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Black ZnO thin film on Ti, Mg and stainless steel substrates via ultrasonic mechanical coating: the study of materials characterization, spectroscopic and photoelectrochemical properties

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ABSTRACT

In this research, the black ZnO thin film were synthesized on Ti, Mg and stainless steel substrates by ultrasonic mechanical coating (UMC), respectively. The ZnO powders were mixed with ethanol to form a suspension solution, which is then spread on to a commercially Ti, Mg and stainless steel substrates. The vibration generator is powered by a piezo motor and applies a high-amplitude oscillation of the resonator at a fixed vibration frequency of 20 kHz and a vibration amplitude of 50, 65 and 80 μm. The stainless steel balls (average diameter 1 to 2 mm) were accelerated with chaotic motion in the chamber, and the bombardments of the stainless steel balls have strong impacts on the surface of the different substrates. The multilayer ZnO powders were bombarded and embedded into the substrate to form a thin film during ultrasonic mechanical coating. The coating treatment was performed for one cycle of 30 seconds. Each sample was subjected to 4 cycles, i.e., 2 minutes for a coating treatment. After the entire coating treatment is completed, the sample is rinsed with alcohol to remove non-adherent powders on the substrate.

The products of ZnO thin film on Ti, Mg and stainless steel substrates by ultrasonic mechanical coating with the color of black by naked eyes observation could be attributed by the non-stoichiometry of oxygen and large amount of defects during the extreme process. The XRD measurements show a typical wurtzite-type structure of the black ZnO_{1-x} thin films even in different substrates. The surface of the black ZnO_{1-x} thin film presents a large numbers of bombardment pits during UMC by optical microscopic observations, and the average grain size is about 100~400 nm with the layered stacking morphology by SEM observations. The black ZnO film was analyzed the absorption spectrum, bonding vibration and luminescence characteristics, Throught the UV-Vis absorbance spectra , Raman spectra (Raman) and Photoluminescence spectra (PL). In addition, the photocatalysis experiments show the black ZnO_{1-x} thin film on Ti, Mg and stainless steel substrates could have significant photodegradation of the methyl orange solution under the UV light irradiation.

The measurement of ZnO Film was measured by the potentiostat, and the basic electrochemical properties of the material can be measured by the three-electrode system, using 300 W xenon lamp; Ag / AgCl as reference electrode of the three-electrode system; Platinum as auxiliary electrode; samples as the working electrode; 0.1 m KOH as the electrolyte, scan rate is 0.1V/s, constant current were set to 1.2 V/cm^2 and 2 V/cm^2, respectively. According to the picture of cyclic voltammetry which is compared to the difference of having light or not.The experiment signs that the curve of the no light is smoother than the curve of light,and the graph will vary with the constant current. The current density vs.time graph obtained by the convective chronoamperometry shows that the change of the constant current will affect the current density. The photoelectrochemistry experiment shows that the black ZnO film on Ti substrate has the best photoelectrochemistry effect under xenon lamp irradiation.

Keywords: Black ZnO thin film; ultrasonic mechanical coating; Materials characterization; Spectrographic analysis; Photoelectrochemical analysis

