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Short Communication

Photoelectrochemical Behavior of Microrod ZnO Coated 316L Stainless Steel Prepared by Hydrothermal Method

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A low-dimensional ZnO film was fabricated on 316L stainless steel (SS) surface by hydrothermal method. Scanning electron microscopy (SEM) showed that the film was consisted of microrods with diameter of about 0.6 μm. X-ray diffraction (XRD) proved the hexagonal phase ZnO of the film. The photoelectrochemical behavior of the microrod ZnO coated electrode was investigated in the presence and absence of UV light irradiation by the open circuit potential (OCP), photocurrent, polarization curve and electrochemical impedance spectrum (EIS) measurements. It was found that the microrod ZnO film exhibited good photo-electrochmical property. The photogenerated current provided noticeable cathodic protection on 316L SS under UV light irradiation. The mechanism of photocurrent cathode protection was discussed.

Keywords: Zinc oxide; Hydrothermal method; Photoelectrochemical property; Photocurrent cathodic protection

1. INTRODUCTION

Semiconductor materials have very wide applications in various fields due to their unique optical and electronic properties. Zinc oxide (ZnO) is an important semiconductor material which has already been widely used in optical waveguides, gas sensors, piezoelectric transducers, bulk acoustic wave devices, transparent conductive films, varistors and solar cell windows [1-6]. With the development of material science, it is commonly believed that ZnO has further application in many fields.

In the past decade, many methods have been employed to prepare ZnO crystals, which can be usually classified into two categories including vapor phase process and solution phase route [7]. The vapor phase approach generally undergoes at relatively high temperatures and a complicate set-up of equipment. On the other hand, solution phase approach has been proven to be a simple and powerful method to prepare ZnO crystals for its low synthesis temperature and potential for mass production. Hydrothermal method, as an important way of solution phase approach, has attracted lots of attention from materials scientists to chemists. Employing this method, a variety of morphologies including nanowires [8], hexagonal clusters [9], nanorods [10], flower-like [11] and whiskers [12] have been synthesized to date.

In order to protect metals from corrosion, sacrificial anodes have been extensively used in applications. Sacrificial anodes are widely used in anti-corrosion measures. While some semiconductor films, such as TiO_2 and ZnO, can be applied at metal surface to act both as coatings and non-sacrificial photoanodes. Under the illuminating of ultraviolet (UV) light, electron-hole pairs can be created at the semiconductor films. The photogenerated current can provide electrons to the matrix metal, and then decrease the potential of the metal to protect metals from corrosion. The semiconductor film would not be consumed or sacrificed. Instead, the water (H_2O) in the system would be the real one that undergoes the anodic reaction. Thus, the investigation of photogenerated cathode protections of metals coated by semiconductor film under UV irradiation is attractive because it is a completely sustainable corrosion protection measure [13-16].

In this work, the microrod ZnO films were prepared on 316L stainless steel (SS) by hydrothermal method. The photoelectrochemical behavior of the ZnO coated 316L SS electrode was investigated in detail. The application of the ZnO film for photocurrent cathodic protection on metal under UV illumination was discussed.

2. EXPERIMENTAL

Chemical reagents used in our experiments are all analytical grade. The deionized water was used for solution preparation. The fabrication of low-dimensional ZnO structures includes two main steps: (1) formation of ZnO crystal nucleus on 316L SS sheet, and (2) growth of low-dimensional ZnO structures by hydrothermal method in autoclave.

The formation of ZnO crystal nucleus on 316L SS was carried out by a sol-gel method [17]. 0.02 mol of $Zn(CH_3COOH)_2\bullet 2H_2O$ was poured into 150 ml diethylene glycol (DEG). Then the solution was kept at 180 °C for 1 h and cooled down to room temperature. The cooled solution was then dropped onto the 316L SS sheet. The sample was annealed at 150 °C for 30 min to remove all the unnecessary substances.

