure have been fabricated by different methods, such as solid-state reaction [24] and electrochemical method [25]. Most recently, a novel type of Cu_2O nanobelt on NP Cu substrate ($\text{Cu}_2\text{O}@\text{NP Cu}$) is synthesized by simply chemical treatment of NP Cu substrate [26, 27], which is expected to exhibit excellent photocatalytic performance.

In this study, NP Cu was prepared by dealloying of the $\text{Ti}_{40.6}\text{Zr}_{9.4}\text{Cu}_{40.6}\text{Ni}_{6.3}\text{Sn}_{3.1}$ amorphous precursor in HF solution. Then, Cu_2O nanobelts were grown on the NP Cu substrate by soaking in dehydrated ethanol. The photocatalytic activity of $\text{Cu}_2\text{O}@\text{NP Cu}$ catalyst to degrade organic dyes was investigated at ambient temperature.

2 Experimental

2.1 Preparation of NP Cu and Cu_2O Nanobelts

$\text{Ti}_{40.6}\text{Zr}_{9.4}\text{Cu}_{40.6}\text{Ni}_{6.3}\text{Sn}_{3.1}$ alloy was prepared by arc melting of the mixture of pure Ti, Zr, Cu, Ni and Sn with the purity higher than 99.99% in an Ar atmosphere. The melt spinning method was used to fabricate $\text{Ti}_{40.6}\text{Zr}_{9.4}\text{Cu}_{40.6}\text{Ni}_{6.3}\text{Sn}_{3.1}$ amorphous ribbons with 30 μm in thickness and 1 mm in width. The dealloying was performed in 0.1 M and 0.2 M HF solutions at 313 K and 333 K for 2 h, 4 h, 6 h and 8 h, respectively. Then, dealloyed ribbons were repeatedly rinsed with deionized water and dehydrated ethanol to remove the residual HF solutions. The Cu_2O nanobelts @NP Cu is prepared by the immersion dealloyed ribbons which are immersed in 0.1 M HF solution at 313 K for 6 h in dehydrated ethanol at room temperature for 1 days, 2 days and 3 days.

2.2 Microstructure Characterization

The phase information of the as-spun $\text{Ti}_{40.6}\text{Zr}_{9.4}\text{Cu}_{40.6}\text{Ni}_{6.3}\text{Sn}_{3.1}$ ribbons and the dealloyed samples was confirmed by using an X-ray diffraction (XRD, Bruker-AXS D8, Karlsruhe, Germany). The surface morphologies of the as-dealloyed samples were observed by a field-emission scanning electron microscope (SEM, Quanta FEG 250, Hillsboro, OR, USA) equipped with an energy-dispersive spectroscopy (EDS). The surface chemical state was analyzed by an X-ray photoelectron spectrometer (XPS, Thermo ESCALAB 250XI, Waltham, MA, USA) with monochromatized AlK_{α} excitation ($h\nu = 1486.6$ eV).

2.3 Photocatalytic Performance of $\text{Cu}_2\text{O}@\text{NP Cu}$

The photocatalytic experiments were carried out by mixing 10–20 mg $\text{Cu}_2\text{O}@\text{NP Cu}$ catalysts into 5 mL 10 mg/L MB aqueous solution and 8–12 mg $\text{Cu}_2\text{O}@\text{NP Cu}$ catalysts into 5 mL 20 mg/L MO aqueous solution. Then, the suspension solutions with catalysts were ultrasonic shocked for 10 min in the dark to achieve adsorption equilibrium. Following the suspensions were exposed to the sunlight for 80 min. The concentrations of degraded methyl orange (MO) and methylene blue (MB) solutions were analyzed by a UV–Vis spectroscopy (Thermo Evolution 220, Waltham, MA, USA).

