Preparation of Nanocomposites of Polypyrrole-metal (or Metal Oxide) on the Surface of V₂O₅ Coated Cathode through a One-step Method

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Abstract. Simultaneous formation of polypyrrole (PPy) and metal (or metal oxide) on a single electrode is particularly challenging because the electrodeposition of PPy and metal (or metal oxide) usually requires opposite potentials. Namely, the preparation of PPy needs an oxidation potential while the metal (or metal oxide) needs a reduction potential. In the present work, nanocomposites of PPy and metal (or metal oxide) were prepared successfully on the cathode by a one-step process, in which V₂O₅ coated titanium sheet was applied as cathode. In fact, two chemical reactions happened here at the same time. The first reaction was the chemical preparation of PPy on the cathode by the use of V₂O₅ as oxidant and the second reaction was the electrochemical formation of metal (or metal oxide) on the surface of the same cathode. As a result, nanocomposites of PPy and metal (or metal oxide) were one-step prepared on a single electrode. The morphology, composition and structure of nanocomposites were investigated via field emission scanning electron microscopy (FESEM), energy dispersive X-ray (EDX) and X-ray diffraction (XRD). Furthermore, PPy-Ag nanocomposite was prepared and used as a sensor to evaluate the electrocatalytic performance of H₂O₂. It was found that the sensor displayed excellent H₂O₂-sensing properties and a feasibility for practical applications. These results imply that the present one-step process not only presents a simple, facile and efficient way for the formation of PPy-based nanocomposites but also exhibits great potential to improve the application performance and broaden the applied fields of the nanocomposites.

Keywords: polypyrrole; V₂O₅; cathode; electrodeposition; nanocomposite; sensor.

1. Introduction
During the past decades, conducting polymer polypyrrole (PPy)-based nanocomposites have addressed considerable attention due to their novel properties and potential applications in various fields [1]. Among numerous PPy based nanocomposites, PPy-metal and PPy-metal oxide nanocomposites have raised particularly interest because the incorporation of PPy with metal or metal oxide may produce nanocomposites with novel properties that derived from effectively incorporation of the feature of parent components [2]. To date, a large number of PPy-metal (or metal oxide) nanocomposites have been prepared and found diverse applications in the fields of actuators [3], sensors [4], fuel cells [5], supercapacitors [6], corrosion protection [7], and drug release [8].

Generally, PPy-metal (metal oxide) nanocomposites were able to be prepared by chemical oxidation or electrochemical oxidation method [9, 10]. Compared with chemical oxidation method, electrochemical
polymerization could obtain functional films with different structure and properties by changing the electrode, electrolyte or electropolymerization methods [11, 12]. For the electrochemical preparation of PPy-metal (metal oxide) composites, it was usually carried out by two steps. PPy was electropolymerized on one anode in the first step. In the second step, metal or metal oxide was electrodeposited on surface of PPy-coated cathode which was used as the anode in the first step. It is obvious that the two-step process for the preparation of PPy-metal (metal oxide) nanocomposites usually requires opposite potentials [13-16]. Therefore, it is always a challenge to achieve pyrrole polymerization and metal nanoparticle formation simultaneously on a single electrode [17].

Recently, a novel method was developed to synthesize PPy-metal nanocomposites on the cathode using a one-step method [18-20]. NO$^+$ generated from cathode in nitric acid electrolyte was used as an oxidizing agent of pyrrole monomers, and then the direct preparation of PPy-metal composites was accomplished on the surface of cathode. However, the polymerization condition of strong acid electrolyte is too hard and dangerous, which limits its wider applicability. Given this point, it is urgent to develop a facial and efficient method to achieve the synthesis of PPy-metal (or metal oxide) nanocomposites by one-step process.

In the present work, the synthesis of PPy-metal (or metal oxide) nanocomposites by one-step process has been successfully accomplished on the surface of V$_2$O$_5$ film coated cathode. As shown in Figure 1, the titanium electrode coated with V$_2$O$_5$ film was used as cathode and immersed in electrolyte containing pyrrole monomers and metal salts. Here, V$_2$O$_5$ acted as an oxidant agent for pyrrole polymerization. After immersion of the cathode, a negative potential was applied. Then the oxidation of pyrrole and the reduction of the metal (or metal oxide) were conducted simultaneously on the V$_2$O$_5$ film. As a result, PPy-metal or PPy-metal oxide nanocomposite could be obtained in one-step process. Energy dispersive X-ray (EDX), field emission scanning electron microscopy (FESEM) and X-ray diffraction (XRD) were conducted to verify the obtained nanocomposites. The feasibility and versatility of this method were demonstrated by successful preparation of several kinds of PPy-metal (metal oxide) nanocomposites, such as PPy-Sn, PPy-Ag, PPy-ZnO, and PPy-NiO/Ni(OH)$_2$ nanocomposites. Furthermore, in order to confirm the applicability of this strategy, PPy-Ag nanocomposite was applied to detect current response of H$_2$O$_2$, and it accessed a satisfactory result. These traits suggest that the one-step process for the preparation of PPy-metal (or metal oxide) may shed a new light for relevant fields in the future.

