Enhancing photocatalytic activity of ZnO nanowires by embedding ITO layer as a photogenerated electron collecting layer

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The photocatalytic performance of a semiconductor is strongly limited by the inefficient separation of photogenerated carries. In this work, an indium tin oxide (ITO) layer was introduced before the conventional growth of vertically aligned ZnO nanowires by chemical vapor deposition using Al-doped ZnO (AZO) as a seed layer on glass substrates. The ITO layer behaving as an efficient collecting layer of photogenerated electrons strongly suppressed the recombination of photogenerated electrons and holes, which was confirmed by the photoluminescence spectra. The UV-induced photocatalytic activities in aqueous solution were evaluated by selecting rhodamine B as the model contaminant. The ZnO nanowires with ITO layer exhibited notably enhanced photocatalytic activity, which was 9.65 times faster than that of ZnO nanowires alone. It has been proposed that the organic molecules were mainly oxidized by holes concentrated in the valence band of ZnO due to the efficient collection of electrons by ITO layer. Our work highlights that addition of electron collecting layer provides an efficient method to enhance the activity of semiconductor photocatalysts.

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1. Introduction

Recently, the worldwide increase in water pollution caused by synthetic dyestuffs has become one of the considerably severe environmental problems. Due to the limited water sources, there is a great need for the development of suitable, inexpensive and rapid waste water treatment techniques [1,2]. The traditional water purification methods, such as electrolytic process [3], adsorption [4–10], oxidant oxidative decomposition (ozone) [11], microbial metabolism decomposition [12] and so on, often introduce the secondary pollution. Photodegradation of these contaminants via photocatalysis has become a very active research topic in the past several decades due to its outstanding catalytic performance, mild reaction conditions, wide availability and no secondary pollution [13–21]. Among many photocatalysts, ZnO is very attractive for photocatalysis. ZnO is a direct wide-band gap (3.37 eV) semiconductor, and has the following advantages: lower cost of production, abundance in nature, chemically-stable crystal structure. Besides, ZnO is easy to form one-dimensional nanostructures (nanowire, nanorod and nanobelt), which have anti-agglomeration performance, relatively high specific surface area and high electron mobility [22]. Meanwhile, 1-D nanostructures can be separated from a solution easily and recycled for waste water treatment. However, the efficiency of pure ZnO photocatalyst is not considerable because of the relatively rapid recombination of the photogenerated electrons and holes. Currently, efforts have been placed on the design of ZnO photocatalyst for achieving large specific surface area, high stability, and high separation efficiency of electron–hole pairs to achieve high photocatalytic efficiency [23–26]. On the other hand, besides the structural design, the decoration of noble metal (such as Ag [27–29], Au [30,31], and Pt [32,33]) or some metal oxide [26,34] onto ZnO is also an effective means to achieve high photocatalytic activity, where noble metal and metal oxide is used to collect photogenerated electrons, achieving the efficient separation of photo-generated carriers (electrons and holes).

As compared to ZnO, indium tin oxide (ITO) presents low electrical resistivity and relatively high work function [35]. Based on the appropriate energy band of ZnO and ITO, it is expected that ITO might be used as a photogenerated electron collecting layer to suppress the recombination of photogenerated electrons and
holes. Herein, we fabricated ZnO nanowires/Al-doped ZnO/ITO (Nws/AZO/ITO) heterostructure photocatalyst on quartz glass substrates via a two-step synthesis method. As a comparison, ZnO nanowires/AZO (Nws/AZO) photocatalyst was fabricated on the same substrate by the same method. The photocatalytic activities of these two samples have been investigated. The results demonstrate that Nws/AZO/ITO has enhanced photocatalysis, and the mechanism has been attributed to effective collection of photo-generated electrons by the highly conductive ITO layer.

2. Experimental details

2.1. Samples fabrication

The ZnO nanowire arrays were prepared by a two-step synthesis method on quartz glass substrates. Quartz glass substrates were cleaned in acetone, ethanol and deionized water successively by ultrasonic treatments to remove the possible attached organic contaminants. In the first step, ITO and AZO thin films were deposited successively by pulsed laser deposition (PLD) with following experiment parameter. The ITO film was fabricated by using a commercial ITO target of 2 cm in diameter. The AZO film growth was carried out using a commercial AZO target of 2 cm in diameter, with Al content of 1.0 at%. Both targets were prepared by conventional solid state reaction method. The films were grown under the base pressure of 1.5 \times 10^{-2} \text{ mbar}, and the distance between target and substrate was kept at 5 cm. The growth temperature was kept at 500 °C for improving ITO and AZO films quality. The ITO thin film was designed to form heterojunction with subsequent ZnO nanowires, and AZO thin film acted as the seed layer for the subsequent nanowire growth. As a reference, only AZO thin film was deposited on the other substrate.