3 Results and Discussion

3.1 Characteristics of the Dealloyed Nanoporous Structures

The XRD patterns of the as-spun and dealloyed $\text{Ti}_{40.6}\text{Zr}_{9.4}\text{Cu}_{40.6}\text{Ni}_{6.3}\text{Sn}_{3.1}$ ribbons are shown in Fig. 1. One

Fig. 1 XRD patterns of the as-spun $\text{Ti}_{40.6}\text{Zr}_{9.4}\text{Cu}_{40.6}\text{Ni}_{6.3}\text{Sn}_{3.1}$ amorphous ribbons *a* and dealloyed ribbons after dealloying in 0.1 M HF at 313 K *b*, 333 K *c*, as well as in 0.2 M HF at 333 K *d* for 4 h

broad diffraction peak appears in the XRD pattern of the as-spun Ti_{40.6}Zr_{9.4}Cu_{40.6}Ni_{6.3}Sn_{3.1} ribbons at around $2\theta = 41^\circ$, indicating that the as-spun Ti_{40.6}Zr_{9.4}Cu_{40.6}Ni_{6.3}Sn_{3.1} ribbons are in an amorphous state. As shown in Fig. 1b–d, dealloyed ribbons exhibit three diffraction peaks at 43.3° , 50.4° and 74.1° , which are assigned to Cu (111), (200) and (220) (JCPDS card no.: 02-1225), respectively. In addition, two weak diffraction peaks at 61.6° and 37° arising from Cu₂O (220) and (111) (JCPDS card no.: 74-1230) are also detected. Thus, it is known that the residue part of dealloyed alloys is composed of face-centered cubic (fcc) Cu and trace Cu₂O under different dealloying conditions. Here, the existence of trace Cu₂O might be the partial oxidation of Cu in the process of dealloying or operation.

Figure 2 presents the nanoporous structure of the as-spun Ti_{40.6}Zr_{9.4}Cu_{40.6}Ni_{6.3}Sn_{3.1} ribbons after dealloying in 0.1 M HF solution and 0.2 M HF solution for 2 h, 4 h, 6 h and 8 h at various temperatures. The homogeneously nanopores are formed on the presented samples, along with the pore size increasing with the increase in dealloying time or temperature. The changes in pore sizes and ligament sizes measured from SEM morphology are summarized in Fig. 3 as a function of dealloying time. The nanopores with a characteristic pore size of 31 nm and 80 nm are formed on Ti_{40.6}Zr_{9.4}Cu_{40.6}Ni_{6.3}Sn_{3.1} ribbons immersed in 0.1 M HF solution at 313 K for 2 h and 8 h, accompanying with the ligament size increasing from 51 to 97 nm. With the temperature increasing to 333 K, the nanopores formed on Ti_{40.6}Zr_{9.4}Cu_{40.6}Ni_{6.3}Sn_{3.1} ribbons after immersion in 0.1 M HF solutions for 2 h and 8 h are 49 nm and 104 nm, accompanying with the ligament sizes increasing from 68 to 106 nm. The nanopore structures formed on Ti_{40.6}Zr_{9.4}Cu_{40.6}Ni_{6.3}Sn_{3.1} ribbons after immersion in 0.1 M HF solution for 2 h at 313 K and 333 K show mean pore sizes of 31 nm and 49 nm and the ligament sizes of 51 nm and 68 nm. The changes in each element in dealloyed Ti_{40.6}Zr_{9.4}Cu_{40.6}Ni_{6.3}Sn_{3.1} ribbons as a function of dealloying time measured from EDS analysis are summarized in Fig. 4. When the as-spun Ti_{40.6}Zr_{9.4}Cu_{40.6}Ni_{6.3}Sn_{3.1} ribbons are soaked for 2 h in 0.1 M HF solution, the atomic percentages of Ti and Zr decrease from designed 40.6% and 9.4% to about 1%, and the relative contents of Sn and Ni do not decline significantly. As a consequence, the atomic percentage of Cu is higher than 80%, especially the content of Cu reaches 96.5% after dealloying in 0.2 M HF at 333 K for 2 h. This phenomenon indicates that main dissolution occurs at the initial period of dealloying. Both Ti atoms and Zr atoms have been almost totally dissolved after dealloying for 2 h, and the contents of Sn and Ni also reduce gradually. In the following dealloying process, atomic percentage of Cu

increases slowly after dealloying for 4 h, which is accompanied by slight decrease in other elements.