2. Materials and Methods

2.1. Materials

The titanium plate was cut into rectangular pieces of 2×1 cm, cleaned with 1500-grit sandpaper firstly, cleaned ultrasonically three times in deionized water, and then polished to a smooth mirror surface on 2000-grit sandpaper, ultrasonically washed three times with distilled water, ethyl alcohol and acetone, and dried in nitrogen ambience. Pyrrole (Py) (98%) was taken from Sigma Aldrich and further purified by

![Figure 1. Schematic illustration of PPy-based composites by one-step process on cathode.](image-url)
twice distillation before use. The V$_2$O$_5$ was prepared as the previous report [21]. Hydrogen peroxide (30 wt% solution) (H$_2$O$_2$) and all other common solvents and reagents were analytical grade and purchased from Sinopharm Group.

2.2. Characterization

Electrochemical deposition and measurements were accomplished with an electrochemical workstation (CHI660D). All electrochemical experiments were employed with a conventional three electrodes system, with a reference electrode (RE) of saturated calomel electrode (SCE), a counter electrode (CE) of Pt wire, and a modified Ti sheet or 3 mm Au as working electrode (WE). The surface topography of all samples was observed by field emission scanning electron microscopy (FESEM, SU-70, Japan). The analysis of the elemental composition was performed with energy dispersive X-ray detector (EDX, SU-70, Japan). Attenuated total reflectance-Fourier transform infrared reflection (ATR-FTIR, is10, USA) spectroscopy was employed to characterize surface features of the modified electrode, by using an ATR accessory which background spectra were obtained by measuring the air directly. The structural analysis of the films was investigated by X-ray diffraction (XRD, Bruker-axs, USA) on a diffractometer with Cu Kα radiation.

2.3. The Preparation of PPy-metal (or Metal Oxide) Nanocomposites

To prepare the PPy-Sn nanocomposites, under the three-electrode system, a 0.1 M HCl solution with 0.01 M SnCl$_2$, 0.1 M NaCl and 0.1 M Py was employed as the electrolyte solution. The pretreated titanium sheet with about 5 μL V$_2$O$_5$ on its surface was used as the working electrode (WE). The reaction was lasted for 120 s with the constant potential of -0.8 V, and the WE was taken out after the electrodeposition was completed. The electrolyte solution used for the preparation of the PPy-Ag nanocomposites included 0.1 M NaNO$_3$, 0.01 M AgNO$_3$, 0.01 M p-toluenesulfonic acid (TsOH) and 0.1 M Py. The electrodeposition was the same as above method at room temperature except the two-electrode system was employed. The co-deposition reaction was performed with constant current of -2.5 mA·cm$^{-2}$ for 150 s. PPy-ZnO nanocomposites was prepared in the electrolyte containing 0.05 M Zn(NO$_3$)$_2$, 0.1 M Py, 0.01 M TsOH, 0.1 M KNO$_3$ at 70 ℃ of water bath temperature, with -0.9 V constant potential for 150 s. The electrolyte including 0.01 M NiSO$_4$, 0.1 M NaNO$_3$ and 0.01 M sodium dodecyl sulfonate (SDS) was used to prepare PPy-NiO/Ni(OH)$_2$ electrode and activated with -0.9 V for 300 s under constant potential mode and constant temperature of 30 ℃. All samples were cleaned three times in deionized water, dried with nitrogen and stored at 4 ℃ for later assessment.

2.4. Construction of Sensors

Under the same system to the preparation of PPy-Ag modified electrode, a 3 mm Au electrode was employed as a cathode (WE). Firstly, about 2 μL of V$_2$O$_5$ was coated evenly on the surface of Au electrode. The electrodeposition reaction was conducted at -2.5 mA·cm$^{-2}$ constant current for 120 s in the above electrolyte, and then it was washed cleaned with deionized water, subsequently dried in the nitrogen and then stored at 4 ℃. All electrochemical detections were conducted in the electrolyte of 0.1 M (pH=6.5) phosphate buffer solution (PBS). The electrolyte were saturated with N$_2$ before electrochemical detection.

