Layer By Layer Assembly with
Sol-Gel Materials and Its Electrochemical Application

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the requirements for the degree of Master of Science

in

Chemical Engineering

by

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The Thesis of Jun Ho Kim is approved, and it is acceptable in quality and form for publication on microfilm and electronically:

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Chair

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ABSTRACT OF THE THESIS

Layer By Layer Assembly with
Sol-Gel Materials and Its Electrochemical Application

by

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Layer by layer assembly, a coating method that uses two opposite charged solutions, has led to functional coating field due to its advantages [1]. Charged
polyelectrolytes are widely used as glue in layer by layer assembly, because they provide opposite charge between the solutions, thus avoiding an agglomerate form of coating.

However, only a few instance of layer by layer assembly without polyelectrolyte are studied. In this study, layer by layer assembly using the sol–gel oxides instead of polyelectrolyte are studied. SnO$_2$ (Tin dioxide) and ZrO$_2$ (Zirconium dioxide) are prepared using the sol-gel method, and six different layer by layer including SnO$_2$ (Tin dioxide)/X (X= Graphene Oxide (GO), Boron Nitride (BN), Iron Oxide (Fe$_2$O$_3$), CuO (Copper Oxide)) and ZrO2 (Zirconium dioxide)/ Y (Y= Graphene Oxide (GO), Boron Nitride (BN)) are assembled. These multilayers are characterized by Scanning Electron Microscopy(SEM). Cyclic Voltammetry (CV) test is used to evaluate the multilayers for supercapasitor.
Chapter 1. Introduction

Layer by layer (LbL) assembly has been receiving increased attention, which has led to the various fields of functional coating, from an electrochemical capacitor (EC) to biomedical applications [2]. The LbL assembly was first introduced in 1966 by Iler, and its application has been expanded with self-assembly technique [3]. Its properties highly depend upon the charged species adsorbed onto the substrates. The typical assembly method is that the two opposite charged solutions or polyelectrolytes, which are coated on the substrate by sequential adsorption, as shown in Figure 1[2]. However, the interaction mechanisms that drive the self-assembly process between the layers is still questionable [4].

The LBL was originally developed for polyelectrolyte/polyelectrolyte systems. Polyelectrolytes are generally conductive polymers that consist of repeating units and are electro-polymerized. They are used as “electrostatic glue” to the structural integrity, thus providing better adsorption between the layers. Due to these reasons, a significant number of polyelectrolytes is reported as a building block and many researchers use it between the targeted materials in the LBL self-assembly process. [5]. As a conventional
polyelectrolyte of layer by layer, poly(allylamine hydrochloride) (PAH), poly(diallyl dimethyl ammonium chloride) (PDDA), polyaniline(PANI), poly(ethyl eneimine) (PEI), poly(sodium styrene sulfonate) (PSS), poly (sodium vinyl sulfonate) (PVS), and poly(acrylic acid) (PAA) are used [6-9]. However, it is inevitable to have another deposition step for utilizing polyelectrolytes during the process. In addition, polyelectrolyte can react solely with the other layers of film at the interface, which may lead to unwanted side reactions during the deposition. Hence, rigidity and chemical stability of the self-assembled layers can be reduced [10].

Recently, researchers have made efforts toward all inorganic multilayers, which do not consist of polyelectrolytes [11]. Each individual inorganic multilayers is coated directly by avoiding polyelectrolytes, thus it performs better and has more desirable functionality depending upon original inorganic materials. In addition, many inorganic multilayered structures are stable at high temperature while partial or all polyelectrolyte assembly are easily damaged after heat treatment. In the same manner, sol-gel metal oxide materials have been used as alternatives of polyelectrolytes [4]. The sol-gel metal oxide films provide not only “glue”, but also homogeneous particle size and corrosion protection on the surface [12].

Here, we report LBL assembly including various sol–gel metal oxides without polyelectrolytes. Tin dioxide (SnO₂) and zirconium dioxide (ZrO₂) are prepared via the sol-gel method, and six different LBL structures including SnO₂/X (X= reduced Graphene Oxide (r-GO), Boron Nitride (BN), Iron Oxide (Fe₂O₃) and copper oxide (CuO)) and ZrO₂/Y (Y= reduced Graphene Oxide (r-GO) and Boron Nitride (BN)) are
assembled. The morphologies of these multilayers are characterized by Scanning Electron Microscopy (SEM). A Cyclic Voltammetry (CV) test is used to evaluate their capacitance for the EC applications.
**Figure 1.** Schematic of layer-by-layer (LbL) self-assembly by using oppositely charged polyelectrolyte [4].
Chapter 2. Background and Motivation