3.2 Estimation of Surface Diffusivity

The surface diffusivity (D_s) of Cu atoms at different dealloying temperatures can be estimated by the following equation [28]:

$$D_s = \frac{[d(t)]^4 kT}{32\gamma t \alpha^4}, \quad (1)$$

where t is the dealloying time, $d(t)$ is the mean pore size at the dealloying time t , k is Boltzmann constant (1.3806×10^{-23} J/K), T is the temperature, γ is surface energy and α is the lattice constant. The surface energy of Cu is 1.79 J m⁻², and the lattice constants of Cu can be obtained from XRD data. The mean pore size, lattice constant and the surface diffusivity are summarized in Table 1. From the results of calculation, the surface diffusivity of the dealloyed ribbons enhances from 9.87×10^{-19} m² s⁻¹ to 201.00×10^{-19} m² s⁻¹ with the dealloying temperature increasing from 313 to 348 K. And the surface diffusivity of the dealloyed ribbon increases 3.70×10^{-18} m² s⁻¹ to 3.14×10^{-17} m² s⁻¹ at 333 K when the concentration of HF solutions increases from 0.1 to 0.2 M. Both temperature and solution concentration affect the diffusion process significantly, inducing different dealloyed microstructures. The nanoporous structure with larger pore sizes is preferentially formed in the highly concentrated HF solutions and the higher dealloying temperatures since long jumps frequently occur at high temperatures, while single or double jumps are more common at low temperatures [29].

In order to further understand the dealloying mechanisms, the activation energy was calculated, because dealloying process can be considered as a thermally activated process. The activation energy can be estimated by the following equation [30]:

$$D_s = D_0 \exp\left(-\frac{E_a}{RT}\right), \quad (2)$$

where D_0 is the diffusion constant, T is the temperature, E_a is the activation energy for the surface diffusion process and R is the gas constant (8.314×10^{-3} kJ/(mol K)). Arrhenius plot of natural logarithm of surface diffusivity of the dealloyed Ti_{40.6}Zr_{9.4}Cu_{40.6}Ni_{6.3}Sn_{3.1} ribbons versus the reciprocal of dealloying temperature after dealloying in 0.1 M HF solution for (4 h) has a linear dependency with the dealloying temperature. Therefore, the activation energy estimated from the slope of fitted line in Fig. 5 is 76.4 kJ/mol for dealloying of Ti_{40.6}Zr_{9.4}Cu_{40.6}Ni_{6.3}Sn_{3.1} ribbons and the diffusion constant is 4.97×10^{-6} m² s⁻¹,

Fig. 2 SEM images of Ti_{40.6}Zr_{9.4}Cu_{40.6}Ni_{6.3}Sn_{3.1} ribbons dealloyed in 0.1 M HF solution at 313 K **a**, 0.1 M HF solution at 333 K **b**, in 0.2 M HF solution at 333 K **c** after 2 h (1), 4 h (2), 6 h (3), 8 h (4)

Fig. 3 The mean pore size, d , and the mean ligament size, l , of dealloyed Ti_{40.6}Zr_{9.4}Cu_{40.6}Ni_{6.3}Sn_{3.1} ribbons as a function of time, in 0.1 M and 0.2 M HF solutions at different temperatures

Fig. 4 The atomic percentages of the elements of dealloyed Ti_{40.6}Zr_{9.4}Cu_{40.6}Ni_{6.3}Sn_{3.1} ribbons as a function of time, in 0.1 M and 0.2 M HF solutions at different temperatures

Table 1 Mean pore size, lattice constant and the surface diffusivity of NP Cu dealloyed by Ti_{40.6}Zr_{9.4}Cu_{40.6}Ni_{6.3}Sn_{3.1} ribbons

HF concentration (M)	Temperature (K)	$d(t)$ (nm)	α (nm)	D_s (10^{-19} m ² s ⁻¹)
0.1 M HF	313	42.3	0.361616	9.87
	333	58.2	0.361643	37.00
	348	87.8	0.361551	201.00
0.2 M HF	333	99.2	0.362073	314.00

which is close to the activation energy and diffusion constant for dealloying of binary amorphous Ti–Cu alloy [31].