3. Results and Discussion

3.1. Synthesis of PPy Using V$_2$O$_5$ as Oxidant

In order to prove that pyrrole can be oxidized by V$_2$O$_5$, V$_2$O$_5$ coated titanium sheet was immersed into a solution of 0.1 M pyrrole for 60 s. Then the sheet was taken out for characterization. It can be seen from insert of Figure 2c, the color of V$_2$O$_5$ coated titanium translated from red (before immersion) to black (after immersion). Figure 2a and Figure 2b displays the microscopic image of the sheet surfaces before and after immersion, respectively. It was found that before immersion V$_2$O$_5$ exhibits wire-like morphology with diameter of about 40 nm. After immersion, the diameter of the nanowire was increased to about 60 nm. Meanwhile, the peaks of C, N element were also found in the EDX spectrum and the molar ratio of C, N is 1.43: 0.38 (Figure 2c), indicating the formation of PPy. Figure 2d displays the ATR-FTIR spectroscopy of the reaction products. The characteristic peaks of PPy at 1169 cm$^{-1}$ and 1092 cm$^{-1}$ were corresponded to C–N in-plane deformations and N–H bonds. The characteristic peaks at 1309
and 1053 cm\(^{-1}\) were attributed to the in-plane \(\text{C}−\text{H}\) deformations. The bands at 1535 cm\(^{-1}\) usually reflects the \(\text{C}=\text{C}\) stretching vibration in the pyrrole ring [22-24]. A weak peak at 1690 cm\(^{-1}\) is attributed to stretching mode of \(\text{V}−\text{O}−\text{C}\) in \(\text{PPy-V}_2\text{O}_5\) composite. The peaks of 1169 and 911 cm\(^{-1}\) also imply the doping state of \(\text{PPy}\) composites [23]. And before the oxidation of \(\text{PPy}\), the spectrum of the \(\text{V}_2\text{O}_5\) is verified by few absorption bands located at 989, 843, and 579 cm\(^{-1}\), which corresponding to the stretching vibration of \(\text{V}=\text{O}\) band (vanadyl oxygen), deformation modes of \(\text{V}−\text{O}−\text{V}\) band [25, 26]. These traits demonstrated the formation of the \(\text{PPy}\) and laid the foundation for the following work.

3.2. Synthesis of \(\text{PPy-metal Nanocomposite}\)

**Figure 2.** The FESEM images of a \(\text{V}_2\text{O}_5\) and b \(\text{PPy}\) oxidized by \(\text{V}_2\text{O}_5\). c The EDX spectrum of \(\text{PPy-V}_2\text{O}_5\), and insert image is \(\text{V}_2\text{O}_5\) coated titanium before and after immersed in the solution of 0.1 M \(\text{pyrrole}\). d The FTIR spectra of \(\text{V}_2\text{O}_5\) and \(\text{PPy}\) oxidized by \(\text{V}_2\text{O}_5\).

Based on the above results, \(\text{PPy-Sn Nanocomposite}\) was synthesized. The synthesis process was illustrated in Figure 1. Figure 3a showed the FESEM image of the \(\text{PPy-Sn Nanocomposite}\). It can be observed numerous aggregated particles with uneven size on the \(\text{PPy}\) film. The chemical constitution of the nanocomposite was carried out by EDX. As displayed in the Figure 4a, EDX spectrum reveals a strong Sn peak, suggesting the existence of Sn element. The peaks of S, Na, Cl, K, presented in EDX spectrum, were caused by unavoidable trace impurities in electrolyte. The crystal analysis of the nanocomposite was made use of XRD analysis and the result showed that the diffraction peaks of 31.2°, 32.5°, 45.4° and 64.2° at 2\(\theta\) values could be assigned to the (200), (101), (121) and (301) tetragonal crystalline planes of Sn, respectively (Figure 5a) [27, 28]. In addition, a broad peak at about 10° could be observed, which reflects the amorphous form of \(\text{PPy}\) [29, 30].
Then PPy-Ag nanocomposite was synthesized following the similar process in order to prove the generality of the present one-step method. The FESEM image of the PPy-Ag nanocomposite was shown in Figure 3b. The typically dendritic crystals are uniformly spread on the surface of the PPy film. The chemical constitution of the PPy-Ag nanocomposite was carried out by EDX. The peaks of Ag are observed, confirming the existence of Ag elements. The peaks of C, N represented the characteristic elements of PPy (Figure 4b). In the previous study, it had been reported that dendritic crystals of silver could be deposited using electrochemical method [31, 32]. XRD was conducted to analyze the crystal structure of the PPy-Ag nanocomposite (Figure 5b). Diffraction peaks at 37.98°, 43.98°, 64.32° and 77.42° were corresponding to (111), (200), (220), (311) and (222) in face-centered cubic crystal of Ag, and it further indicated that the dendritic structures belong to silver crystal [33, 34]. We can infer from above results that a large amount of Ag nanoparticles were one-step co-deposited with PPy film on the V_2O_5 coated titanium electrode. Compared with the method of Ag could be reduced with PPy directly, the process of this strategy is more fast and convenient [35].
3.3. Synthesis of PPy-metal Oxide Nanocomposite

