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Research Article

The Effects of Dilute Sulfuric Acid on Sheet Resistance and Transmittance in Poly(3,4-thylenedioxythiophene): Poly(styrenesulfonate) Films

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The conductivity of poly(3,4-thylenedioxythiophene): poly(styrenesulfonate) (PEDOT: PSS) films by adding various molar concentrations of sulfuric acid (H_2SO_4) was improved and studied in this paper. The sheet resistance of the doped PEDOT: PSS film was enhanced with increasing the ratio of H_2SO_4, but it drops after the maximum sheet resistance. The reason for this phenomenon is resulting from the fact that the H_2SO_4 preferentially react with the sorbitol which is so-called the pinacol rearrangement. The nonconductive anions of some PSS^- were substituted by the conductive anions of hydrogen sulfate (HSO_4^-) when the residual H_2SO_4 reacted with PSS. In addition to the substitution reaction, PEDOT chains were increasingly aggregated with increasing the ratio of H_2SO_4. After doped H_2SO_4, the sheet resistance of H_2SO_4-doped PEDOT: PSS film is improved nearly 36%; the surface roughness is reduced from 1.268 nm to 0.822 nm and the transmittance is up to 91.9% in the visible wavelength range from 400 to 700 nm.

1. Introduction

The poly(3,4-thylenedioxythiophene): poly(styrenesulfonate) (PEDOT: PSS) is a conductive polymer blend, which mainly consisted of two substances, PEDOT and PSS. The PEDOT is a polymer of the 3,4-thylenedioxythiophene (EDOT), which is insoluble in water. The solubility of the PEDOT increased through being combined with the PSS. Therefore, the PEDOT: PSS becomes easier to use.

The PEDOT: PSS was widely applicated to electronic devices such as organic solar cells, actuators, capacitors, organic light-emitting devices, and sensors [1–3]. One of the fundamental requirements for operation of all organic optoelectronic devices is a stable anode interface. Indium tin oxide (ITO) has been widely used for organic optoelectronic devices due to its high optical transparency and high conductivity. However, the work function of ITO is low. The most common way is to be coated with a buffer layer on the top of ITO surface. The buffer layer can export the carriers more efficiently.

Among these buffer layers, the PEDOT: PSS is superior to other materials due to its structural stability, optical transparency, and process ability. The PEDOT: PSS as the buffer layer not only increases the work function of the ITO but also planarizes the surface of ITO substrate. The insufficient conductivity of the PEDOT: PSS is a restriction for application in optoelectronic devices, although the PEDOT: PSS has the above advantages. Therefore, the topic of enhancement on conductivity of the PEDOT: PSS was studied by many researchers. The research of the PEDOT: PSS indicates that the conductivity of the PEDOT: PSS film can be increased by the addition of organic solvents, such as sorbitol [4–7], dimethyl sulfoxide (DMSO) [7–10], glycerol [7, 11–13], ethylene glycol (EG) [14–16], or polyethylene glycol (PEG) [17].

In this paper, the conductivity of PEDOT: PSS solutions was improved through adding the inorganic solution, dilute sulfuric acid. The PEDOT: PSS solutions were prepared with different molar concentrations of dilute sulfuric acid to induce variations on the surface morphology and the electrical properties of PEDOT: PSS films. The mechanism of enhancement conductivity for PEDOT: PSS films was further studied through measuring instruments. These experimental results provided further evidences for our proposed mechanism.

2. Experimental

The SIGMA D-Sorbitol (98%) doped the Clevios PH 500 PEDOT: PSS was used as the solution for preparation of thin films by the spin-coating method. The sorbitol was added to the PEDOT: PSS solution directly, and then the doped PEDOT: PSS solution was stirred for 30 min at room temperature. The mixed solution was doped again by adding different molar concentrations of dilute sulfuric acid. At last, the mixed PEDOT: PSS solution is the so-called double doped PEDOT: PSS solution. Glass substrates with an area of $2 \times 2\,\text{cm}^2$ were precleaned with acetone, methanol and deionized (DI) water in an ultrasonic bath for 10 min each time, sequentially. Finally, glass substrates were dried with nitrogen. The double doped PEDOT: PSS solution was coated by spinner on the cleanly glass substrate and formed the double doped PEDOT: PSS film. The spin-coating was performed at a rotation rate of 3500 rpm for 20 sec. The double doped PEDOT: PSS film was heated at 150°C for 20 min on a hotplate in ambient lab conditions.