3.3 Fabrication and Photocatalytic Activity of Cu₂O@NP Cu Photocatalysts

Figure 6 illustrates the surface morphologies of Cu₂O nanobelts obtained on the surface of nanoporous copper after immersion in dehydrated ethanol for different times. The Cu₂O nanobelts in 2D dimension with width of 10–15 nm and length of 1 μ m are seen along the surface of the NP Cu. With the extension of the immersion time from 1 to 3 days, the more Cu₂O nanobelts are grown on the surface of the NP Cu with the width of Cu₂O nanobelt

increasing from 12 to 25 nm and coverage fraction ranging from 26.9 to 57.2%, as presented in Fig. 7.

The surface element information of the NP Cu after immersion in dehydrated ethanol for 3 days is analyzed by XPS. As presented in Fig. 8, the Cu 2*p* spectrum is separated by two peaks at 932.5 and 952.5 eV, assigned to Cu 2*p*_{3/2} and 2*p*_{1/2}, respectively. Cu 2*p*_{3/2} peak is composed of one peak at 932.2 eV raising from Cu⁰ and one peak at 934.3 eV generating from Cu⁺. Cu₂O nanobelts are considered to be grown from the Cu₂O species during immersion in dehydrated ethanol [26, 27]. The present combination of dealloying solutions and immersion in dehydrated ethanol led to the formation of the Cu₂O nanobelts on NP Cu substrate. The initial microstructure of NP Cu substrate might affect the final characteristics of the

Fig. 5 Arrhenius plot of natural logarithm of surface diffusivity, $\ln(D_s)$, of dealloyed $\text{Ti}_{40.6}\text{Zr}_{9.4}\text{Cu}_{40.6}\text{Ni}_{6.3}\text{Sn}_{3.1}$ ribbons versus the reciprocal of dealloying temperatures, $1000/T$, after dealloying in 0.1 M HF solution for 4 h

Fig. 7 Relationship between width, coverage fraction of Cu_2O nanobelts and NP Cu after immersion in dehydrated ethanol for different times

Fig. 6 SEM images of Cu_2O obtained after soaking in dehydrated ethanol for 1 days **a, b**, 2 days **c, d**, 3 days **e, f**

Fig. 8 XPS spectra of the Cu 2p **a**, Sn 3d **b**, Ni 2p **c**, O 1s **d** in the dealloyed samples after soaking in dehydrated ethanol for 3 days

surface Cu₂O nanobelts, which is investigated in another work [32]. As it is shown in Fig. 8b, c, the XPS spectra of Ni and Sn illustrate that the trace amounts of Ni and Sn are all oxidized during dealloying.

UV–Vis spectra of MO and MB solutions degraded by the Cu₂O@NP Cu catalysts are presented in Fig. 9. The maximum absorbance peaks at 463.5 nm of MO solution are observed under different conditions, which decline significantly with the increase in the amount of Cu₂O@NP Cu or immersion time in dehydrated ethanol, as shown in Fig. 9a, b. Degradation efficiency, P , can be deduced by the equation $P = (A_0 - A_t)/A_0 \times 100\%$, where A_0 presents the absorption peak of the original solutions and A_t stands for the absorption peak intensity of the MO solutions after degradation time t . The calculated degradation efficiencies of the MO solution degraded by Cu₂O@NP Cu catalysts obtained in dehydrated ethanol for different times are listed in Table 2. The data degraded by NP Cu without Cu₂O nanobelts are also shown for the comparison. The degradation efficiencies of MO solutions are 7.1%, 88%, 92% and 93.6% degraded by NP Cu, Cu₂O@NP Cu soaked in dehydrated ethanol for 1, 2 and 3 days, hinting that most of MO are degraded by the catalysts soaking in dehydrated ethanol for 3 days. Furthermore, the degradation efficiency increases with the increase in the amount of Cu₂O@NP Cu,