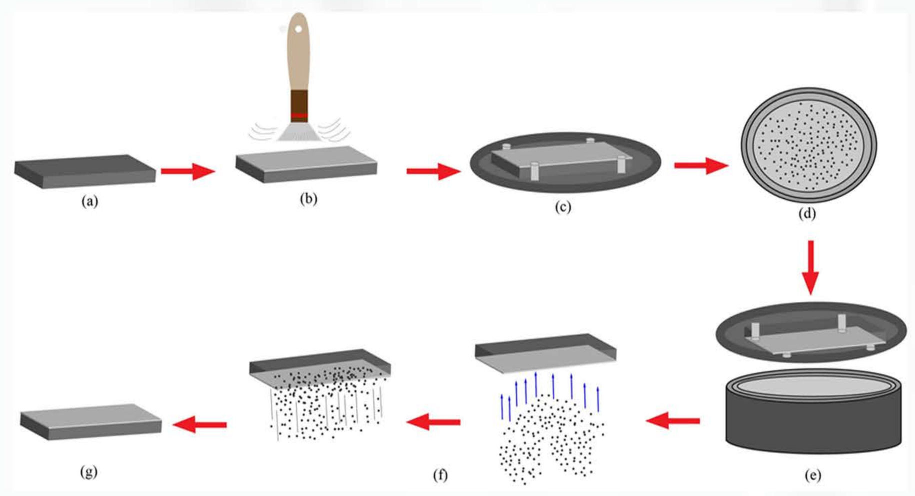


Figure 1. Ultrasonic shot peening process: (a) selecting a suitable substrate; (b) brushing the alcohol and ZnO powder mixed solution on a selected substrate and making it evenly distributed; (c) fixing the substrate with colloidal ZnO on platform; (d) putting stainless steel balls in the holder; (e) covering the platform on the holder; (f) running ultrasonic shot peening; (g) final product.

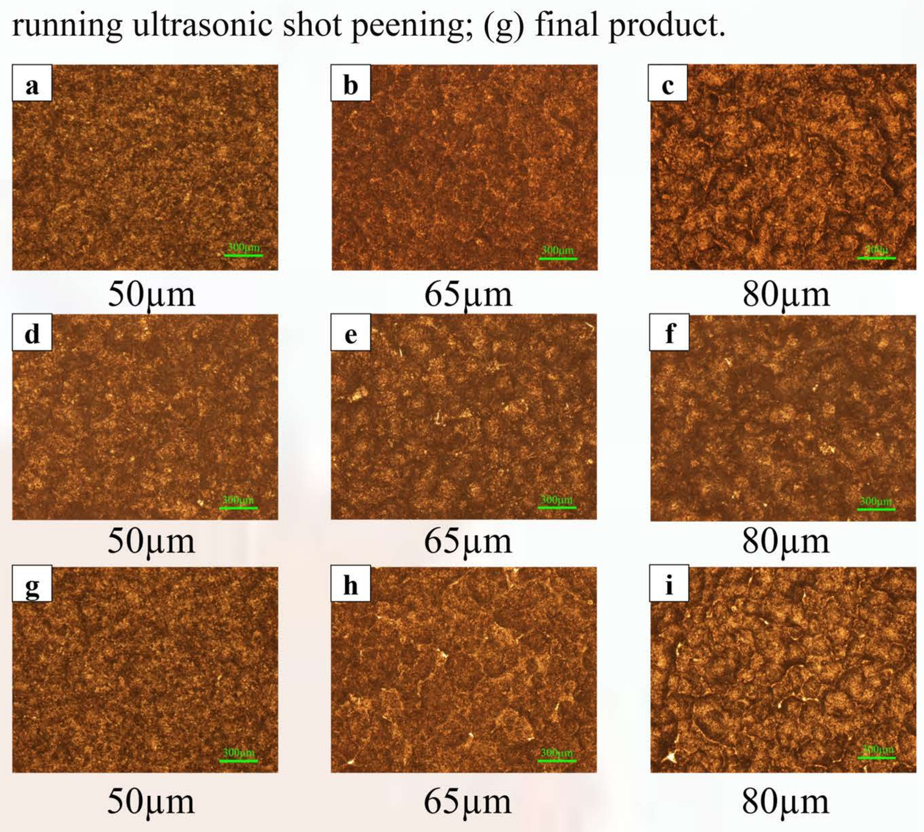


Figure 2. The optical microscopic observations on three different substrates: (a) to (c) for Ti, (d) to (f) for Mg, and (g) to (i) for 304Sus with the UMC amplitudes of 50, 65, and 80 μm, respectively.