In the second step, the vertically aligned ZnO nanowire arrays were then synthesized on AZO/ITO/glass and AZO/glass by chemical vapor deposition (CVD) processes. Zinc sheets (99.9%) and high purity oxygen (99.99%) were used as the zinc source and oxygen source, respectively. In order to control the release rate of the source, zinc sheets were loaded in half-open small quartz tube of 10 mm in diameter and 60 mm in length, which was put in an alumina boat. Then the boats with source materials and substrates were positioned in the center of the quartz tube. Unlike most of the reports, in our experiment the substrate was placed horizontally on the upstream side of the source at a distance of 6 cm, as displayed in Fig. 1. Thus Zn vapors can diffuse slowly to the substrate, which is in favor of fabricating regular ZnO nanowire arrays. During the growth of ZnO nanowires, a flow of 1500 sccm high purity Ar passed continuously through the quartz tube. Then the quartz tube was heated to 600 °C at a heating rate of 40 °C/min. Once the desired temperature was reached, 200 sccm O2 was introduced into the quartz tube, with growing time maintained for 30 min. The atmospheric pressure was maintained at 150 Pa. After the growth of nanowires, the tube was naturally cooled down to room temperature. With this two-step process, two samples, Nws/AZO/ITO and Nws/AZO were prepared. All chemicals for synthesis and analysis were commercially available and used without further treatments.

2.2. Characterization

General characterization methods have been applied to the samples [20,36]. Field emission scanning electron microscope (SEM, FEI Inspect F50) with highest spatial resolution of 1 nm was used to observe the morphology of samples. An energy dispersive spectrometer (EDS) is attached on SEM for the elemental detection and mapping. The crystalline structure was investigated by X-ray diffraction (XRD, Rigaku SmartLab3) with Cu Kα radiation from a 3 kW X-ray generator, and the smallest step of angle is 0.0001°. The photoluminescence (PL) spectra of the samples were acquired at room temperature with acquisition time of 0.1 s by excitation with the 340 nm line of a Xe lamp (Horiba Jobin Yvon Fluorolog-3) in the wave range between 200 nm to 800 nm with resolution ≤ 0.1 nm and signal to noise ratio of higher than 10,000:1.

2.3. Photocatalytic measurement

To examine the photocatalytic activity of the samples, photo-degradation of rhodamine B (RhB) in aqueous solution was investigated. A 500 W Xenon lamp with emission wavelength range at 190–1100 nm without filter was used as the light source, and the light intensity is 425 mW/cm². In a typical test, the sample sample was horizontally immersed into a beaker containing 150 mL of about 12.5 mg/L RhB aqueous solution with continuous magnetic stirring. After the stirring for 30 min in dark to reach an adsorption–desorption equilibrium between the photocatalyst and RhB, the solution was irradiated by the light source. At a certain time interval, 3 mL treated solution was taken out. The relative concentration of RhB in the treated solution was calculated by measuring the absorbance value at 554 nm by means of a UV–vis spectrophotometer (UV–vis, HITACHI U3900). In order to confirm that the degradation of RhB is caused by the photocatalyst rather than self-degradation, the controlled experiment was also carried out without photocatalyst under the same conditions.

3. Results and discussion

3.1. Structure and morphology

The cross-sectional and top-view SEM images of Nws/AZO/ITO are shown in Fig. 2(a) and (b). From the cross-sectional view of the sample (Fig. 2(a)), ZnO nanowires were grown vertically on the substrate. As shown in the figures, the ITO layer and AZO seed layer deposited by PLD in the first step is about 200 nm totally in thickness. The average length and diameter of ZnO nanowires are about 16 μm and 350 nm, respectively. Similar SEM image has been observed for Nws/AZO. As can be seen in Fig. 2(a), a thin continuous ZnO layer was firstly formed on the AZO layer, then ZnO nanowires were grown on the ZnO layer. The growth mechanism of ZnO nanowires can be understood by the different growth rates and surface energies on different crystal facets of ZnO [37], the formation of nanowires is mainly determined by its inherent c-axis orientation growth feature [38]. Fig. 2(b) is the top view image of the sample, which shows that the entire substrate was coated with uniform ZnO nanowires. Furthermore, it can be seen that there is enough spacing among these nanowires, which is ideal for pollutants adsorption and transformation. We also performed the elemental mapping (O, Zn, Al, In and Sn) by EDS attached on SEM, and the ITO layer was confirmed to be on the substrate surface and under the AZO layer, as shown in Fig. 2(c).