as shown in Fig. 9b. Figure 9c, d shows that absorption spectra of MB solutions show the maximum absorbance at 663 nm under different conditions. Similar degradation behavior of MB solution degraded by Cu₂O@NP Cu is observed with that of MO solution. When the Cu₂O@NP Cu catalysts were prepared by soaking in dehydrated ethanol for 3 days, the Cu₂O@NP Cu catalysts exhibit a high degradation efficiency of 95.9% for MB solution (Fig. 9c, d). By contrast, the degradation efficiency of MB by NP Cu is only 7.7%. In other words, the more Cu₂O nanobelts grow on the surface of NP Cu, the higher photocatalytic performance of the Cu₂O@NP Cu catalysts will be obtained. Correspondingly, the photogenerated electrons and holes can transfer to the Cu₂O surface more quickly, avoiding the recombination of electron–hole pairs, due to the plenty of the heterojunctions between NP Cu and Cu₂O, resulting in the improvement in the quantum efficiency.

The degradation kinetic behavior of MO and MB solutions degraded by Cu₂O@NP Cu catalysts is also investigated based on UV–Vis spectra versus time. For MO solution, as shown in Fig. 10a, the absorbance peak at about 463.5 nm corresponding to color radical decays with the evolution of time in the UV–Vis spectra. The absorbance peaks almost disappear after degradation for 60 min. The normalized concentration C_t/C_0 variation of MO

Fig. 9 UV-Vis spectra of MO **a**, **b**, MB solutions **c**, **d** degraded by $\text{Cu}_2\text{O@NP Cu}$

Table 2 Degradation efficiency and reaction rate constant of MO and MB solutions degraded by $\text{Cu}_2\text{O@NP Cu}$ soaking in ethanol for different days

Forming time for Cu_2O nanobelts (days)	Degradation efficiency (%)		K_{obs} (min^{-1})	
	MO	MB	MO	MB
0	7.1	7.4	—	—
1	88.0	69.1	—	—
2	92.0	80.1	—	—
3	93.6	95.9	0.0624	0.0544

Fig. 10 UV-Vis spectra of: MO **a**; MB **b** versus time during the degradation process by $\text{Cu}_2\text{O@NP Cu}$ catalysts. The inset is the normalized concentration (C_t/C_0) versus time of: MO and MB solutions

against time derived from UV-Vis spectra is shown in the inset of Fig. 10a. Here, C_0 and C_t are initial and real-time (t) concentrations of azo dye solutions. It is found that

C_t/C_0 decreases drastically in the case of degradation MO by $\text{Cu}_2\text{O@NP Cu}$ catalysts. Meanwhile, the UV-Vis spectra for MB have obvious peaks centered at 663 nm

before degradation treatment in Fig. 10b. As the degradation reactions undergo, the normalized concentration C_t/C_0 of MB shows similar variation with that of MO. Both the degradation of MO and MB solutions by Cu₂O@NP Cu catalysts follows the pseudo-first-order kinetic mode ($C = C_0 \exp(-k_{\text{obs}}t)$, $R^2 > 0.95$). The reaction rate constants k_{obs} calculated from fitting results are 0.0624 min⁻¹ and 0.0544 min⁻¹ for MO and MB solutions, as given in Table 2, which are higher than graphene oxide- or Fe-based amorphous powders, due to the difference in degradation mechanism [19, 33].