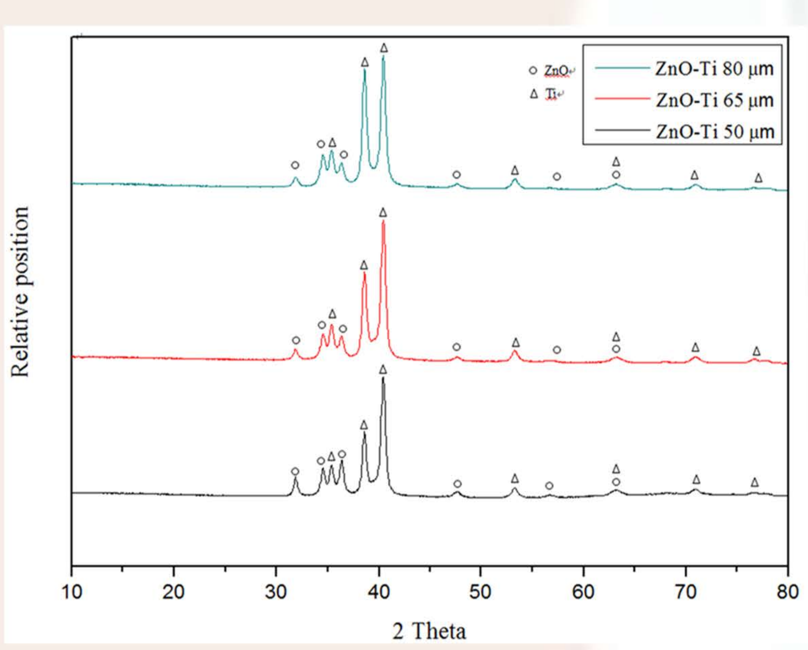


Figure 3. The XRD of black ZnO thin film on Ti substrate with the UMC amplitudes of 50, 65, and 80 μm, respectively.

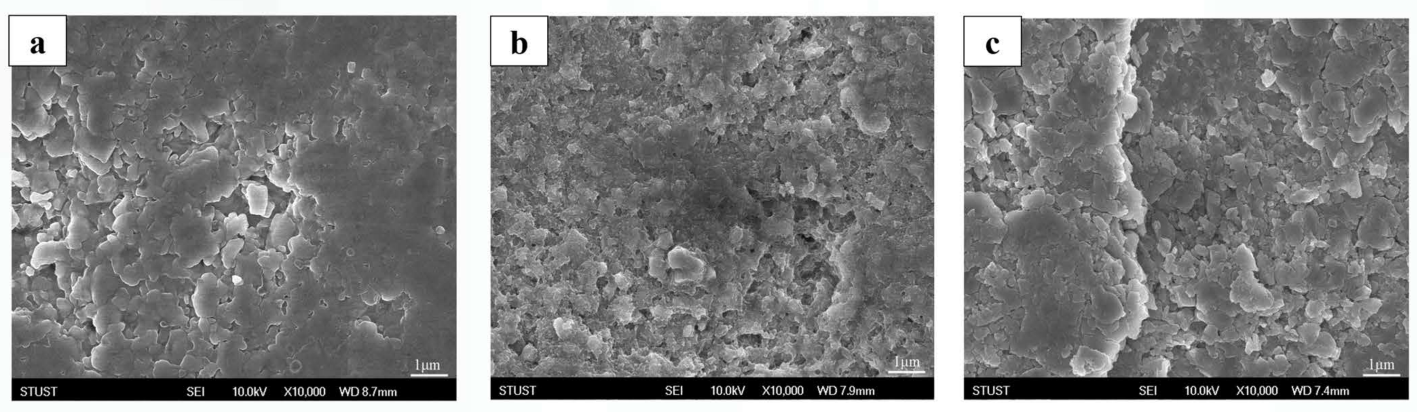
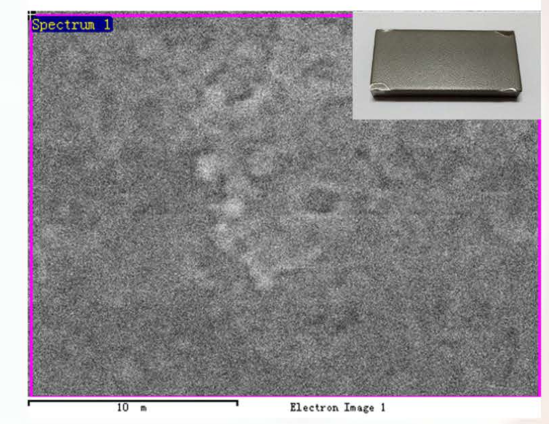