In the second step, hydrothermal method was used to synthesize the low-dimensional ZnO structures. The precursor was prepared by $Zn(NO_3)_2\bullet 6H_2O$ and hexamethylenetetramine (HMT), with the concentration of 0.1 mol/L (zinc ions) and the molar ratio of 1:1 (Zn^{2+}: HMT). Ammonia solution

(25%) was used as titrate solutions for increasing pH value. The prepared solution was added into a Teflon-lined autoclave (volume: 50 ml) with a filling capacity of about 30%. Afterwards, a ZnO crystal nucleus coated 316L SS sheet was put into the bottom of the autoclave. The autoclave was then placed into an oven and kept at 120 °C for 8 hours. After the experiment, the 316L SS sheet, with the final ZnO structure on the surface, was thoroughly washed with deionized water and acetone, and finally dried in air.

The photoelectrochemical measurements were conducted with an AUTOLAB PGSTAG 30 Electrochemical Measurement System. A 100W high voltage mercury lamp was used as UV source. All the potentials reported in the paper were relative to a saturated calomel electrode (SCE), and the counter electrode was platinum. Open circuit potential (OCP) measurements were carried out as soon as soaking the working electrode into the electrolyte. The variations of OCP with different surface conditions with time were recorded for 5500 seconds. In polarization curve measurements, the potential range was from -250 mV to +250 mV (vs. SCE). The scanning rate was 0.5 mV/s. The i-t measurement was conducted at OCP, with alternative switching on and off the light. The V-t measurement also carried out at OCP, with the same pattern of i-t measurement. In electrochemical impedance (EIS) measurements, a perturbation potential of 10 mV amplitude was applied over the frequency range of 10^{-2}-10^{5} Hz. All the tests were carried out at ambient temperature.

The morphology of low-dimensional ZnO structures at 316SS sheet surface was observed by scanning electron microscope (SEM, JSM-6490LV). The crystal structures of samples were also tested using X-ray diffraction (XRD, BEDE-DI, with Cu-Kα radiation, λ=1.542 Å), with Bragg angle ranging from 20 ° to 80 °.