The sheet resistance of double doped PEDOT: PSS films was measured with four point sheet resistivity meter (SRM103, Solar Energy Tech., Taiwan). The surface morphology and roughness of double doped PEDOT: PSS films were measured by atomic force microscopy (AFM, Park Systems, XE-70). And the transmittance of double doped PEDOT: PSS films were measured by UV/visible spectrometer (HITACHI, U-3900).

3. Results and Discussion

The electrical property of the PEDOT: PSS is strongly dependent on its chemical and physical structures. The chemical structures of the PEDOT and the PSS are shown in Figure 1. The –OH groups of the PSS structure were dissociated to H^+ in the water. And the H^+ actively attacked the double bond of the thiophene of the PEDOT to form hydrogen bonding. However, electrons of the C–O shared electron pairs were attracted by O due to its higher electronegativity. The phenomenon led to the fact that the C of the C–O bond became a positive charge. Finally, the ionic bond was formed between the C^+ of the PEDOT structure and the O^- of the PSS structure. The reaction of the PEDOT and the PSS was shown in Figure 2.

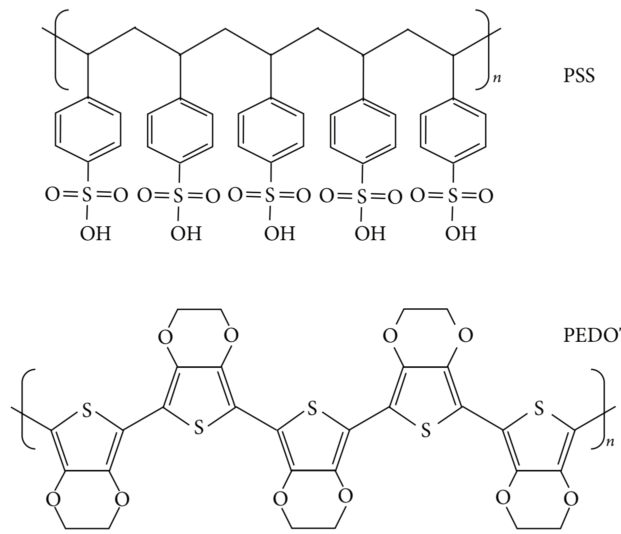

Figure 1: Chemical structure of PEDOT: PSS.

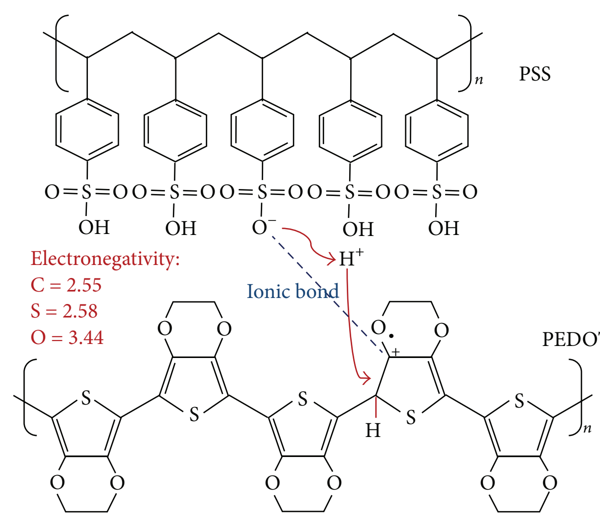

Figure 2: Schematic illustration of the reaction between PEDOT and PSS.

The conductivity of the PEDOT: PSS was enhanced through adding the solvent, such as sorbitol. The sorbitol treatment screens the ionic interaction between PEDOT and PSS to form ionic bonding. The screening effect led to better phase separation between PEDOT and PSS. Thus, the coiled type of PEDOT and PSS chains was reoriented to the linear type of PEDOT and PSS chains [18–20]. The schematic illustration of the reorientation of PEDOT: PSS was shown in Figure 3. In addition, additives of the polyol caused PEDOT chains aggregation [16, 21, 22].

The conductivity of the PEDOT: PSS was further enhanced through adding the dilute sulfuric acid again. Figure 4 shows that the sheet resistance and surface roughness of the doped PEDOT: PSS film through adding 1.5 M H_2SO_4 was measured by four-point probe and AFM,

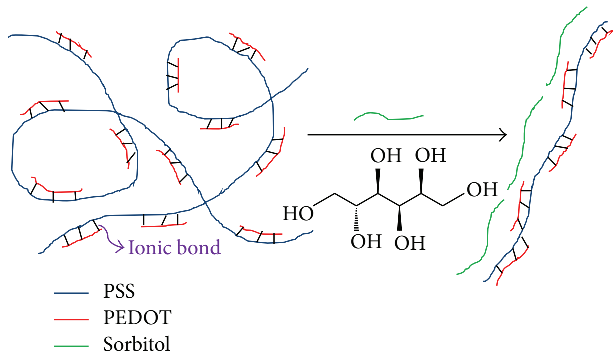

Figure 3: Schematic illustration of the reorientation of PEDOT: PSS by sorbitol.