4 Discussion

As presented above, bicontinuous nanoporous Cu structures were fabricated by dealloying of Ti–Zr–Cu–Ni–Sn amorphous alloys. The sizes of nanopores and ligaments formed on Ti_{40.6}Zr_{9.4}Cu_{40.6}Ni_{6.3}Sn_{3.1} ribbons increase more than tens of nanometers when the concentration of the HF solutions rises from 0.1 to 0.2 M, after immersion at 333 K for the same periods. The larger pores formed in higher concentration F⁻ solution are attributed to the difference in the concentration of the F⁻ anions, which react with Ti to form the water-soluble [TiF₆]²⁻. Compared with the samples dealloyed in 0.1 M HF solution, higher content of Cu and less content of Ti, Zr, Ni, Sn are detected in the samples dealloyed in 0.2 M HF solution, demonstrating that the increase in F⁻ concentration accelerates the dissolution of active component, leading to the increase and coarseness of the pores and ligaments [31]. Through the above data analysis, the formation of NP Cu can be explained by the following reasons. On the one hand, the native TiO₂ layer in TiZrCuNiSn amorphous ribbons is broken down since the fluoride ions triggered the formation reactions of highly soluble fluoride complex (i.e., TiF₆²⁺, TiF₂²⁺) [34]. Meanwhile, the Ti element in the substrates is attacked by F⁻ anions continuously, which is a selective dissolution process of Ti atoms from TiZrCuNiSn matrix. Actually, the standard electrode potentials of Ti, Zr, Ni, Sn and Cu are -1.630 V versus the standard hydrogen electrode (SHE) for Ti/Ti²⁺, -1.529 V versus SHE for Zr/Zr⁴⁺, -0.25 V versus SHE for Ni/Ni²⁺, -0.136 V versus SHE for Sn/Sn⁴⁺ and 0.342 V versus SHE for Cu/Cu²⁺. The large differences in the standard electrode potentials between Cu and Ti, Zr, Ni and Sn are 1.972 V, 1.871 V, 0.592 V and 0.478 V, respectively. The large potential differences ensure the selective dissolution of Ti, Zr and other elements in the HF solution. The bicontinuous structures with the pores and ligaments are formed by the rapidly active dissolution of Ti, Zr, Ni and Sn atoms, as well as the diffusion and rearrangement of Cu atoms. With increasing immersion time, dealloying reaction is carried

out more thoroughly with more dissolution of Ti, Zr, Sn and Ni. Correspondingly the sizes of pores and ligaments of nanoporous Cu also are increased and coarsened. On the other hand, with the increase in dealloying temperature the diffusion of atoms will be accelerated, including fast dissolution of Ti, Zr, Ni, Sn atoms and rapid rearrangement of Cu atoms, resulting in the increase in the sizes of the pores and ligaments. As mentioned that fluorine ion reacts with Ti and Zr to form a high solubility of fluoride ion TiF₆²⁻/ZrF₆²⁻. Therefore, Zr and Ti atoms take the lead in dissolution, and the dissolution rate is very fast and the dissolution of Ni, Sn elements is slower because of lower potential difference between them and Cu. Finally, the residue of dealloyed alloys contains mainly Cu and a trace of Ni and Sn elements. Here, the trace elements might act as diffusion inhibitor for refining of the nanopores [17]. As a consequence of increasing F⁻ anions, the large nanopores and wider ligaments are formed. In addition, the diffusion and rearrangement of Cu adatoms are regarded to be the prominent steps for the formation of the ligament of NP Cu. These steps evoke mainly at the interfacial regions, and the surface diffusion controlled processes exhibit a strong dependency on temperature [35]. Therefore, in the research, the rough nanoporous structures are formed at higher temperatures since the diffusion and rearrangement of Cu adatoms proceed in a relative large scale length due to long-range jump of Cu adatoms, i.e., large nanopores and wider ligaments are obtained at high temperatures.

Furthermore, the formation of Cu₂O nanostructures was controlled by the substrate, solvent, reductant, treatment time, dissolved oxygen and so on [24–26]. Different from reported Cu₂O [36] nanowires or Cu₂O nanocubes [37], belt-shaped nanostructured Cu₂O along the NP Cu substrate was synthesized in the research, which might be attributed to the existence of dehydrated ethanol molecules serving as a stabilizing agent by orientated growth of Cu₂O species [26]. The Cu₂O octahedral was synthesized controllable by adjusting ammonia solution and NaOH solution [38]. The shapes of Cu₂O nanostructures were affected by the stabilizing agent and the ratio of the reagents [38]. Cu₂O nanobelts in width of several tens to several hundred nanometers were grown against the NP Cu template [26, 27, 32]. It was believed that Cu₂O species nucleated preferentially at lamellar defects during the rearrangement of Cu adatoms, which was caused by the synthesis effect of geometrical structure of NP Cu, local pH, diffusion of ions and water molecules. Once Cu₂O species are formed, the Cu₂O will grow continuously along the (111) planes to form the belt-shaped structure since ethanol molecules act as stabilizing agents although the suppression mechanism of growth by ethanol molecules is needed for further investigation [27]. Here, thinner and homogeneously distributed Cu₂O nanobelts formed might be ascribed to