3. RESULTS AND DISCUSSION

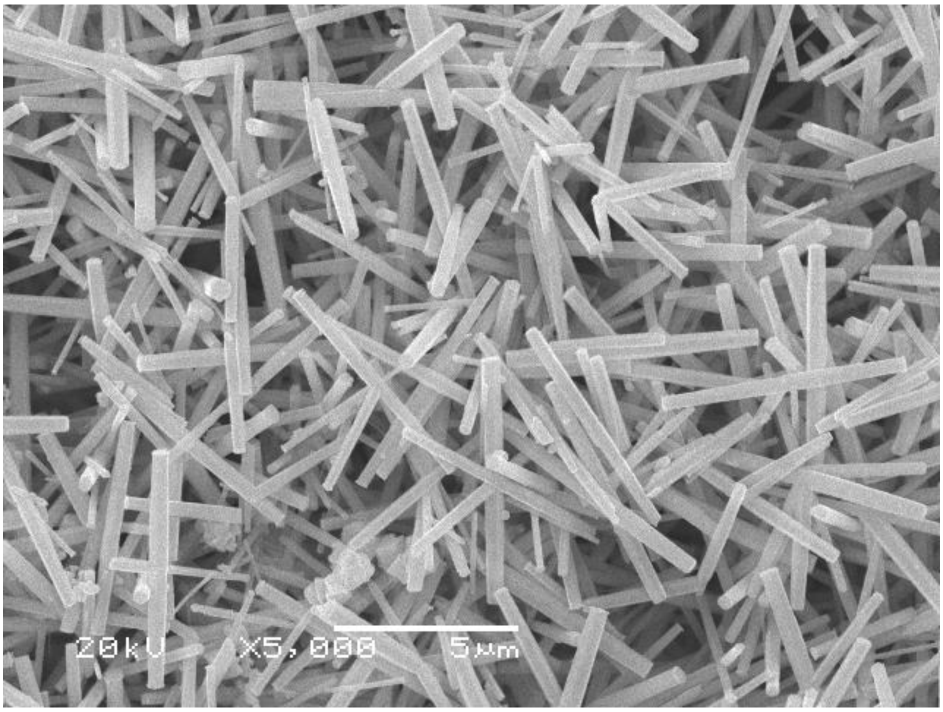

Figure 1. SEM image of microrod ZnO film

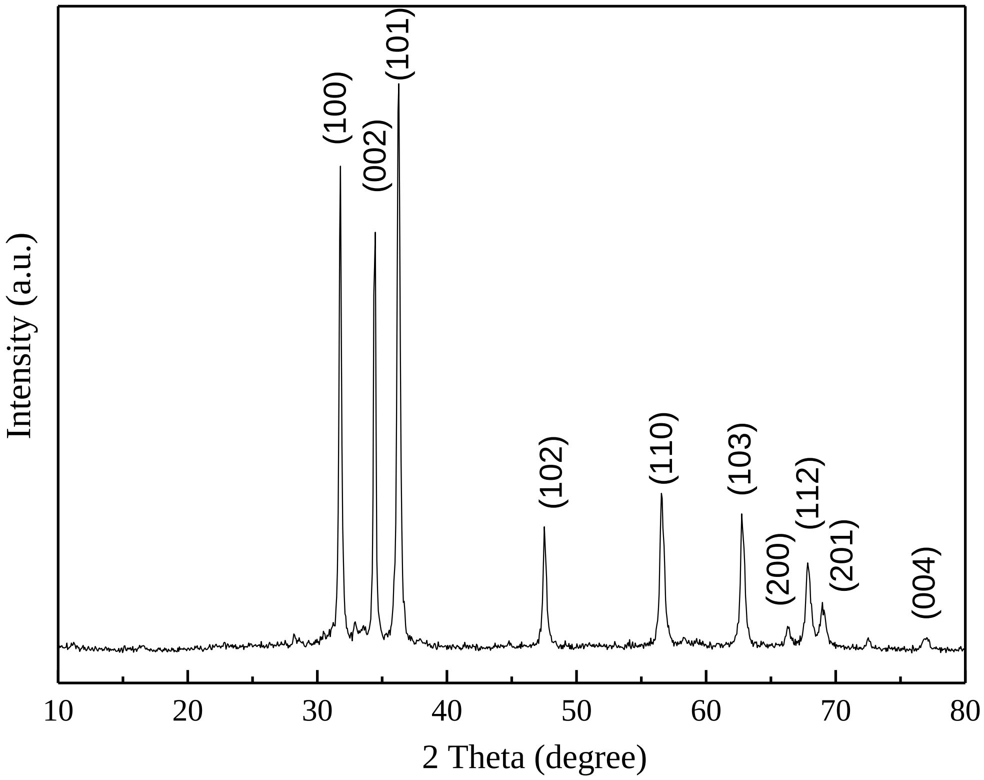

Figure 2. XRD pattern of microrod ZnO film

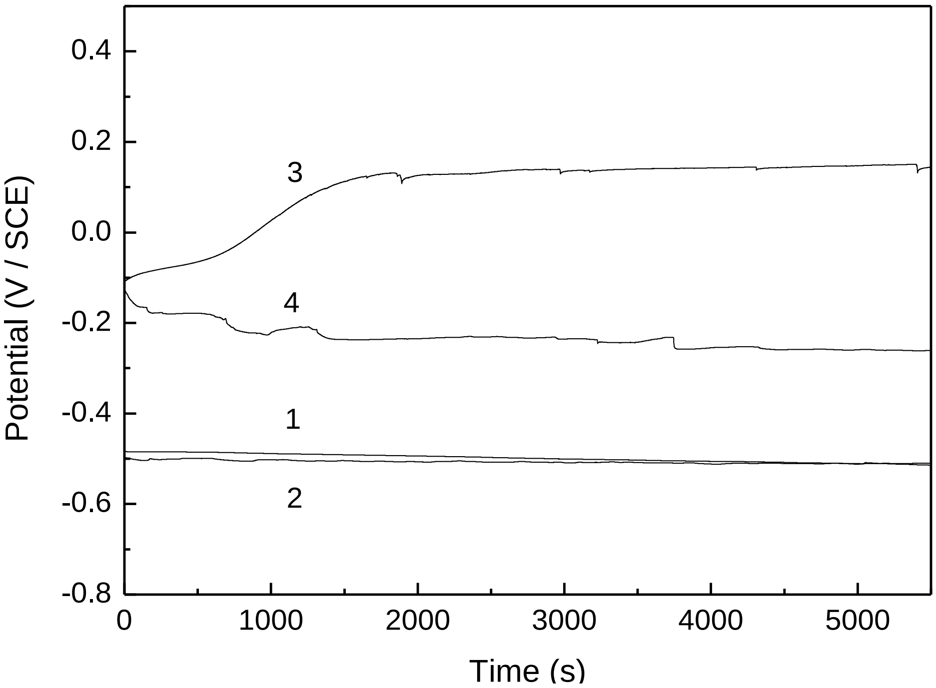

Figure 3. Open circuit potentials (vs. SCE) vs. time in the presence and absence of UV light irradiation of bare 316L SS and ZnO coated steel. (1) Bare SS in the dark. (2) Bare SS under UV irradiation. (3) ZnO film in the dark. (4) ZnO film under UV irradiation.

Fig. 1 shows the morphology of ZnO film on 316L SS surface. The film is consisted of microrods with diameter of about 0.6 μm. The XRD results obtained from the ZnO film on 316L SS in Fig. 2. It shows the presence of ZnO with good crystallinity. All the diffraction peaks can be indexed as the hexagonal phase ZnO reported in the standard card (JCPDS 36-1451). No obvious characteristic peaks are observed for other impurities.

The photoelectrochemical behavior of the ZnO microrod film on 316L stainless steel surface was investigated in the presence and absence of UV light irradiation in 3 wt. % NaCl solution. The open potential circuit (OCP) results are presented in Fig. 3. It is shown that, on bare metal surface (curve 1 and 2), UV light irradiation has only limited influence on OCP. It is generally believed that the protective passive film can be formed on metal surface in corrosive aqueous solution [18]. Cr_2O_3 and Fe_2O_3 compound film exists on 316L stainless steel surface in aqueous solution. The compact film can be very stable and exhibit excellent corrosion resistance. The semiconductor compound can generate photoelectrons under UV light irradiation [7, 8]. While the Cr_2O_3 and Fe_2O_3 compound does not exhibit apparent photoelectrochemical performance and can not generate enough photoelectrons to change the OCP remarkably. Therefore the OCP values of the both curves remain stable and only slightly shift negatively with the immersion time. As for the sample coated with ZnO microrods, OCP increases with the time in the dark, and stabilizes at about 0.1V gradually. The increase of potential can be ascribed to the penetration of Cl^- on ZnO film. The stable OCP indicates the stability of mass and electron transfer on stainless steel surface through ZnO film. When the microrod ZnO film is under UV light irradiation, the OCP moves in positive direction gradually and stabilized eventually. It can be attributed to the photoelectrons offered by the ZnO film. The accumulated electrons on metal surface lead to the moving of OCP.