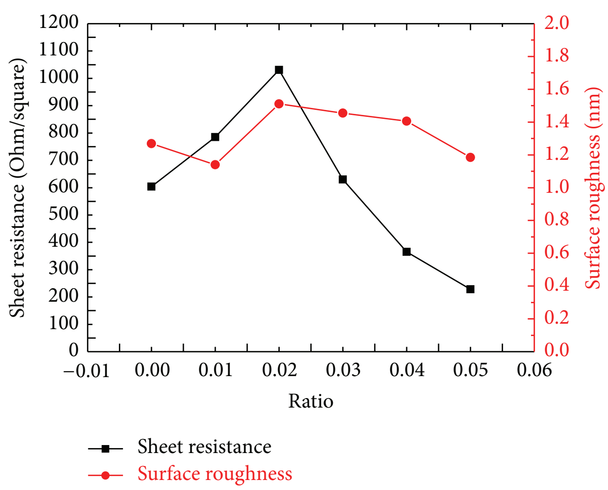

Figure 4: The sheet resistance and surface roughness of doped PEDOT: PSS with different weight ratios of 1.5 M H_2SO_4 to PEDOT: PSS.

respectively. It is clear that the sheet resistance of the doped PEDOT: PSS film is affected by adding the various ratios of H_2SO_4. The sheet resistance of the doped PEDOT: PSS film enhanced with increasing the ratio of H_2SO_4, but it drops after the maximum sheet resistance. The value of sheet resistance is reduced from 604 to 228 Ω/sq. The surface roughness of the double doped PEDOT: PSS film is not almost changed.

Figure 5 shows the sheet resistance and surface roughness of the doped PEDOT: PSS film through adding 1 M H_2SO_4. The sheet resistance value is reduced from 604 to 255 Ω/sq. The surface roughness of the 1 M H_2SO_4 doped PEDOT: PSS film was smoother as compared with the 1.5 M H_2SO_4 doped PEDOT: PSS film. Although the sheet resistance and surface roughness were improved slightly, we cannot clearly find the tendency from the 1 M and 1.5 M H_2SO_4 doped PEDOT: PSS films. This is due to the fact that the reaction rate of high concentration of H_2SO_4 is too fast. Thus, we reduce the molar concentration of H_2SO_4 again.

The reaction rate of H_2SO_4 was slowed down when the molar concentration of H_2SO_4 was 0.5 M. The results are shown in Figure 6. The sheet resistance and surface roughness

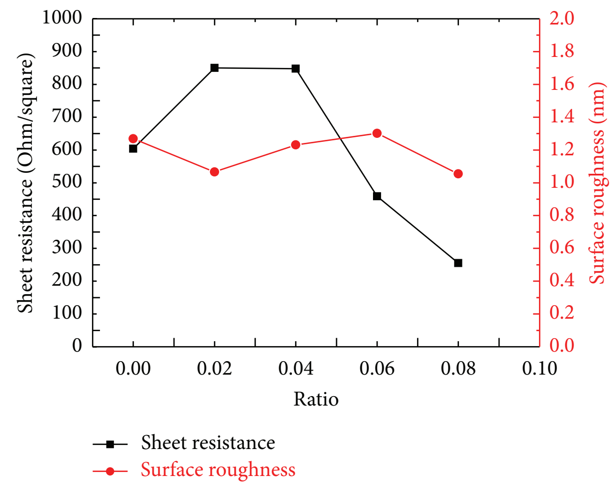

Figure 5: The sheet resistance and surface roughness of doped PEDOT: PSS with different weight ratios of 1 M H_2SO_4 to PEDOT: PSS.