2. 1. Multilayer assembly for Electrochemical Capacitor

Layer by layer (LBL) is a simple and versatile coating method, thus it is applied to a large variety of applications including electrochemical energy storage devices such as EC [13, 14] LBL assembly had not receive much attention until Decher’s pioneering work in 1992. He suggested the use of polyelectrolytes on a charged surface, and this technique received great attention in the functional thin film field [7, 15]. His method has been made great impact on the electrochemical capacitor field, and people have been conventionally used PAH, PDDA, PEI, PANi for the positive charge, and PSS, PVS, PAA for the negative charge [16,17].

One of the limitations to the capacitance of electrochemical capacitors (ECs) is the surface area of the conductor. Therefore, graphene has been found to be excellent electrode material due to its high electrical and thermal conductivities, great mechanical strength, and large specific surface area [18, 19, 20, 21]. Recently, Ashis K. Sarker’s group demonstrated the use of the graphene layer and PANi to apply to the supercapacitor. A Graphene Oxide (GO)nanosheet and PANi are successfully assembled, and three different samples are prepared by changing the concentration of both GO and PANi. Samples of GO and PANi are denoted S-1(0.5 mg/mL PANi, 2 mM GO) S-2 (0.25 mg/mL PANi, 1 mM GO) and S-3(0.125 mg/mL PANi, 0.5 mM GO). The schematic
view of the interaction between the two layers is shown in figure 2. Hydroiodic acid (HI) reduction is performed to convert GO to reduced GO (rGO), and its influence on the surface is observed by topographical 2D and 3D Atomic Force Microscopy (AFM) images. Figure 3(a) shows the measured thickness of one bilayer using a cross-sectional SEM image. Their results (1.17 nm per one layer) agreed with literature value (~1.3 nm). They also demonstrate the CV curve of samples in 1 M Na$_2$SO$_4$ solution at a scan rate of 1000 mV/s and Galvanostatic charge/discharge curves at current density of 3 A/cm$^2$ as shown in figure 4. The S-3 sample shows the highest volumetric capacitance of 584 F/cm$^3$ at a current density of 3.0 A/cm$^2$, while S-1 and S2 show 213 F/cm$^3$ and 389 F/cm$^3$ respectively. Since the reported value of carbon-based supercapacitor is 170 F/cm$^3$ at 100 A/cm$^3$, their results can be concluded that this PANi/r-GO assembly facilitates the application of a supercapacitor [22, 23, 24].

For the EC applications, manganese dioxide (MnO$_2$) has also shown to be a promising material due to its low cost and high specific capacitance (200 F/g) in mild aqueous electrolyte [25, 26, 27, 28]. Li et al., researched on MnO$_2$ nanosheet and graphene multilayer assembly with polyelectrolytes. Figure 5 illustrates the schematic procedure of multilayer construction. As-prepared PSS-GS to provide positive charge and negatively charged PDDA are sequentially adsorbed on the substrate, and then MnO$_2$ is applied onto the layers. This can be confirmed by cross-sectional SEM image as shown in figure 6(b). After 10 cycles of dip coating, the multilayer assembly exhibits a layered structure with a uniform thickness of about 200 (figure 7). Electrochemical performance of MnO$_2$/PDDA/PSS-Graphene films are then tested by Galvanostatic charge/discharge
tests and CV curve at 5, 10, 20, 40, and 80 mV/s in 0.1 M Na$_2$SO$_4$ solutions. All CV curve exhibits rectangular shape, and calculated specific capacitance are 263 F/g while reported value of the pure GO-MnO$_2$ exhibits 197.2 F/g. This result indicates that the assembled MnO$_2$/PDDA/PSS-Graphene multilayer can aid to advance the EC applications. [29]

In summary, these results imply that the use of polyelectrolyte in the multilayer assembly facilitates electrochemical applications. However, these multilayer assemblies have some disadvantages; using polyelectrolytes requires more insertions or dipping steps, which slows down the process. Furthermore, the use of polyelectrolytes may cause a potential side reaction between target layers and polyelectrolyte layers.
Figure 2. Schematic view of multilayer film LbL-assembled based on multiple interactions[22]
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(c) Specific capacitance with current density for ITO/(PDDA/PSS-GS/PDDA/MnO$_2$)$_{10}$ electrode
(d) Cycling stability of ITO (PDDA/PSS-GS/PDDA/MnO$_2$)$_{10}$ electrode at current density of 1.41 A/g [29]
2.2. Multilayer assembly without polyelectrolytes

To date, many multilayers have been assembled with polyelectrolyte. However, only a few multilayers have been made without polyelectrolyte. The first electrostatically assembled layer by layer without polyelectrolytes is introduced by Ilber in 1966 [3]. This multilayer assembly did not attract research attention until Lee. et al. suggested “all-inorganic” multilayers of titanium dioxide (TiO₂) and silicon dioxide (SiO₂) nanoparticles without polyelectrolyte in 2006. Lee’s group further developed this concept with two different charged SiO₂ nanoparticles [30, 31].

