

Photocatalytic Performance of Cu/TiO_{2-x}N_x Nanotube Arrays Enhanced by Surface Plasmon Resonance and Application in Hydrogen Evolution by Water Splitting

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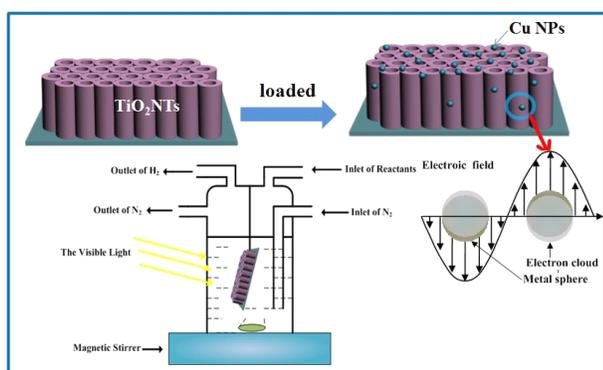
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ABSTRACT

TiO₂ nanotube arrays (TiO₂ NTs) are fabricated by anodic oxidation of titanium in NH₄F+H₃PO₄ electrolyte, and Cu nanoparticles (Cu NPs)-loaded and N-doped TiO₂ nanotube arrays (Cu/TiO_{2-x}N_x NTs) are obtained using microwave-assisted reduction, followed by annealing under the atmosphere of (95%) N₂ and (5%) H₂ under 450 °C. Results show that Cu NPs are well dispersed on the surface of TiO_{2-x}N_x NTs, which can enhance the visible absorption and Raman properties of TiO₂ based on the local surface plasmon resonance effect (LSPR) of Cu NPs. The experiment of photocatalytic water splitting to generate hydrogen indicates that Cu/TiO_{2-x}N_x NTs exhibits better photocatalytic activity than that of pure TiO₂ NTs, the photocatalytic mechanism on the Cu/TiO_{2-x}N_x NTs is proposed as well.

ultraviolet (UV) light ($\lambda < 387$ nm) for activation, and the percentage of UV light in the solar spectrum is about 5%, which is very low compared with that of the visible light (48%). The low-usage of sunlight has been restraining the photocatalytic efficiency of pure TiO₂. Meanwhile, the combination of the photo-generated electrons and holes of TiO₂ can reduce the quantum efficiency of the light. Therefore, many efforts have been reported to overcome the limitations, the highly ordered TiO₂ nanotube arrays with high surface-to-volume ratios show better photocatalytic activity than any other form of TiO₂ [5]. Recently studies reveal that noble metal (Au, Ag, Pt) nanoparticles can improve the photoresponse property of TiO₂ in the visible region based on the localized surface plasmon resonance (LSPR) effect, and thus enhance the activity of TiO₂, and noble metal loading was proved to be an effective way to restrain the recombination of photo-generated electron-hole pairs. Based on the above results, transition metal Cu is employed to modify the N doped TiO₂ (TiO_{2-x}N_x) nanotube arrays in this study, because Cu exhibits the similar electronic structure compared with the Au, Ag, Pt [6,7]. In addition, the photocatalytic water splitting to generate hydrogen on Cu/TiO_{2-x}N_x NTs is investigated and the photocatalytic mechanism is discussed.



Keywords: localized surface plasmon resonance, nanotube arrays, nanoparticles, photocatalysis, water splitting

1 INTRODUCTION

Nano TiO₂-based materials are widely applied in the fields of solar cell, water splitting, environment remediation and sterilization [1-4]. However, the widespread use of TiO₂ is inhibited by its wide band gap (3.2 eV) that requires

2 EXPERIMENTAL

2.1 Preparation of Cu/TiO_{2-x}N_x NTs

Titanium sheets (>99 % purity, 45×21 mm) were cleaned by sonication in acetone and deionized water respectively, then the cleaned Ti sheets were chemically etched in a mixture solution (HF-HNO₃-H₂O 1:4:5 in v/v) for 10min. Subsequently, rinsed with deionized water and dried in air. A two-electrode system was applied with Ti foils as the working electrode and graphite as the counter electrode. The TiO₂ NT was obtained by anodization at 40 V for 2 h in 100 mL phosphoric acid solution containing 0.3wt% NH₄F. Subsequently, Cu NPs were dispersed on TiO₂ NTs by microwave-assisted reduction. Sodium phosphinate monohydrate (NaH₂PO₂·H₂O) was used as a