Figure 4. The SEM images of black ZnO thin film on Ti, Mg, and 304Sus substrates with the UMC amplitude of 50 μm.



Element	Weight%	Atomic%
C K	2.30	6.46
O K	21.10	44.48
Al K	2.36	2.96
Ti K	41.49	29.21
Zn L	32.75	16.89
Totals	100.00	

Figure 5. The SEM image and related EDX spectrum of black ZnO thin film on Ti substrate with the UMC amplitude of 50 μm. The inset shows the image of the thin film taken by camera.

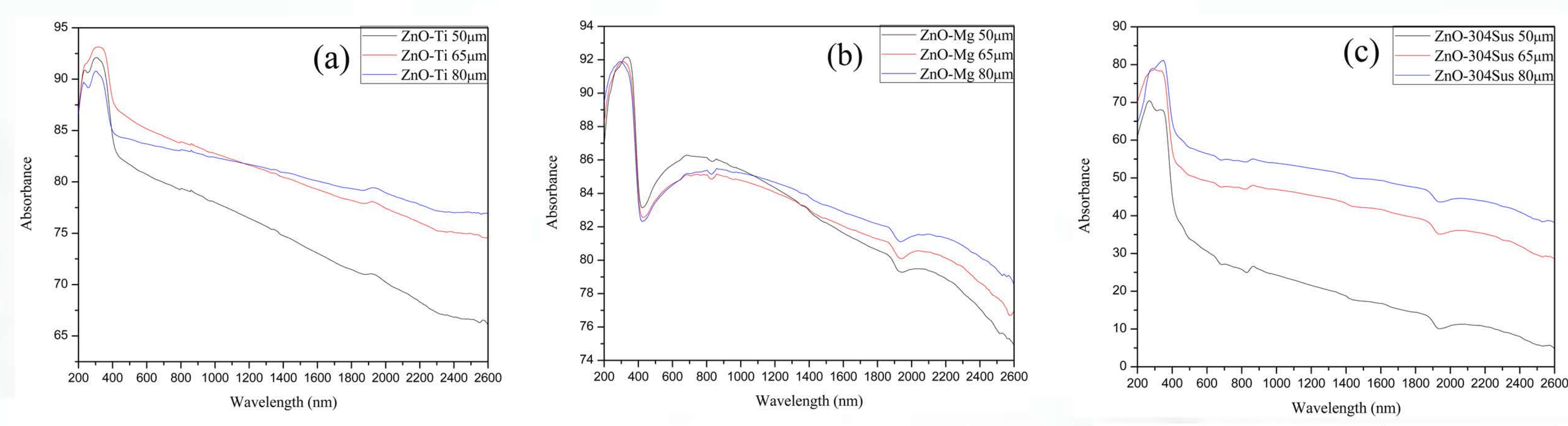


Figure 6. The UV-Vis absorbance spectra of black ZnO thin films on Ti, Mg, and 304Sus substrate with the UMC amplitude of 50 μm, 65 μm, and 80 μm, respectively.