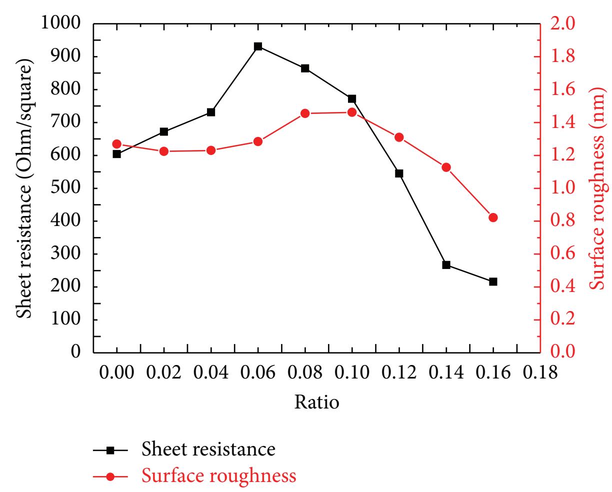

Figure 6: The sheet resistance and surface roughness of doped PEDOT: PSS with different weight ratios of 0.5 M H_2SO_4 to PEDOT: PSS.

were reduced significantly. The sheet resistance is reduced from 604 to 216 Ω/sq and the surface roughness is also reduced from 1.268 to 0.822 nm. Furthermore, we further decreased again the molar concentration of H_2SO_4. However, the PEDOT: PSS solution was diluted with the lower molar concentration of H_2SO_4.

The various molar concentrations of H_2SO_4 were added to the PEDOT: PSS. It can be seen that there is a common phenomenon. The sheet resistance was slightly increased with adding a small amount of H_2SO_4. The reason for this phenomenon is that the sulfuric acid was reacted with sorbitol preferentially. The reaction is called the pinacol rearrangement. It resulted that the reorient and aggregation effect combined PEDOT grains with sorbitol was destroyed. After the reaction of the pinacol rearrangement, the residual H_2SO_4 reacted with PSS. The chemical reaction can be written as $H_2SO_4 + PSS^- \rightarrow HSO_4^- + PSSH$. The HSO_4^-