These recent efforts have led to the development of “all inorganic” multilayer assembly. In 2010, Hao Chen et al. expanded on the multilayer assembly without polyelectrolyte which consists of exfoliated montmorillonite(MMT) and zirconia (ZrO₂). Their study aims to observe film growth kinetics controlling the sol–gel ZrO₂ layer deposition on the MMT surfaces. MMT suspensions and sol-gel ZrO₂ are successfully assembled, as shown in figure 8. The effect of ZrO₂ sol-gel suspension concentration and dipping time on the thickness of multilayer films was also investigated. Figure 9 shows the influence of the concentration of ZrO₂ sol-gel suspension on thickness, and this result insists that the thickness of 45 seconds of dipping time exhibits an s-shape graph while the thickness of 0 and 10 minutes of dipping time are constant with higher concentration. In case of 45 s holding time, the film thickness rapidly increases at higher concentration of ZrO₂ suspension (0.15-0.3 M). To estimate the growth during 0 to 45 s dipping time, the difference of the film thicknesses of 0 to 45 s dipping time are also plotted in figure...
9b. Cross-sectional SEM image of different concentrations are also presented in figure 9c.

In summary, the film growth rate can be controlled via varying the precursor concentration and the holding time in the precursor solution. Their results imply the feasibility of controlling films of assembly without polyelectrolyte [4].

To date, TiO$_2$, which is a semiconductor oxide, is widely used in various applications such as photo-catalysis, solar cells, and photo electrochromic device. Recently, TiO$_2$ has been demonstrated as a high-performance electrochemical capacitor by Wen-wen Liu et al. They successfully synthesized graphene nanosheet and TiO$_2$ multilayers without polyelectrolyte and compared its electrochemical properties as electrode for supercapacitor with pure GNS and TiO$_2$ [32, 33].

Indium tin oxide (ITO)-coated glass substrate are firstly dipped with PDDA solution for 15 minutes to be positively charged, but polyelectrolytes then are not used during the dip coating process. The number of layers (1, 5, 10 and 15) for \{GNS\}, \{TiO2\} and \{GNS/TiO2\} multilayer films are successfully assembled as shown in figure 10. Figure 11 shows the CV curve of \{GNS\}, \{TiO$_2$\}, and \{GNS/TiO$_2$\} after 15 cycles of dip coating. All samples exhibit a rectangular shape, and \{GNS/TiO$_2$\} shows the highest specific capacitance. TiO$_2$ and graphene multilayer assembly without polyelectrolyte represents better specific capacitance than TiO$_2$ or graphene only [34].

Therefore, their results motivate us to study other inorganic materials without polyelectrolyte that have higher capacitance than TiO$_2$. In this study, we aim to develop...
both the method of layer by layer assembly without polyelectrolyte and the application for electrochemical capacitance. Therefore, we investigate the assembly of multilayer with all-inorganic materials, which might provide higher specific surface and capacitance. In this study, \{\text{BNNS}_x-(\text{SG ZrO}_2)\}_n, \{\text{BNNS}_x-(\text{SG SnO}_2)\}_n, \{\text{Fe}_2\text{O}_3\text{NS}_x-(\text{SG SnO}_2)\}_n, \{\text{CuONP}_x-(\text{SG SnO}_2)\}_n, \{r-\text{GNS}_x-(\text{SG SnO}_2)\}_n, and \{r-\text{GNS}_x-(\text{SG SnO}_2)\}_n are studied [35].
Figure 8. An SEM image of air-dried [MMT/(sol–gel ZrO$_2$)]$_{30}$ multilayer [4].
Figure 9. (a) The relationship between the film thickness and precursor solution concentration.

(b) The relationship between the estimated net thickness for the sol–gel layers grown during 45 second holdings in precursor solutions and the precursor solution concentration.