reducing agent added into diethyleneglycol with poly (*N*-vinylpyrrolidone) acting as the capping molecule. The mixed solution was exposed to microwave irradiation for 5 min at 140 °C, and cooled to room temperature naturally, then TiO₂ NTs was placed into above solution, followed by adding Cu(NO₃)₂ solution. The Cu/TiO₂ NTs was obtained by microwave irradiation the mixture solution for 1 h, then Cu/TiO₂ NTs was washed by ethanol and dried at room temperature, followed by annealing under the atmosphere of (95%)N₂ and (5%) H₂ at 450 °C for 2 h, to obtain the N doped Cu/TiO₂ NTs (Cu/TiO_{2-x}N_x NTs).

For short, hereafter Cu/TiO_{2-x}N_x NTs-I and Cu/TiO_{2-x}N_x NTs-II denote the samples prepared in 1 and 1.5 mM Cu(NO₃)₂ solution respectively.

2.2 Characterization

The crystalline phase of samples was identified by X-ray diffractometer (Shimadzu, XRD-6000, Cu K α radiation). The morphology was observed using a scanning electron microscope (SEM, JSM-6390A). The absorption property of samples was recorded using UV-vis spectrophotometer (Shimadzu, UV-3600). Raman spectra were collected on a Raman spectrometer (Renishaw in Via Reflex).

3 RESULTS AND DISCUSSION

Fig. 1 show SEM images of the samples. The TiO₂ NTs are orderly aligned on the Ti substrate after anodization, with a diameter of approximately 120 nm, a well thickness of 30 nm. Cu NPs on the surface of TiO_{2-x}N_x are obtained by microwave-assisted reduction of Cu(NO₃)₂. The presence of Cu NPs does not damage the morphology of TiO_{2-x}N_x. Most of Cu NPs are distributed on the exterior mouth of TiO_{2-x}N_x NTs, In top view, we can just observe the less amount of Cu NPs loaded on nanotubes.

The XRD patterns of TiO₂ NTs and Cu/TiO_{2-x}N_x NTs-I are showed in Fig. 2. The diffraction peaks of anatase TiO₂ are observed in all the samples, which are in good agreement with those in the standard JCPDS cards NO.21-1272. The loaded Cu NPs does not affect the crystal structure of TiO₂ NTs and the diffraction peaks of Cu NPs were not observed in Fig. 2, which may be related to the lower concentration of the Cu(NO₃)₂ during the experiment.

To investigate the optical properties of samples, the UV-vis absorption spectra were measured. As is shown in Fig. 3, all samples exhibit strong absorption in the range below 387 nm, comparing with pure TiO₂ NTs, the absorption of Cu/TiO_{2-x}N_x NTs increases significantly in the visible region due to the SPR effect of Cu NPs with the absorption center approximately at 610 nm. According to the reported [8], the resonance absorption of Cu NPs should be at 580nm, which may be related to the size and shape of nanoparticles. N element was doped by annealed at N₂ atmosphere can result in the red-shift of the UV-vis. absorption spectra because the N_{2p} and O_{2p} orbit hybrid can change the electronic band structure of TiO₂. However, it is

not obvious, a further study on the doping amount of N in TiO₂ NTs is underway for this phenomenon.

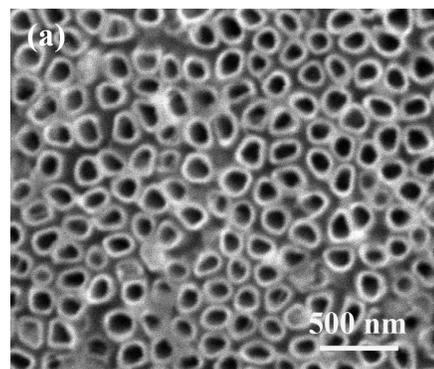
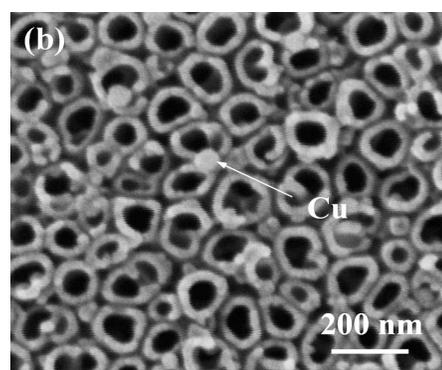