To further demonstrate the versatility of this one-step method, co-deposition of metallic oxide and PPy on V$_2$O$_5$ coated titanium cathode was performed. In this regards, PPy-ZnO nanocomposite was prepared first. Figure 3c represents the FESEM image of the obtained PPy-ZnO nanocomposite. It clearly shows that the crystal exhibited a three-dimensional petaliform structure on the surface of rough PPy film. XRD peaks of 31.77°, 34.42° and 36.25° corresponded to (100), (002), (101) of hexagonal phase ZnO (Figure 5c) [36, 37]. Moreover, the characterization of EDX also shows the intensive peak of Zn, implying the Zn was existed in petaliform crystal (Figure 4c).

Figure 5. XRD patterns of a PPy-Sn, b PPy-Ag, c PPy-ZnO and d PPy-NiO/Ni(OH)$_2$, respectively. In addition, another nanocomposite of PPy-metal oxide, PPy-NiO/Ni(OH)$_2$ nanocomposite, was also prepared. Figure 3d shows FESEM image of the nanocomposite. Similar to the previous report [38, 39], NiO/Ni(OH)$_2$ prepared with electrodeposition presented the morphology of compact blocky grains. The PPy substrate was completely covered by lots of NiO/Ni(OH)$_2$ nanoparticles. Moreover, two peaks of Ni are found from EDX spectrum (Figure 4d), suggesting the existence of Ni element. On the other hand, it could not find out any relative characteristic peak from the result of XRD analysis (Figure 5d), maybe the NiO/Ni(OH)$_2$ was essentially poor crystallization or amorphous structure under this preparation system [40, 41]. All of the above results confirmed that various PPy-metal (or metal oxide) nanocomposites could be synthesized by the present one-step method and thus consolidated its versatility for preparing PPy-metal or PPy-metal oxide nanocomposites in a fast, simple, and efficient way.

3.4. The Sensor Application of PPy-Ag Composite

Given the good catalytic properties of Ag nanoparticles for H$_2$O$_2$ [34], PPy-Ag nanocomposites was designed to be a non-enzyme sensor for H$_2$O$_2$ detection. From the Figure 6a, the response current of parallel electrodes was shown when 0.1 mM H$_2$O$_2$ was added. The response current of PPy-Ag modified electrode exhibited several times higher than the Ag modified electrode after 0.1 mM of H$_2$O$_2$ was added, while it has hardly any changes on bare Au electrode. Intrinsically, the linear PPy structure provided a larger specific surface area and reaction sites for Ag particles, and the overpotential characteristics of PPy would also contribute to the catalytic reaction of H$_2$O$_2$ [29]. The large area of current response also reflected the excellence pseudocapacitance properties of PPy [42]. The PPy-Ag modified electrode
exhibited an increasing current response with increased concentrations of \( \text{H}_2\text{O}_2 \) to the electrolyte, suggesting that \( \text{H}_2\text{O}_2 \) could be easily reduced on PPy-Ag modified electrode in a wide concentration range (Figure 6b). The peak value of response current also increased with the square root of scan rates linearly, implying the response process to \( \text{H}_2\text{O}_2 \) was diffusion controlled (Figure 6c). In comparison, we investigated the \( \text{H}_2\text{O}_2 \) sensing ability of bare Au electrode, Ag, and PPy-Ag by chronoamperometry (Figure 6d). The bare Au electrode showed a negligible response to the added \( \text{H}_2\text{O}_2 \). The Ag modified electrode exhibited an observed increase with the continuous addition of \( \text{H}_2\text{O}_2 \). However, the response current increment of the PPy-Ag electrode was enhanced significantly and the response time was only 3 s inferred from the insert image (Figure 6d), indicating an excellent detection performance. From Figure 7a, the response current was linearly increased with the concentration of \( \text{H}_2\text{O}_2 \) ranging from 0.01 mM to 43.55 mM and the correlation coefficient is calculated as 0.99951 (Figure 7b). The linear regression equation for the \( \text{H}_2\text{O}_2 \) detection is presented as \( I \text{ (mA)} = -0.0145-0.0435\times C \text{ (mM)} \). The sensitivity of the modified electrode is \( 621.43 \mu \text{A} \cdot \text{mM}^{-1} \cdot \text{cm}^{-2} \), and the detection limit is 4.52 \( \mu \text{M} \) (S/N=3). Based on the previous study, the PPy-Ag modified electrode is comparative or superior to most of Ag-based \( \text{H}_2\text{O}_2 \) sensors (Table 1).