(c) Representative cross-sectional SEM images. The precursor solution concentrations are labeled; holding time = 45 s [4].
Figure 10. \{GNS\}_n, \{TiO_2\}_n and \{GNS/TiO_2\}_n multilayer films (n = 1, 5, 10 and 15) on ITO substrates [34].
Figure 11. (a) CV curves of the {GNS}, {TiO$_2$}, {GNS/TiO$_2$} and {GNS} + {TiO$_2$} multilayer film after 15 dipping cycles with the scan rate of 100 mV/s in 0.5 M Na$_2$SO$_4$ aqueous electrolyte; (b) the specific capacitance at different scan rate from 10 mV/s to 100 mV/s [34].
Chapter 3. Experimental

3. 1. Synthesis of Materials

3.1.1 Synthesis of Sol-Gel Zirconium Dioxide (SG ZrO$_2$)

Sol–gel ZrO$_2$ precursors are prepared by adding zirconium acetate hydroxide into deionized water. 0.15 M of zirconium acetate hydroxide was added into 30 ml of deionized water. The mixture is then ultrasonicated for 20 minutes. The resulting ZrO$_2$ precursors (was likely an aqueous “sol”) was then aged at 60°C for 2 hours [4].

3.1.2 Synthesis of Sol-Gel Tin Dioxide (SG SnO$_2$)

10.12 g of SnCl$_2$·2H$_2$O is dissolved into 100 ml of anhydrous ethanol. The mixture is refluxed and mixed in a closed vessel. The temperature of the mixture is maintained at 80°C for 2 hours and then cooled to room temperature. The resulting SnO$_2$ solution is aged for 24 hours at 30°C [36].

3.1.3 Synthesis of Graphene Oxide Nanosheets(r-G$^{NS}_x$)
GO (Graphene Oxide) is synthesized from natural graphite powder (325 mesh, GAK-2, Ukraine) by Hummer’s method. 3 g of Graphite powder are added into an 80°C mixture of H₂SO₄ solution (12 mL), K₂S₂O₈ (2.5 g), and P₂O₅ (2.5 g). This mixture is kept 80°C for 4.5 hours. The mixture is then cooled down to room temperature and 0.5 L of deionized water was added. After 10 hours, the mixture is filtered with additional deionized water to remove the residual acid by using 0.2 micron Nylon Millipore filter. Graphene powder is transferred into 120 mL of 0°C concentrated H₂SO₄. 15 g of KMnO₄ is added gradually under stirring and the temperature of the mixture is kept to be below 20°C. The mixture is under stirring at 35°C for 2 h, and additional 250 mL of deionized water is added. In order to reduce heat, additional 250 mL of ice water is added to keep the temperature below 50 °C. The mixture is stirred for 2 hours, and another 0.7 L of deionized water is added. 20 mL of 30% H₂O₂ is added to the mixture, and the color of mixture changed into brilliant yellow. In order to remove residual metal ions and the acid, filtration is performed with 1 L of 1:10 HCl aqueous solution and 1 L of deionized water. The dark brown product is dried in air and diluted to make a GO dispersion (0.5% w/w).

Lastly, dialysis is performed to remove the remaining metal species for one week [37].

3.1.4 Synthesis of Iron Oxide Nanosheets (Fe₂O₃NS)

The iron oxide nanosheets is prepared by mixing two equivalent molar ratio of an aqueous solution of NaOH and ferrous ammonium sulfate (Fe(NH₄)₂(SO₄)₂·6H₂O). 0.1 M NaOH is added into 0.1 M Fe(NH₄)₂(SO₄)₂·6H₂O under continuous stirring at room temperature. Centrifugation (3000rpm) is performed to separate the resulting deposits. The product is washed several times with deionized water [38].
3.1.5 Synthesis of Boron Nitride Nanosheets (BN$_{NS}$)

Boron Nitride nanosheets is prepared through exfoliation of h-BN microsized particles. BN powder (1 g, Aldrich) is added into 40 mL of N,N-dimethylformamide (DMF). The mixture is then vigorously ultrasonicated to disperse the powder for 10 hours. The exfoliations is performed at 5000–8000 rpm to remove residual large-size BN particles [39].

3.1.6 Synthesis of Copper Oxide Nanoparticles (CuO$_{NP}$)

Copper oxide nanoparticles is prepared by adding copper acetate aqueous solution into acetic acid. 0.5 mL of acetic acid is dissolved into 80 mL of 0.02M copper acetate aqueous solution. The temperature of mixture is kept at 100 °C. 20 mL of 0.04 M NaOH solution is rapidly added into the mixture under vigorous stirring. After neutralization of the mixture, the temperature is cooled to room temperature. Centrifuging and washing are repeated, and lastly the mixture is dispersed in 100 ml of deionized water [40].