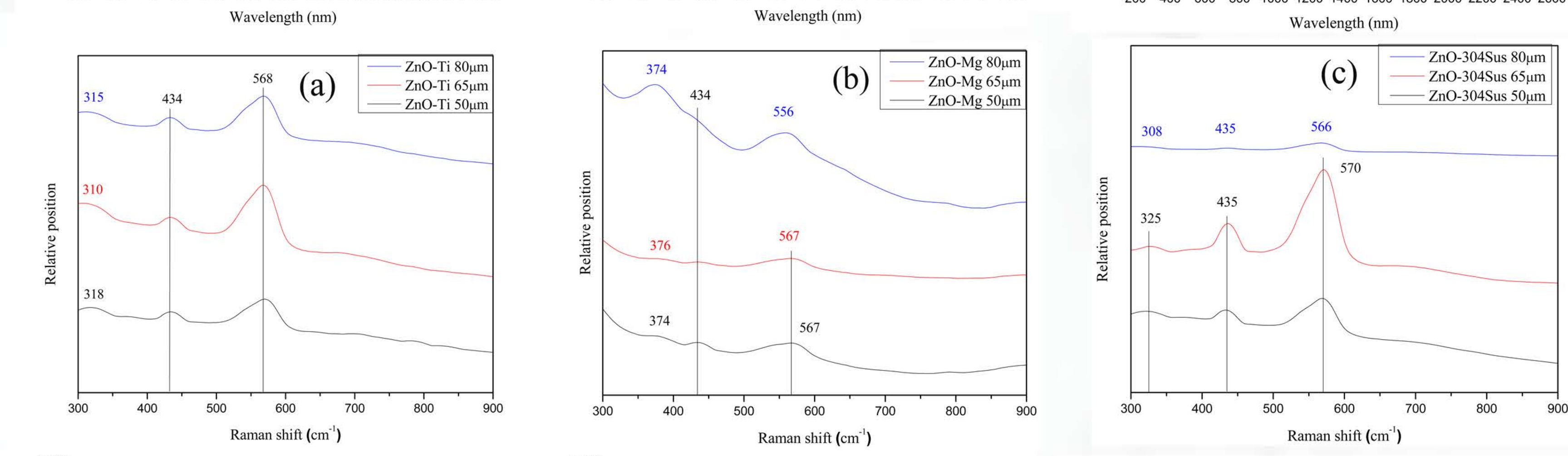


Figure 7. The Raman spectra of black ZnO thin film on Ti, Mg, and 304Sus substrate with the UMC amplitudes of 50, 65, and 80 μm, respectively.