different microstructures and element distributions of the porous substrate obtained from Ti–Zr–Cu–Ni–Sn quinary amorphous alloy. Cu₂O preferentially forms in an alkaline solution because OH[−] induced reduction reaction of Cu²⁺ cations to Cu⁺ cations [39, 40]. In the research, small amount of H₂O molecules in dehydrated ethanol support OH[−] which are predominant to the formation of Cu₂O by the reaction $2\text{Cu} + 2\text{H}_2\text{O} \rightarrow 2\text{H}_2 + \text{Cu}_2\text{O} + [\text{O}]_{\text{SA}}$. The rate of reaction speeds up with absorbed oxygen in dehydrated ethanol, resulting in more Cu₂O particles to form new nanobelts or to gradually refine the nanobelts. Moreover, dehydrated ethanol might limit the growth of Cu₂O nanobelts [26–28], so that the nanobelts can only grow in the two-dimensional direction of the porous surface. The nanobelts are getting wider and more with increasing immersion time in dehydrated ethanol, which is attributed to more adsorption of dissolved oxygen in dehydrated ethanol to the nanoporous surface. The water molecules react with dissolved O₂ to generate OH[−], and then the solution pH shifts to a weak alkaline, serving as a reservoir of OH[−]. Cu₂O nanobelts grown on the surface of NP Cu, are excited to produce electrons and holes by exposing to the sunlight. The photoelectrons and holes initiate photodegradation reactions when the catalysts are contacted with the organic dye solutions by forming the superoxide anions and hydroxyl radicals, to make the organic molecule oxidize and decompose [23, 41]. The core–shell architected NP Cu@Cu₂O also shows superior photocatalytic activity for the MO degradation ascribed to the synergistic effects between unique core–shell structure and 3D nanoporous network with high surface area and fast mass transfer channel [42]. With the increase in soaking time, the coverage fraction of Cu₂O nanobelts increases, accompanied with the increase in the numbers of heterojunctions between Cu and Cu₂O, which are beneficial to inhibiting the recombination of photogenerated electrons and holes by forming flowing path of electrons. Therefore, the photogenerated electrons and holes can be effectively separated, decreasing the probability of the recombination of photoelectrons and holes and enhancing the quantum efficiency. Consequently, the photocatalytic activity of the Cu₂O@NPCu catalysts with more Cu₂O on the NP Cu substrate is improved significantly.

5 Conclusions

The evolution of the nanoporous structure dealloyed from quinary amorphous Ti_{40.6}Zr_{9.4}Cu_{40.6}Ni_{6.3}Sn_{3.1} alloys has been investigated. The three-dimensional bicontinuously nanoporous structure of fcc Cu with a pore size of 30–100 nm and a ligament size of 50–200 nm was formed at different temperatures in various concentrations of HF

solutions for different immersion times. Cu₂O nanobelts have been fabricated via immersion NP Cu in dehydrated ethanol. Both water molecule reactant acting as OH[−] reservoir and the ethanol molecule serving as stabilizing or capping reagent are responsible for the formation of two-dimensional Cu₂O nanoarchitectures. Cu₂O@NP Cu composites exhibit excellent photocatalytic properties in degrading organic dyes of MB and MO under the irradiation of the sunlight. The degradation efficiencies are 93.6% and 95.4% for the photocatalytic degradation of MB and MO solutions when the coverage fraction of Cu₂O nanobelts is 57.2% on NP Cu substrate. The high photodegradation ability of Cu₂O@NP Cu is attributed to the coexistence of Cu₂O nanobelts and large amount of heterojunctions between Cu and Cu₂O.

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