3. 2. Layer by layer assembly

3.2.1 Preparation of substrates

ITO (Indium Tin Oxide) glass and p-type single-crystal silicon wafers (MEMC Electronic Materials, Inc., St. Peters, MO) are used as substrate for layer by layer assembly. Prior to deposition, ITO glass plates are ultrasonically washed with ethanol for 20 minutes. ITO glass are then ultrasonically cleaned in deionized water for 20 minutes.
These two steps are repeated and dried in air. The dipping and withdrawing speeds of substrates are kept at a value of 20 mm per minute.

Small pieces of silicon wafers are ultrasonically cleaned in 0.1 M NaOH solutions for 20 minutes. Silicon wafers are immersed into piranha solutions (3 volume of 95–98 wt.% H₂SO₄ : 1 volume of 30 wt.% H₂O₂) for 20 min. Silicon wafers are then washed with deionized water four times for 20 minutes, and dried in air.

3.2.2 Dip Coating

Dip coater (Nima Technology Ltd., Coventry, UK) is used to deposit layer by layer assembly. Layer by layer assembly is performed with four steps. A pre-cleaned substrate is firstly dipped into a sol–gel oxide precursor solution. A substrate is then moved into deionized water to rinse. A substrate is then dipped into a nanosheets or nanoparticles precursor. Lastly a substrate is washed with deionized water. Therefore, one deposition cycle is made with these four steps. Every compositions are dip coated 10 cycles and 20 cycles, respectively. For GO samples, thermal treatment in argon atmosphere is performed to convert from GO to rGO (reduced Graphene Oxide). In case of ZrO₂ sol-gel oxide (SG ZrO₂)- BN nanosheets (BNNS), SnO₂ (sol-gel oxide)- BN (nanosheets), and SnO₂ (sol-gel oxide)- Fe₂O₃ (nanosheets), magnetic stirring is applied to avoid precipitation.

3.3 Electrochemical Characterization

3.3.1 Cyclic Voltammetry Test
In order to evaluate the electrochemical properties of assembled multilayer films, cyclic voltammetry are performed using a three electrodes cell. Ag/AgCl electrode, Pt and assembled multilayer films on ITO glass were used as reference, counter and working electrodes. The potential is scanned from -0.7 to 0.3 V in 1 M H₂SO₄ for \{GNSₓ-(SG ZrO₂)\}_n multilayers, 0.1 to 0.6 V in 1 M H₂SO₄ for \{BNNSₓ-(SG ZrO₂)\}_n multilayers, -0.4 to 0.8 V in 1 M H₂SO₄ for \{BNNSₓ-(SG SnO₂)\}_n multilayers, -0.6 to 0.1 V in 0.1 M H₂SO₄ for \{Fe₂O₃NSₓ-(SG SnO₂)\}_n multilayers, -0.2 to 0.8 V in 0.1 M KCl for \{CuONPₓ-(SG SnO₂)\}_n multilayers, and 0 to 1.0 V in 1.0M Na₂SO₄ for \{r-GNSₓ-(SG SnO₂)\}_n multilayers. The scan rate is varied from 5 to 100 mV/s [41, 42, 43, 44].

The specific capacitance (Cₘ) is calculated by following equation 1.

\[
C_m (F/g) = \frac{\int i}{m \cdot s} \text{ (eq. 1) [44]}
\]

Where Cₘ = the specific capacitance in farads per gram,

\[\int i\] = the integrated area of the CV curve,

m = the mass of the electrode material in grams,

s = the scan rate in volts per second
Chapter 4. Results and Discussion

4.1. Preparation of Stable Suspensions

Figure 12 shows an image of as-prepared solutions of different materials for dip coating process. Figure 12 (a) shows synthesized ZrO$_2$ sol after gelation and Figure 12(b-f) represent the suspensions for CuO, SnO$_2$, BN, Fe$_2$O$_3$, and GO respectively. Most of suspensions are mono-dispersed and homogeneous. Except for BN and Fe$_2$O$_3$ suspensions, all the other suspensions are stable even after a few weeks. However, in case of BN and Fe$_2$O$_3$, magnetic stirring was used during dip coating to avoid precipitation due to instability of suspension. Further studies are required in order to prepare stable suspensions of BN and Fe$_2$O$_3$ by changing the pH of solution, synthesis temperature, etc.
Figure 12. Synthesized precursors (a) ZrO$_2$ sol-gel oxide, (b) CuO nanoparticles, (c) SnO$_2$ sol-gel oxide, (d) BN nanosheets, (e) Fe$_2$O$_3$ nanosheets, and (f) GO nanosheets.
4.2. Characterization of LbL multilayer morphology