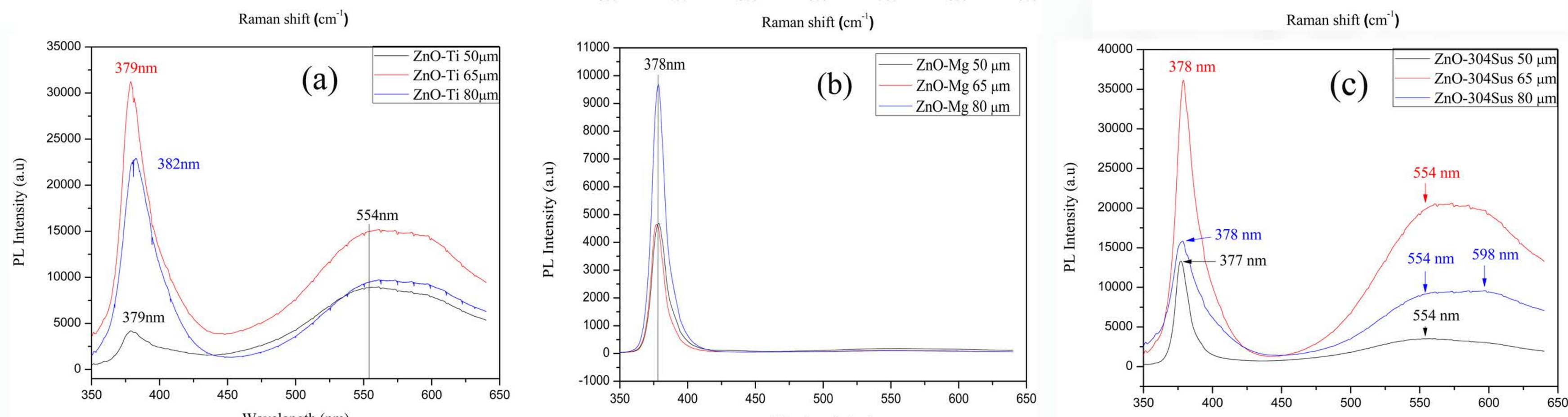


Figure 8. The Photoluminescence spectra of black ZnO thin film on Ti, Mg, and 304Sus substrate with the UMC amplitudes of 50, 65, and 80 μm, respectively.

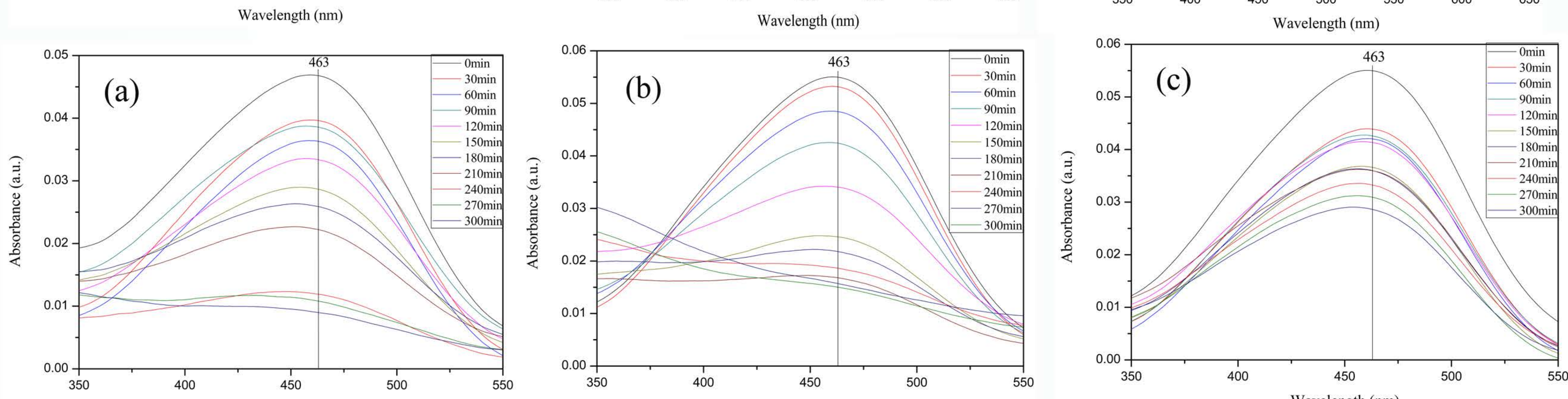


Figure 9. Photodegradation of the methyl orange solution under the UV light irradiation subjected to the black ZnO thin film on Ti, Mg, and 304Sus substrate with the UMC amplitude of 50 μm.