**Figure 6.** a CVs of bare electrode, Ag and PPy-Ag modified electrode with and without 0.1 mM \( \text{H}_2\text{O}_2 \) at a scan rate of 50 mV·s⁻¹. b CVs of PPy-Ag modified electrode with different concentrations of \( \text{H}_2\text{O}_2 \) at a scan rate of 50 mV·s⁻¹. c CVs of PPy-Ag modified electrode at different scan rates (from a to j: 10, 20, 30, 40, 50, 60, 70, 80, 90, 100 mV·s⁻¹), and inset image displays the plot of the peak current vs. square root of scan rates. d I-t curves depending on the response of bare electrode, Ag and PPy-Ag modified electrode to \( \text{H}_2\text{O}_2 \) in 0.1 M PBS (pH=6.5) at -0.3 V upon successive addition of 0.5 mM \( \text{H}_2\text{O}_2 \) under continuous stirred conditions.
Figure 7. a I-t curve of PPy-Ag modified electrode with the subsequent addition of H$_2$O$_2$ into 0.1 M PBS (pH=6.5) at -0.3 V, and insert image is enlarged curve at low concentrations of H$_2$O$_2$. b Correlation between different H$_2$O$_2$ concentrations and current. c I-t curves of the PPy-Ag modified electrode by addition of 1 mM H$_2$O$_2$ and other interfering substances with the same concentration under stirring condition, applied potential at -0.3 V. d The current response of five different PPy-Ag modified electrodes with the addition of 2 mM H$_2$O$_2$, each test repeated five times. e The current response of sensors with 1 mM H$_2$O$_2$ every five days for one month.

Moreover, the selectivity, reproducibility and time stability of the sensor were also examined. Figure 7c shows the influence to current response of interferents including ascorbic acid (AA), glucose, uric acid (UA) and KCl with the same concentration. Markedly, the PPy-Ag modified electrode displayed the highest electrochemical response to H$_2$O$_2$. The electrode reproducibility was assessed by measuring the current values of five different electrodes, and the RSD is 4.46% (Figure 7d). The time stability of the PPy-Ag modified electrode was examined every five days at the same condition for one month. The response current of the modified electrode still retained 86.84% after one-month test, indicating the

Table 1. Comparison of typical H$_2$O$_2$ sensors.

| Sensors                        | Sensitivity (μA mM$^{-1}$ cm$^{-2}$) | Linear range (mM) | LOD (μM) | References |
|-------------------------------|------------------------------------|-------------------|----------|------------|
| Ag Nanowires                  | 26.6                               | 0.1~3.1           | 29.2     | [43]       |
| Ag-SBA-16/CPE                 | 816.6                              | 0.02~20           | 2.95     | [44]       |
| Ag NPs-PPy-Fe$_3$O$_4$/GCE    | 18.71                              | 0.005~11.5        | 1.7      | [45]       |
| Ag-FeOOH/GCE                  | 8.07                               | 0.03~15           | 22.8     | [46]       |
| Ag-Cu$_2$O-polyimide films    | null                               | 0.05~0.5          | 4.0      | [47]       |
| Nf-Pd Ag-rGO-NH$_2$/GCE       | 1307.46                             | 0.002~19.5        | 0.7      | [48]       |
| PPy-Ag/Au                     | 621.43                             | 0.01~43.55        | 4.52     | This work  |
electrode present a considerable long-term stability (Figure 7e). When a real sample of H$_2$O$_2$ disinfectant (3 wt%) was detected with the electrode, good recoveries (98.44~121%) were shown among different concentrations, and the RSD of the five measurements was less than 7.24% (Table 2). The above results indicate an excellent performance of the PPy-Ag sensor and thus provide a feasibility for practical applications.