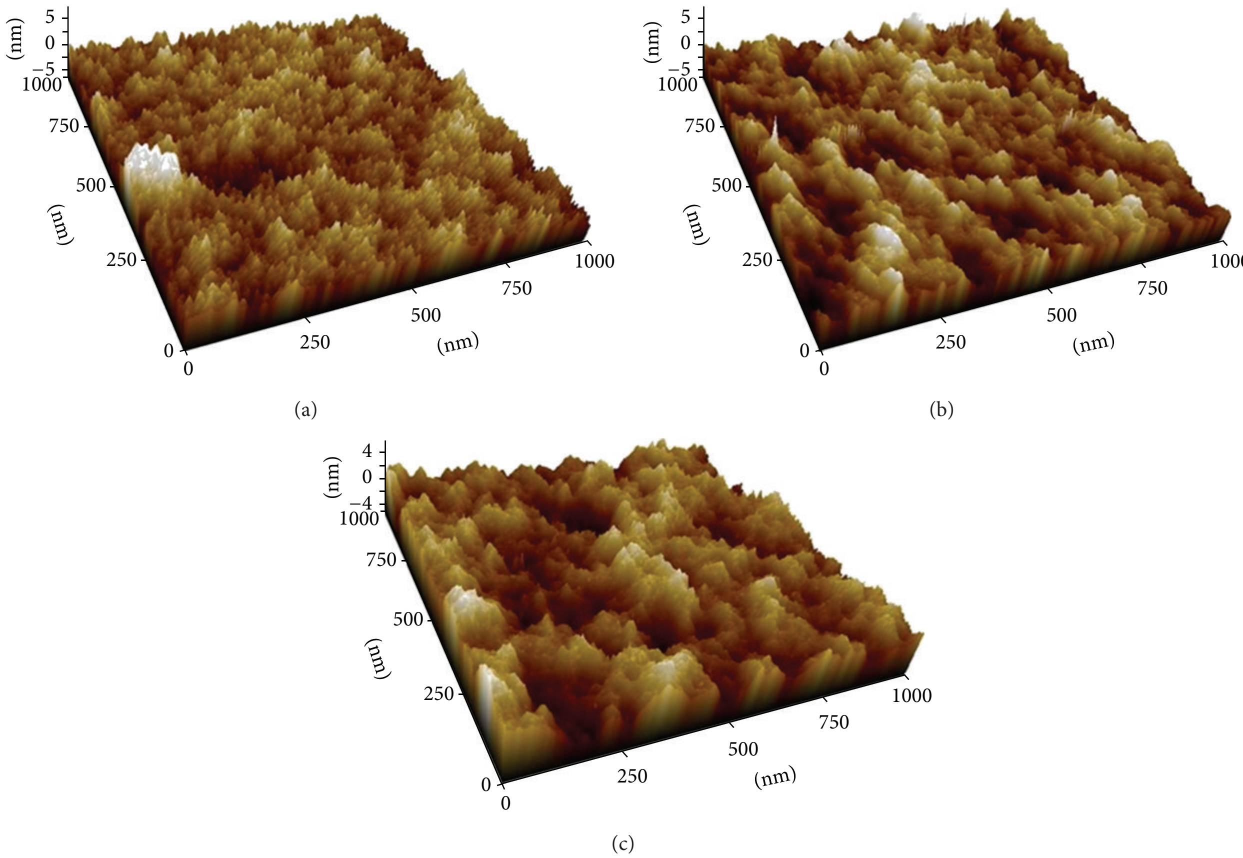

Figure 7: The surface morphology of (a) pristine PEDOT: PSS; (b) doping ratio of PEDOT: PSS to dilute H_2SO_4 is 25 : 2; (c) doping ratio of PEDOT: PSS to dilute H_2SO_4 is 25 : 4.

formed an ionic bond with the PEDOT, even that the nonconductive anions of some PSS^- were substituted by the conductive anions of HSO_4^- [23]. The ionic bond reaction is similar to Figure 2. And the substitution reaction caused more aggregation of PEDOT chains. The results are shown in Figure 7. The higher phase signal in Figure 7 corresponds to the PEDOT, and the lower phase was the PSS [15, 22, 24]. It's clear that PEDOT chains were increasingly aggregated with increasing the ratio of H_2SO_4. Thus, the substitution reaction will be favorable for the conductivity enhancement.

Figure 8 shows the doped PEDOT: PSS films with different molar H_2SO_4 concentrations as a function of weight ratio of H_2SO_4 to PEDOT: PSS. The transparency of the doped PEDOT: PSS film can be affected by the H_2SO_4 treatment. The transmittance of the doped PEDOT: PSS film was decreased with increasing the ratio of H_2SO_4 to PEDOT: PSS. The lowest sheet resistance of 216 Ω/sq is obtained at 0.5 M H_2SO_4-doped PEDOT: PSS film and at the weight ratio of 0.16 whose transmittance in the visible wavelength range from 400 to 700 nm is 91.9%. The high transparency and low sheet resistance indicated that the 0.5 M H_2SO_4-doped PEDOT: PSS films can be used as the transparent conductive electrode of optoelectronic devices.

4. Conclusions

In this paper, it was employed the noncontact AFM, four point sheet resistivity meter, and U-3900 spectroscopy to investigate the origin of the sheet resistance decrease of H_2SO_4-doped PEDOT: PSS films. The doped PEDOT: PSS solution by adding the different molar concentrations of H_2SO_4 strongly affects the surface roughness, sheet resistance, and transmittance. After doped H_2SO_4, the surface roughness is reduced from 1.268 nm to 0.822 nm. It's indicated that the surface of H_2SO_4-doped PEDOT: PSS film was smoother compared with the doped PEDOT: PSS film. The pinacol rearrangement occurred by adding the dilute sulfuric acid, but the sheet resistance was improved from 604 to 216 Ω/sq. The decrease of the sheet resistance is due to the fact that the nonconductive anions of some PSS^- were substituted by the conductive anions of HSO_4^-. And the substitution reaction caused more aggregation of PEDOT chains; namely, the substitution reactions will be favorable for the conductivity enhancement. The transmittance of the doped PEDOT: PSS film is decreased with increasing the weight ratio of H_2SO_4 to PEDOT: PSS. The transmittance of the 0.5 M H_2SO_4-doped PEDOT: PSS film is above 91% in the visible wavelength range from 400 to 700 nm. However, the high transparency and low sheet resistance reveal that

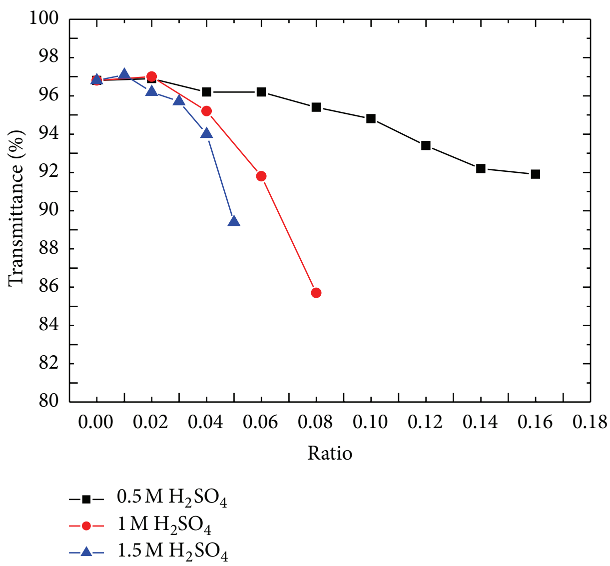

FIGURE 8: The transmittance of the doped PEDOT: PSS with different molar concentrations of H_2SO_4 as a function of weight ratio of H_2SO_4 to PEDOT: PSS.