To study the crystal structure of samples, XRD studies were carried out and the results are shown in Fig. 3. The data were collected over diffraction angle in the range of 20–80° with a step

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**Fig. 1.** Schematic depiction of the oxygen and zinc vapor flow in the furnace.
of 0.02°. As indicated in Fig. 3, both patterns reveal the strong diffraction peaks corresponding to (002) and (004) planes, from the standard card (PDF# 800020) for the hexagonal wurtzite structure of ZnO. Only the sharp diffraction peaks of (002) and (004) confirms that ZnO nanowires were preferentially grown along the c-axis. The intensity of (004) peak is much lower than that of (002), which is due to that (004) peak is the second order diffraction.

The possible reason is as following. The (002) surface of ZnO has the lowest free energy, resulting in a smooth surface in the equilibrium state. Therefore, ZnO nanowires have a faster growth rate along the c-axis than other orientation, resulting in the fabrication of vertical ZnO nanowires [39]. The low roughness and high crystallinity of the seed layer AZO would contribute to the good vertical alignment of obtained ZnO nanowires [40]. The growth mechanism was further confirmed by the SEM image of ZnO nanowires grown at low Zn vapor pressure which stopped at the initial growth stage, as shown in Fig. 2(d).

3.2. Photocatalytic performance

The photocatalytic performance was studied via the
degradation of RhB, a typical organic pollutant which is extensively generated by the printing and textile industry. Fig. 4 shows the UV–vis absorption spectra of the aqueous solution of RhB with Nws/AZO/ITO and Nws/AZO under exposure to UV light irradiation for different period of time. From 30 to 0 min, the aqueous solution of RhB was in dark for ensuring an adsorption/desorption equilibrium of RhB on samples. The results indicated there are almost no adsorption and self-degradation. It should be noted that we tested the photocatalyst activity using visible light using a light filter in ranges of 400–700 nm, but only negligible effect was observed, indicating that only the ultraviolet light can be absorbed by both samples. This is consistent with the band gap of about 3.37 eV. As can be seen, after 180 min of light exposure, the characteristic adsorption peak of RhB aqueous solution is all at 554 nm, and in the degradation process no new absorption peaks occurred in the wavelength range of 400–700 nm, which suggests that the catalytic mechanism is mainly due to the destruction of conjugated structure of RhB [41]. This demonstrates Nws/AZO/ITO has more excellent photocatalytic performance than Nws/AZO. The degradation rates of RhB under UV irradiation using Nws/AZO/ITO and Nws/AZO were shown in Fig. 5(a), respectively. The controlled experiment without photocatalysts presented shows the negligible self-degradation effect of RhB under UV irradiation (less than 4%). It is obviously observed that the degradation rate of RhB molecules by Nws/AZO/ITO is much higher than the Nws/AZO in the given time.

The photocatalytic degradation kinetic reaction could be interpreted by the pseudo-first-order kinetics which can be described below [42,43]

\[
\ln\left(\frac{C_0}{C}\right) = kt,
\]

where \( k \) is a pseudo-first-rate kinetic constant and \( t \) is the irradiation time, \( C \) is the concentration of RhB at photodegradation time of \( t \) and \( C_0 \) is the initial concentration. The variation of \( \ln\left(\frac{C_0}{C}\right) \) as a function of irradiation time are shown in Fig. 5(b). The values of the squares of linear correlation coefficients (\( R \)) are 0.983 and 0.984 for Nws/AZO/ITO and Nws/AZO (seen in the table of
We can draw conclusion from the above results that Nws/AZO/ITO displays higher photocatalytic activity than Nws/AZO. It is well known that the photocatalytic reaction is usually stimulated by photo-generated electrons and holes, so generally the photocatalytic activity of photocatalyst mainly depends on the separation and transfer of photogenerated electron–hole pairs. The separation capability of the photo-induced carriers can be evaluated by PL technique. The PL signal results from the radiative recombination process of self-trapped excitations. A lower PL intensity means a smaller recombination probability of the photogenerated electron–hole pairs. Fig. 10 presents the PL emission spectra of Nws/AZO/ITO, Nws/AZO and pure glass substrate. It can be seen that, ~385 nm, ~500 nm, ~570 nm and ~670 nm emissions are observed in the PL spectrum of Nws/AZO/ITO and Nws/AZO, when excited by a short wavelength light of 325 nm. The 570 nm and 670 nm emissions are also observed in pure glass substrate, and no strength variation can be observed, which indicates their origination from glass substrate. The ~385 nm UV emission can be assigned to the near-band-edge emission of the band gap of ZnO, while the ~500 nm emission is a common defect emission, can be attributed to the defect state located at the surface of ZnO [45], i.e. the oxygen vacancies [46], and the zinc interstitials [47]. It can be seen from PL spectrum, the emission intensity of the PL signal for Nws/AZO is higher than that for glass substrate, while the emission intensity of the PL signal for Nws/AZO/ITO is obviously lower than that for Nws/AZO. It suggests that with the integration of ITO layer in Nws/AZO/ITO, the recombination of photogenerated charge carriers is effectively inhibited, which is highly favorable for the enhancement of the photocatalytic activity.