**Table 2.** Determination of H$_2$O$_2$ in real sample.

| Sample No. | Added (mM) | Measured by sensor (mM) | Recovery (%) | RSD (%) |
|------------|------------|-------------------------|--------------|---------|
| 1          | 0.1        | 0.121                   | 121          | 1.18    |
| 2          | 1          | 1.026                   | 102.6        | 4.51    |
| 3          | 5          | 4.972                   | 98.44        | 7.24    |

4. Conclusions

This work presented an effective strategy to prepare PPy-metal (or metal oxide) nanocomposites on the surface of V$_2$O$_5$ coated cathode through one-step process. Essentially, the polymerization of pyrrole oxidized by V$_2$O$_5$ was synchronously proceed with electrodeposition of metal (or metal oxide) on the same cathode. As a result, PPy-Sn, PPy-Ag, PPy-ZnO, and PPy-NiO/Ni(OH)$_2$ nanocomposites were successfully prepared and proved the feasibility and versatility of this method. Moreover, the application of H$_2$O$_2$ non-enzyme detection was investigated on PPy-Ag modified electrode. The results exhibited a comparative or superior performance of H$_2$O$_2$-sensing to other parallel sensors. Predictably, such a fast, simple and efficient way for the preparation of PPy-based nanocomposites is expected to develop more competitive and promising nanocomposites in the future.

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References

[1] Diaz AF, Castillo JJ, Logan JA and Lee WY 1981 Electrochemistry of conducting polypyrrole films *Electroanal Chem* vol 129 pp 115-132
[2] Gangopadhyay R and De A 2000 Conducting polymer nanocomposites: A brief overview *Chem Mater* vol 12 p 2064
[3] Tadesse Y, Brennan J, Smith C, Long TE and Priya S 2010 Synthesis and characterization of polypyrrole composite actuator for jellyfish unmanned undersea vehicle *Proc Spie* p 7642
[4] Rehman AU, Ikram M, Kan K, Zhao YM, Zhang WJ, Zhang JW, Liu Y, et al 2018 3D interlayer nanohybrids composed of reduced graphenescheme oxide/SnO$_2$/PPy grown from expanded graphite for the detection of ultra-trace Cd$^{2+}$, Cu$^{2+}$, Hg$^{2+}$ and Pb$^{2+}$ ions *Sensor Actuat B-Chem* vol 274 pp 285-295
[5] Fard LA, Ojani R, Raoof JB, Zare EN and Lakouraj MM 2017 Poly (pyrrole-co-aniline) hollow nanosphere supported Pd nanoflowers as high-performance catalyst for methanol electrooxidation in alkaline media *Energy* vol 127 pp 419-427
[6] Wang C, Liu H, Jiang M, Wang YD, Liu RN, Luo ZP, Liu XQ, et al 2017 Ammonium vanadate polytpyrrole manganese dioxide nanowire arrays with enhanced reversible lithium storage *Appl Surf Sci* vol 416 pp 402-410
[7] Aravindan N and Sangaranarayanan MV 2016 Influence of solvent composition on the anti-corrosion performance of copper-polypyrrole (Cu-PPy) coated 304 stainless steel *Prog Org Coat* vol 95 pp 38-45
[8] Wu MX, Yan HJ, Gao J, Cheng Y, Yang J, Wu JR, Gong BJ, et al 2018 Multifunctional
supramolecular materials constructed from polypyrrole UiO-66 nanohybrids and pillararene nanovalves for targeted chemophotothermal therapy. *Acs Appl Mater Inter* vol 10 pp 34655-34663

[9] Xu YD, Zhang X, Li Y, Zhang YJ, He LJ and Zhao JW 2018 Effect of electrolyte cations on the capacitive performance of the hexagonal-MoO3/polypyrrole hybrid. *Mater Lett* vol 210 pp 314-316

[10] Pruna A, Shao Q, Kamruzzaman M, Li YY, Zapien JA, Pullini D, Mataix DB, et al 2017 Effect of ZnO core electrodeposition conditions on electrochemical and photocatalytic properties of polypyrrole-graphene oxide shielded nanoarrays. *Appl Surf Sci* vol 392 pp 801-809

[11] Li YF and He GF 1998 Effect of preparation conditions on the two doping structures of polypyrrole. *Synth Met* vol 94 pp 127-129

[12] Zhang J, Liu XH, Zhang LX, Cao BQ and Wu SH 2013 Reactive template synthesis of polypyrrole nanotubes for fabricating metal/conducting polymer nanocomposites. *Macromol Rapid Comm* vol 34 pp 528-532