the H_2SO_4-doped PEDOT: PSS films can be used as the transparent conductive electrode of optoelectronic devices.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgments

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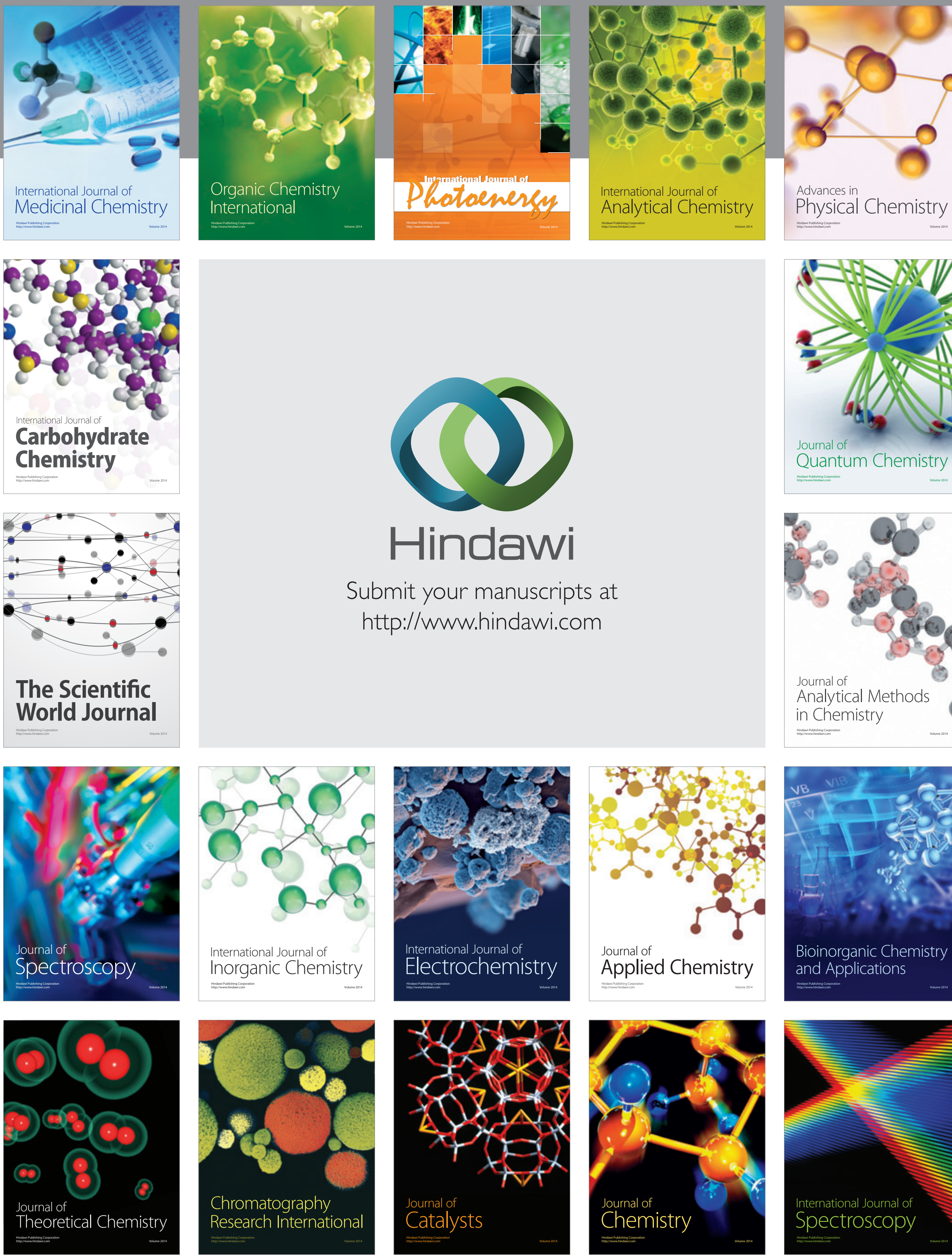
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