The enhanced photocatalytic activity of Nws/AZO/ITO can be ascribed to the matched band edge positions of ZnO Nws, AZO and ITO as well as the heterojunction formations among them. The pure ZnO is a semiconductor with electron affinity of 4.2 eV [48]. As we all know, Al is usually used as n-type dopant of ZnO, so the conductivity of AZO (Al doped ZnO) is much higher than pure ZnO and Fermi level is closer to the conduction band maximum [49,50]. ITO with a band gap of ~3.6 eV [51] is a degenerately doped n-type semiconductor with Fermi level is closer to the conduction band maximum [49,50]. ITO with a band gap of ~3.6 eV [51] is a degenerately doped n-type
transparent conductive oxide, subsequently its Fermi level, \(\text{Ef}\), is positioned slightly above the conduction-band minimum, \(\text{E}_C\). The work function of ITO is \(\sim 4.7\) eV [35]. When ZnO, AZO and ITO closely contact with each other, these semiconductors should have the same Fermi level, leading to the shift of their conduction and valance bands. Consequently, the photo-generated electrons can be injected from the ZnO conduction band to the AZO and afterwards ITO conduction band, while photo-generated holes migrate to the opposite direction. An approximate equilibrium energy-band diagram and schematic diagram for the sample is shown in Fig. 11. In such a way, the photo-generated electrons and holes are efficiently separated and the recombination of electron–hole pairs is suppressed.

![Fig. 8.](image)

Fig. 8. (a) Absorption spectra for the degradation of RhB using Nws/AZO/ITO with 10 \(\mu\)m long ZnO nanowires (the initial concentration of RhB = 12.5 mg/L) and (b) the photocatalytic performances of Nws/AZO/ITO with (1) 10 \(\mu\)m and (2) 16 \(\mu\)m long ZnO nanowires for degradation of RhB under UV irradiation.

![Fig. 10.](image)

Fig. 10. PL spectra of Nws/AZO, Nws/AZO/ITO and glass substrate.

![Fig. 11.](image)

Fig. 11. (a) Band diagram and (b) schematic diagram to illustrate the degradation process of RhB by Nws/AZO/ITO under UV irradiation.

![Fig. 9.](image)

Fig. 9. Five photocatalytic degradation cycles of RhB using Nws/AZO/ITO.
The photogenerated holes can oxidize the -OH anions in aqueous solution to produce -OH which is responsible for degradation of RhB. Meanwhile, on the edge of the ITO layer, a small amount of electrons are trapped by electron acceptors such as adsorbed O₂ to produce superoxide radical anions of O₂−. Next, the O₂− radicals and e− can further react with H₂O to form -OH radicals. A possible photodegradation process of RhB in the presence of Nws/AZO/ITO can be proposed as the following Eqs. (1)–(5):

\[
\begin{align*}
\text{Nws/AZO/ITO} + h\nu & \rightarrow \text{Nws/AZO/ITO} (h^+ + e^-) \quad (1) \\
\text{H}^+ + \text{OH}^- & \rightarrow \text{H}_2\text{O} \quad (2) \\
e^- + \text{O}_2 & \rightarrow \text{O}_2^- \quad (3) \\
2\text{O}_2^- + 2\text{H}_2\text{O} + e^- & \rightarrow \text{OH}^- + 3\text{OH}^- \quad (4) \\
\text{RhB} + \text{OH}^- & \rightarrow \text{CO}_2 + \text{H}_2\text{O} \quad (5)
\end{align*}
\]

It should be noted that the holes might take the main role in the photodegradation process, since the ITO layer is covered by AZO with only the edges exposed to RhB solution which is a very small area.

4. Conclusions

Well aligned perpendicular ZnO nanowires have been fabricated by CVD on glass substrate with AZO as seed layer. By inserting an ITO layer before the growth of AZO layer, enhanced photocatalytic performance has been observed by the RhB degradation under UV irradiation. The enhanced photocatalytic activity could be attributed to the highly efficient separation of the electron–hole pairs induced by the Nws/AZO/ITO heterostructure, due to the effectively collection of photogenerated electrons by the inserted ITO layer.

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References