[13] Meenach SA, Burdick J, Kunwar A and Wang J 2007 Metal/conducting-polymer composite nanowires. *Small* vol 3 pp 239-243

[14] Sonavane AC, Inamdar AI, Dalavi DS, Deshmukh HP and Patil PS 2010 Simple and rapid synthesis of NiO/PPy thin films with improved electrochromic performance. *Electrochim Acta* vol 55 pp 2344-2351

[15] Vorotyntsev MA, Skompska M, Rajchowska A, Borysiuk J and Donen M 2011 A new strategy towards electroactive polymer-inorganic nanostructure composites: Silver nanoparticles inside polypyrrole matrix with pendant titanocene dichloride complexes. *J Electroanal Chem* vol 662 pp 105-115

[16] Ali Y, Kumar V, Sonkawade RG, Shirsat MD and Dhaliwal AS 2013 Two-step electrochemical synthesis of Au nanoparticles decorated polyaniline nanofiber. *Vacuum* vol 93 pp 79-83

[17] Kishore PS, Viswanathan B and Varadarajan TK 2008 Synthesis and characterization of metal nanoparticle embedded conducting polymer-polyoxometalate composites. *Nanoscale Res Lett* vol 3 pp 14-20

[18] Jung YJ, Singh N and Choi KS 2009 Cathodic deposition of polypyrrole enabling the one-step assembly of metal-polymer hybrid electrodes. *Angew Chem-Int Edit* vol 48 pp 8331-8334

[19] Hnida KE, Socha RP and Sulka GD 2013 Polypyrrole–silver composite nanowire arrays by cathodic co-deposition and their electrochemical properties. *J Phys Chem C* vol 117 pp 19382–19392

[20] Cui X, Huang X, He Y, Dai L, Wang S, Sun Y, Shi W, et al 2014 Cathodic protection: A new strategy to enable the formation of nanostructured polypyrrole on magnesium. *Synth Met* vol 195 pp 97-101

[21] Xiong CR, Aliev AE, Gnade B and Balkus KJ 2008 Fabrication of silver vanadium oxide and V2O5 nanowires for electrochromics. *Acs Nano* vol 2 pp 293-301

[22] Wang JG, Liu HY, Liu HZ, Hua W and Shao MH 2018 Interfacial constructing flexible V2O5 polypyrrole core-shell nanowire membrane with superior supercapacitive performance. *Acs Appl Mater Inter* vol 10 pp 18816-18823

[23] Bai MH, Bian LJ, Song Y and Liu XX 2014 Electrochemical codeposition of vanadium oxide and polypyrrole for high-performance supercapacitor with high working voltage. *Acs Appl Mater Inter* vol 6 12656-12664

[24] Arora K, Chaubey A, Singhal R, Singh RP, Pandey M, Samanta S, Malhotra B, et al 2006 Application of electrochemically prepared polypyrrole–polyvinyl sulphonate films to DNA biosensor. *Biosens Bioelectron* vol 21 pp 1777-1783

[25] Huguenin F, Girotto EM, Torresi RM and Buttry DA 2002 Transport properties of V2O5/polypyrrole nanocomposite prepared by a sol-gel alkoxide route. *J Electroanal Chem* 536: 37-45

[26] Yang J, Lan TB, Liu JD, Song YF and Wei MD 2013 Supercapacitor electrode of hollow spherical V2O5 with a high pseudocapacitance in aqueous solution. *Electrochim Acta* vol 105 pp 489-495

[27] Ardhi REA, Liu G, Tran MX, Hudaya C, Kim JY, Yu H and Lee JK 2018 Self-relaxant superelastic matrix derived from C-60 incorporated Sn nanoparticles for ultra-high-performance
Li-ion batteries *Acs Nano* vol 12 pp 5588-5604

[28] Shimizu M, Shimizu S, Katada A, Uejima M and Arai S 2018 Electrochemical preparation of free-standing carbon-nanotube/Sn composite paper *Mater Lett* vol 220 pp 182-185

[29] Nalage SR, Navale ST and Patil VB 2013 Polypyrrole-NiO hybrid nanocomposite: Structural, morphological, optical and electrical transport studies *Measurement* vol 46 pp 3268-3275

[30] Roy S, Mishra S, Yogi P, Saxena SK, Mishra V, Sagdeo PR and Kumar R 2018 Polypyrrole-vanadium oxide nanocomposite: polymer dominates crystallinity and oxide dominates conductivity, *Appl Phys a-Mater* vol 124 p 53