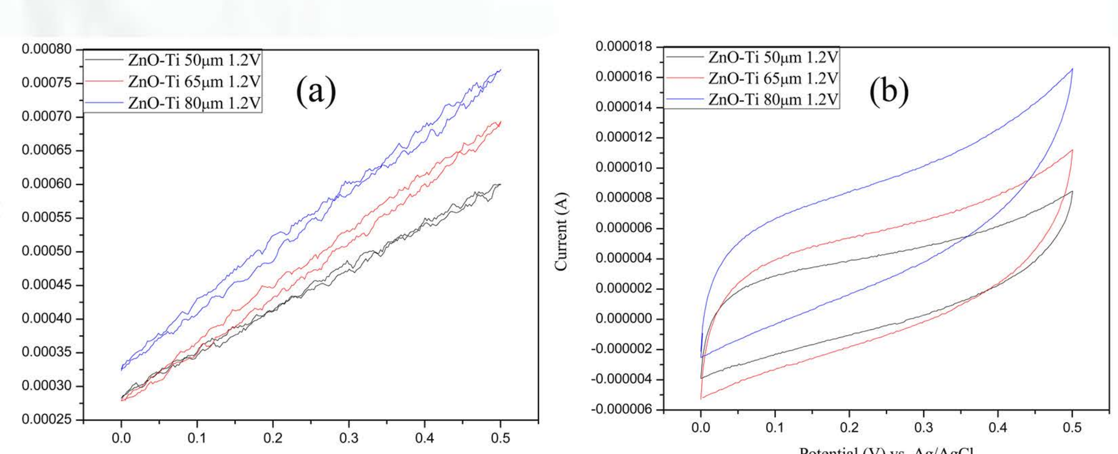


Figure 10. The cyclic voltammetry images of black ZnO thin film on Ti substrate with the UMC amplitudes of 50, 65, and 80 μm, respectively.

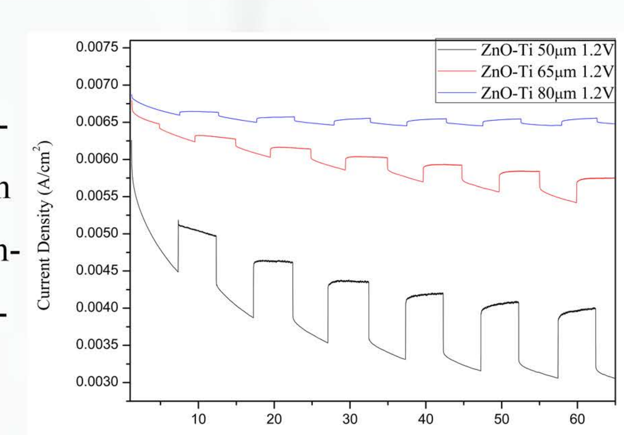


Figure 11. The photoelectrochemistry images of black ZnO thin film on Ti substrate with the UMC amplitudes of 50, 65, and 80 μm, respectively.

CONCLUSION

1. The optical microscopic observations show the bombardment pits on the surface of black ZnO thin film have become more obvious as the amplitude increases, and this kind of effect is more serious on the harder the substrates like Ti and 304 Sus.
2. The results of XRD show that the black ZnO_{1-x} thin film is wurzite structure, and the crystallinity decreased as the UMC amplitude increased.
3. The average grain size of the black ZnO thin film is about 100~400 nm with the layered stacking morphology by SEM observations.
4. The Photoluminescence spectra shows that using 325 nm wavelength as excitation light. With the black ZnO thin films on Ti , Mg , and 304Sus substrate ,which the UMC amplitude of 50 μm, 65 μm, and 80 μm have zinc oxide fluorescent signals at wavelength of 379 nm. Only the thin films on 304Sus and Ti substrate have a fluorescent signal at 554 nm.
5. The Raman spectra show that there are wurtzite structure of the black ZnO and characteristic peaks of oxygen defects at 330 cm^{-1}, 434 cm^{-1}, and 568 cm^{-1}.
6. The UV-Vis absorbance spectra show the huge absorbance enhancement in visible light range comparing to white ZnO.
7. The photocatalysis experiments show the black ZnO thin film on Ti, Mg and stainless steel substrates could have significant photodegradation of the methyl orange solution under the UV light irradiation. Comparing to all the cases, the black ZnO thin film on Ti substrate has the best performance.
8. According to the image of cyclic voltammetry which is compared to the difference of having light or not. The experiment signs that the curve of the no light is smoother than the curve of light,and the graph will vary with the constant current. The current density vs. time graph obtained by the convective chronoamperometry shows that the change of the constant current will affect the current density. The photoelectrochemistry experiment shows that the black ZnO film on Ti substrate has the best photoelectrochemistry effect under xenon lamp irradiation.

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