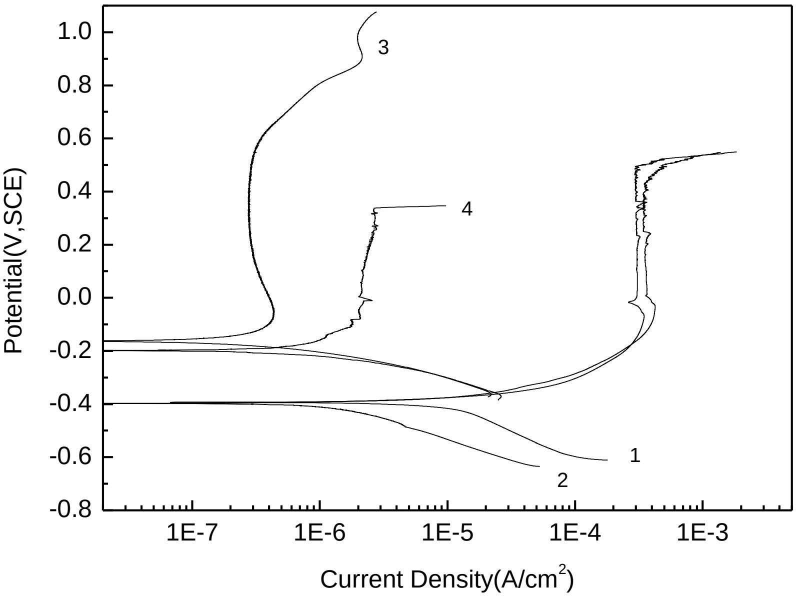

Figure 4. Comparison of the polarization curves for the bare 316L SS and the ZnO coated one in the dark and under UV irradiation, with the potential scanning range from -250mV to 250 mV (vs. SCE) and scanning rate of 0.5 mV/s. (1) Bare SS in the dark. (2) Bare SS under UV irradiation. (3) ZnO film in the dark. (4) ZnO film under UV irradiation.

Potentiodynamic polarization measurements show that on bare 316L SS surface, the anodic polarization curves exhibit apparent passivity (Fig. 4). Meanwhile, the current transients can be observed which indicates the occurrence of metastable pitting [19]. The passive current density of the ZnO coated electrode is less than bare stainless steel. Especially the ZnO sample without UV irradiation, the passive current density is less than 1 μA. The good passivity means excellent protection effect on metal substrate. The passive current density increases when the ZnO coated electrode is under UV irradiation. The photoelectrons elevate the current density, which is in accordance with the OCP behaviors. In addition, compared to bare 316L SS, the pitting tendency of the ZnO coated electrode decreases, which can be obtained from the current fluctuation intensity in the passive region of the anodic polarization curves [20].

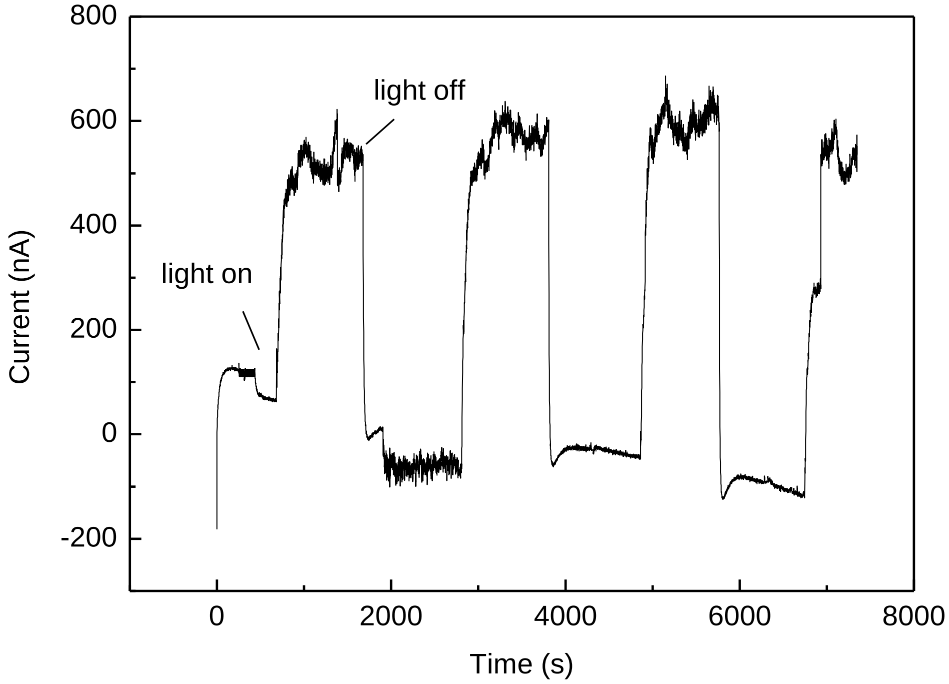

Figure 5. The influence of UV irradiation on current of ZnO coated 316L SS.

Fig. 5 shows the current-time (I-t) curve obtained from potentiostat measurement (under OCP). It indicates the influence of UV irradiation on the photogenerated electrons. Under UV irradiation, the current increases rapidly and finally fluctuates at a relatively constant range. The current goes down sharply as soon as UV light switches off. And the photocurrent returns back to the original value as soon as the light irradiates again. It indicates that the current increase under irradiation is completely due to the occurrence of the photogenerated electrons.