[31] Cho FH, Kuo SC and Lai YH 2017 Surface-plasmon-induced azo coupling reaction between nitro compounds on dendritic silver monitored by surface-enhanced Raman spectroscopy *Rsc Adv* vol 7 pp 10259-10265

[32] Qin X, Wang HC and Shan RF 2018 Morphology-controlled synthesis of Ag nanoparticle decorated glassy carbon electrode and its electrochemical performance *Ionic* vol 24 pp 1765-1772

[33] Wei GD, Nan CW, Deng Y and Lin YH 2003 Self-organized synthesis of silver chainlike and dendritic nanostructures via a solvothermal method *Chem Mater* vol 15 pp 4436-4441

[34] Hao H, Sheng QL and Zheng JB 2017 Ag C core-shell structure composites-decorated Ag nanoparticles: zero current potentiometry for detection of hydrogen peroxide *Chem Pap* vol 71 pp 535-542

[35] Qin X, Lu W, Luo Y, Chang G and Sun X 2011 Preparation of Ag nanoparticle-decorated polypyrrole colloids and their application for H2O2 detection *Electrochem Commun* vol 13 pp 785-787

[36] Wu CL, Qiao XL, Chen JG and Wang HS 2007 Controllable ZnO morphology via simple template-free solution route *Mater Chem Phys* vol 102 pp 7-12

[37] Xie J, Li P, Li YT, Wang Y J and Wei Y 2009 Morphology control of ZnO particles via aqueous solution route at low temperature *Mater Chem Phys* vol 114 pp 943-947

[38] Jia D, Ren Q, Sheng L, Li F, Xie G and Miao Y 2011 Preparation and characterization of multifunctional polypyrrole–Au coated NiO nanocomposites and study of their electrocatalysis toward several important bio-thiols *Sensor Actuat B-Chem* vol 160 pp 168-173

[39] Jiang L, Syed JA, Gao YZ, Lu HB and Meng XK 2018 Electrodeposition of Ni(OH)2 reinforced polyaniline coating for corrosion protection of 304 stainless steel *Appl Surf Sci* vol 440 pp 1011-1021

[40] Ahn KS, Nah YE and Sung YE 2002 Surface morphological, microstructural, and electrochromic properties of short-range ordered and crystalline nickel oxide thin films *Appl Surf Sci* vol 199 pp 259-269

[41] Zhou C, Lin LN, Ma YZ, Huang LY, Li J, Liu ZP and Dong ZX 2017 Fabrication of amorphous mesoporous Ni(OH)2 hollow spheres with waxberry-like morphology for supercapacitor electrodes *Chemselectrochem* vol 4 pp 2314-2320

[42] Asen P, Shahrokhiann S and Zad AI 2017 One step electrodeposition of V2O5/polymer/graphene oxide ternary nanocomposite for preparation of a high performance supercapacitor *Int J Hydrogen Energ* vol 42 pp 21073-21085

[43] Kurowska E, Brzozka A, Jarosz M, Sulka GD and Jaskula M 2013 Silver nanowire array sensor for sensitive and rapid detection of H2O2 *Electrochim Acta* vol 104 pp 439-447

[44] Azizi SN, Ghasemi S, Samadi-Maybodi A and Ranjbar-Azad M 2015 A new modified electrode based on Ag-doped mesoporous SBA-16 nanoparticles as non-enzymatic sensor for hydrogen peroxide *Sensor Actuat B-Chem* vol 216 pp 271-278

[45] Qi C and Zheng J 2015 Novel nonenzymatic hydrogen peroxide sensor based on Fe3O4/PPy/Ag nanocomposites *J Electroanal Chem*. vol 747 pp 53-58

[46] Zhang J and Zheng JB 2015 An enzyme-free hydrogen peroxide sensor based on Ag/FeOOH nanocomposites *Anal Methods-Uk* vol 7 pp 1788-1793

[47] Antink W H, Choi Y, Seong KD and Piao Y 2018 Simple synthesis of CuO/Ag nanocomposite electrode using precursor ink for non-enzymatic electrochemical hydrogen peroxide sensing *Sensor Actuat B-Chem* vol 255 pp 1995-2001
[48] Guler M, Turkoglu V, Bulut A and Zakhakiran M 2018 Electrochemical sensing of hydrogen peroxide using Pd Ag bimetallic nanoparticles decorated functionalized reduced graphene oxide *Electrochim Acta* vol 263 pp 118-126