Fig.1 SEM images (a) pure TiO₂ NTs;



(b) Cu NPs loaded on TiO_{2-x}N_x-I NTs

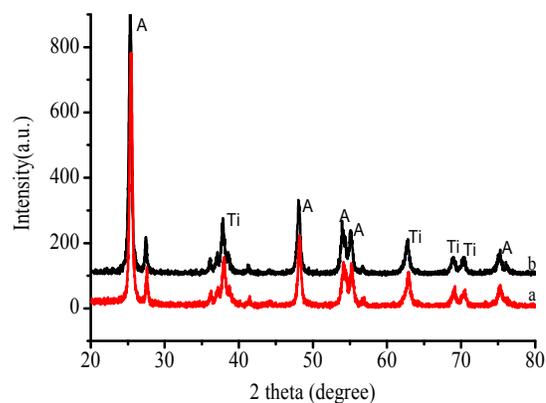


Fig.2 XRD patterns. spectra (a) TiO₂ NTs; (b) Cu/TiO_{2-x}N_x NTs-I.

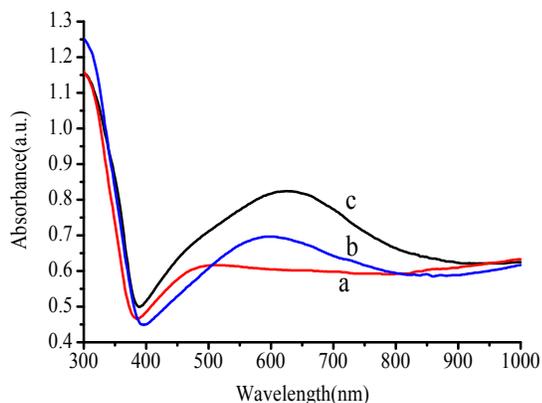


Fig.3 UV-vis. spectra (a) TiO₂ NTs; (b) Cu/TiO_{2-x}N_x NTs-I; (c) Cu / TiO_{2-x}N_x -II.

Fig.4 exhibits the photoluminescence (PL) emission spectrum of samples. PL emission spectrum is an important tool to study the efficiency of charge carrier trapping and transfer [9]. PL emission mainly results from the recombination of excited electron-hole pairs, so it can be used to study the electron transfer between TiO₂ and Cu NPs. The emission spectra of samples were recorded under 250 nm excitation. As Fig. 4 shows, the emission spectra of Cu/TiO_{2-x}N_x NTs samples appear to be similar with pure TiO₂, which means that the loading of Cu NPs has not induced new photoluminescence. There are two main emission peaks at 400 nm (3.10 eV) and 465 nm (2.67 eV). The peaks are assigned to electronic transition from the bottom of the conduction band to the top of the valence band and the defect levels formed by oxygen vacancies respectively. It can be found that the spectrum of curve b and c are weakened after Cu loading, indicating the recombination of photogenerated electrons and holes is suppressed effectively.

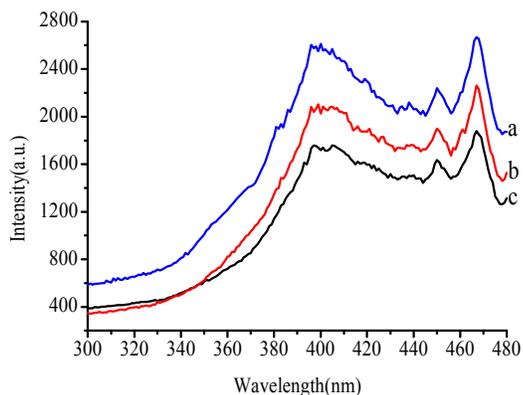


Fig. 4 PL spectra: (a) TiO₂ NTs.; (b) Cu/TiO_{2-x}N_x NTs-I; (c) Cu/TiO_{2-x}N_x NTs -II.

Fig.5 shows the Raman scattering spectra of the samples. Anatase TiO₂ belongs to D_{4h} point group, and its

characteristic Raman active modes are at 147 cm⁻¹ (Eg), 398 cm⁻¹ (B1g), 515 cm⁻¹, (B1g), 637 cm⁻¹(Eg), which was agreement with the observed spectra. In Fig. 5b and 5c, the above characteristic Raman peaks of TiO₂ are enhanced with loading of Cu NPs. The enhancement is due to SERS from Cu NPs. The local electronic field nearby the surface of Cu NPs can greatly strengthened and achieve the strong Roman signal[10, 11]. Moreover, the scattering peaks of appeared the minor red-shift due to the interface structure between Cu and TiO₂.