The photocurrent cathodic protection property of microrod ZnO film on substrate metal under UV irradiation has also been investigated. Fig. 6 shows the influence of UV irradiation on the photogenerated potential. Upon irradiation with UV light, we observe a sudden drop of potential (in negative position). The amplitude of potential shift is more than 100 mV. Although the shifted potential is still more than the one of the substrate metal, it still offers cathodic protection effect.

However, the potential returns to a steady state and ceases to provide cathodic protection effect as soon as the irradiation stops. This phenomenon is attributed to the charge recombination [9].

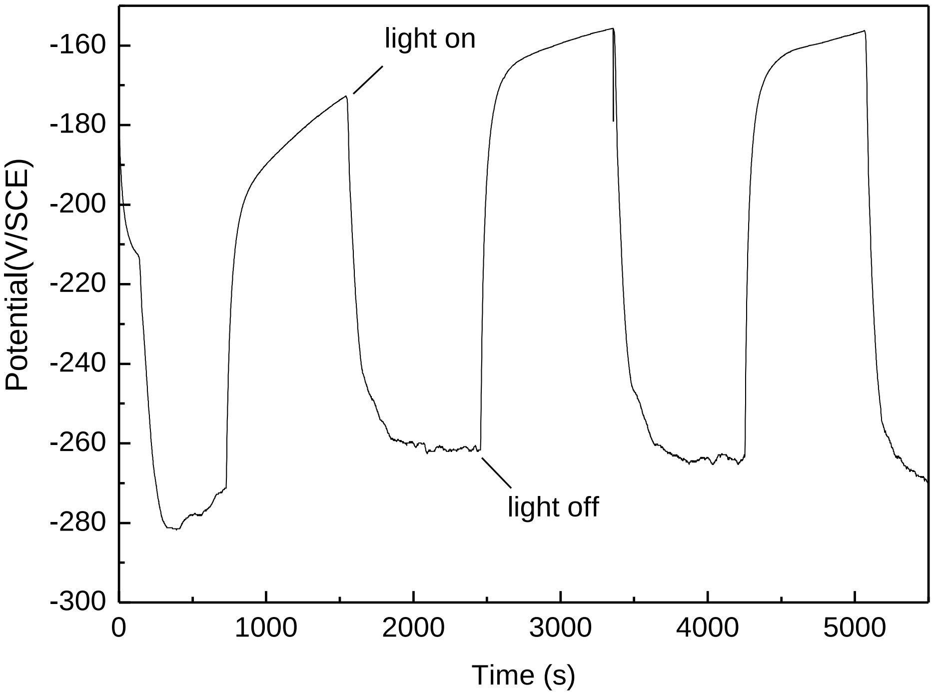

Figure 6. The influence of UV irradiation on OCP of ZnO coated 316L SS.