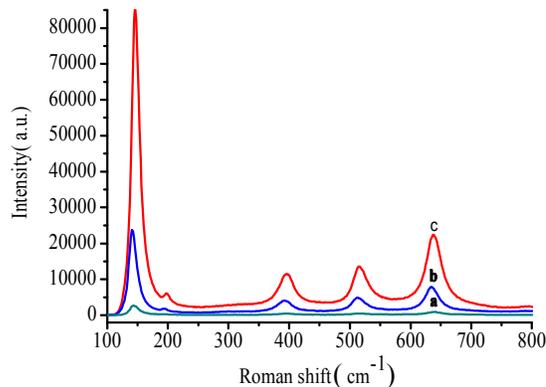


Fig.5 Raman spectra of (a) TiO₂ NTs (b) Cu/TiO_{2-x}N_x NTs-I; (c) Cu/TiO_{2-x}N_x NTs-II.

Photocatalytic water splitting to generate hydrogen was used to evaluate the activity of catalyst using ethanol as a sacrificial agent. The curve b and c in Fig. 6 are the hydrogen evolution rate of Cu/TiO_{2-x}N_x NTs irradiated by UV and visible light, comparing with the curve-a in Fig. 6, the hydrogen evolution rate were higher than the pure, the evolution rate of Cu/TiO_{2-x}N_x NTs-I and II are 1.01 and 1.12 μmol/(cm²·h), both higher than that of pure TiO₂ NTs under the same condition. The SPR effect is induced by the visible light and it could trapped the energy from the exited light leading to a better photocatalytic activity [12, 13].

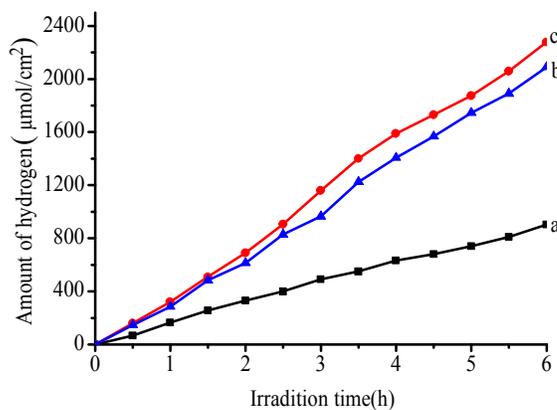


Fig. 6 Hydrogen evolution from: (a) TiO₂ NTs, (b) Cu/TiO_{2-x}N_x NTs -I, (c) Cu/TiO_{2-x}N_x NTs - II.

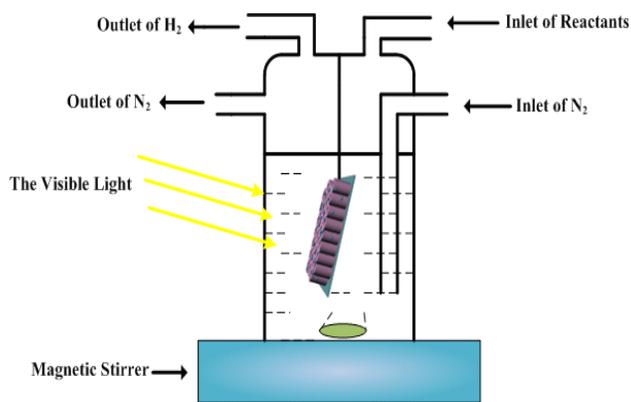


Fig. 7 Photo-reaction equipment of H₂ evolution by water splitting

4 CONCLUSIONS

Cu/TiO_{2-x}N_x NTs were prepared by anodation oxidation and microwave-assistant reduction. The absorption of the samples was enhanced in the visible light based on the surface plasmon resonance effect of Cu NPs. In addition, Cu NPs could effectively restrain the recombination of photo-generated electron-hole pairs and the electron from the conduction band of TiO₂ to the metal surface so that composite particles can trap the more energy from sunlight. The experiment indicated that the hydrogen evolution rate of Cu/TiO₂ NTs samples irradiated by UV and visible light improved in various degrees compared with pure TiO₂, the hydrogen evolution rate of Cu/TiO_{2-x}N_x NTs is 2.9 times higher than that of pure TiO₂.

5 ACKNOWLEDGEMENTS

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