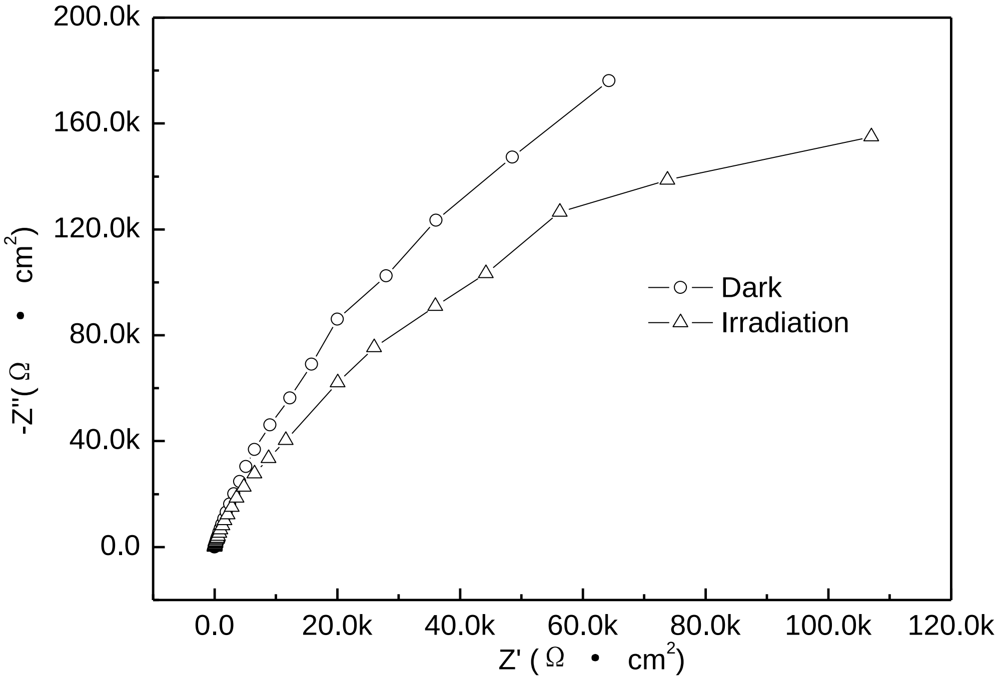

Figure 7. Nyquist plots of ZnO microrod film in the dark and under UV irradiation.

In order to obtain further information on the electrochemical behavior of the film, EIS was carried out at OCP in 3 wt. % NaCl solution under UV irradiation and in the dark, respectively. The Nyquist plot is shown in Fig. 7.

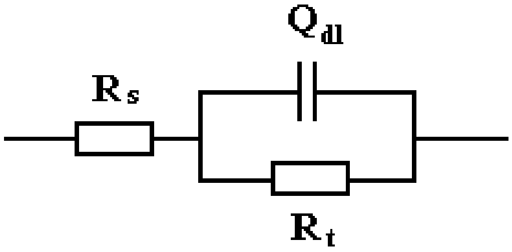

Figure 8. Equivalent circuit of the electrochemical system ZnO film/solution.

There is only one capacitive arc on the Nyquist plot. Therefore, the equivalent circuit is shown in Fig. 8, in which R_s represents the electrolyte solution resistance, R_t and Q_{dl} stand for the charge transfer resistance and double layer capacitance, respectively. Table 1 shows the fitting impedance parameters with the equivalent circuit.

Table 1. Fitting result of Nyquist plots using the equivalent circuit.

	$R_s(\Omega\cdot\mathrm{cm}^2)$	$R_p(\Omega\cdot\mathrm{cm}^2)$	$\mathrm{CPE}(\Omega^{-1}\mathrm{s}^{-n}\mathrm{cm}^{-2})$	n
In the dark	19.05	9.51×10^5	5.97×10^{-5}	0.90
Under UV irradiation	19.84	4.18×10^5	5.15×10^{-5}	0.91

The arc shape of both Nyquist plots, in the dark and under irradiation, is quite similar. But upon irradiation condition, the arc diameter is remarkably decreased compared with the dark. Under UV irradiation, the photogenerated electrons penetrate the ZnO film and reach the 316L SS surface, which can increase the current of the system. Therefore, the electrochemical reaction rate increases. In addition, the R_t and Q_{dl} change due to the reaction between the photogenerated electrons and the dissolved O_2 in the solution [7].

4. CONCLUSIONS

In this work, ZnO film was successfully prepared on 316L SS surface by hydrothermal method. The film consists of microrods with diameter of about 0.6 μm. The photoelectrochemical behaviors of ZnO coated 316L SS were investigated. OCP measurements show that on bare metal surface, UV light irradiation has only limited influence on OCP. UV irradiation has noticeable influence on the electrode coated with ZnO film. The potential shifts negatively and provides cathode protection effect. Polarization curves also proved that the photoelectrons increase the passive current density, which is in accordance with the OCP behaviors. UV light irradiation on ZnO coated electrode can increase the current of the system and decrease the potential simultaneously. Meanwhile, the current and potential return back to the original level as soon as the irradiation stops. It indicates that the photoelectrons occurred under UV irradiation can offer cathode protection to metal substrate. Lastly, EIS measurements approved that the photoelectrons increase the system current and electrochemical reaction rate.

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