4.2.1 \{r-GNS_{x}^{SG}\{ZrO_{2}\}\}_{n} multilayers

To confirm the morphologies of LbL assemblies, cross-sectional SEM images of \{r-GNS_{x}^{SG}\{ZrO_{2}\}\}_{n} were taken (Figures 13a and b). After 10 and 20 cycled depositions (Figures 13a and b), the layers are all shown as very clear and uniform multilayers. It can be plainly seen that the layers of r-GNS are periodically stacked onto the substrate, which indicates that the thermal treatment for GO (500 °C) did not cause the agglomeration of graphene sheets and the ZrO_{2} sheet. The relationship between the film thickness and the number of deposition cycles were also plotted in Figure 14. The film thickness lineally increases with the number of deposition cycles. The film thickness after 20 cycles was \~130\ nm. According to the SEM measured value, it can be calculated that its growth rate, elucidated with the thickness increment per deposition cycle, to be \~6.5\ nm per deposition cycle.
**Figure 13.** SEM images of \( \{r\text{-GNS}_x(SG \text{ ZrO}_2)\}_n \) multilayers (a) after 10 cycled and (b) 20 cycled deposition.
Figure 14. The relationship between the \( \{r^{-G^\text{NS}_x}(\text{SG} \text{ZrO}_2)\}_n \) multilayers thickness and number of deposition cycles.
4.2.2. \( \{\text{BN}^{\text{NS}}_{x-x}(\text{SG} \text{ ZrO}_2)\}_n \) multilayers

As-prepared \( \{\text{BN}^{\text{NS}}_{x-x}(\text{SG} \text{ ZrO}_2)\}_n \) multilayers were confirmed through the cross-sectional SEM images. In Figure 15, a dip coated layer can be seen, and the film is uniformly coated onto the substrate. Specifically, more agglomeration was spotted for the first few cycles (~ 10 cycles). As in the previously mentioned BN suspension, it is known that the solution was not stable during the dip coating process. However, its precipitation did not lead to the inhomogeneous phase and interfere the formation of uniform surface films after 10 cycles. Therefore, these results suggest that the magnetic stirring was successful. The film thickness also linearly increases with the number of deposition cycles. The film thickness after 20 cycles was ~258 nm with the growth rate of ~13 nm/cycle.
Figure 15. SEM images of $\{\text{BN}^\text{NS}_x(\text{SG ZrO}_2)\}_{\text{n}}$ multilayers (a) after 10 cycled and (b) 20 cycled deposition.
Figure 16. The relationship between the \(\text{BN}^{\text{NS}}_{x-(\text{SG} \ ZrO_2)n}\) multilayers thickness and number of deposition cycles.
4.2.3. $\{\text{BN}^{\text{NS}}_x^{-(\text{SG SnO}_2)}\}_n$ multilayers

Figure 17 shows the SEM images of the multilayer structure of $\{\text{BN}^{\text{NS}}_x^{-(\text{SG SnO}_2)}\}_n$ with the 10 and 20 cycle depositions, respectively. Dip coated multilayers are observed after 10 and 20 cycles (Figures 17 a, b), and films are very uniform. After 10 cycles, the thickness dramatically increases. Since the s- shape graph is expected, further experiments for higher number of deposition are required. The repeated and detailed observation of the relationship between the thickness and the number of deposition cycles within 5 cycles is needed to understand the agglomerative behavior. After the 20 cycles deposition, the thickness of the $\{\text{BN}^{\text{NS}}_x^{-(\text{SG SnO}_2)}\}_n$ multilayers was ~ 810 nm with a growth rate of ~40.5 nm/cycle.
Figure 17. Cross-sectional SEM images of $\{\text{BN}^{NS}_{x-(SG \text{ SnO}_2)}\}_n$ multilayers after (a) 10 and (b) 20 cycles deposition.
Figure 18. The relationship between the \( \{ \text{BN}^{NS_x} (\text{SG SnO}_2) \}_n \) multilayer thickness and number of deposition cycles.
4.2.4. \( \{\text{Fe}_2\text{O}_3^{\text{NS}_x-(\text{SG SnO}_2)}\}_n \) multilayers

In Figure 19, cross-sectional SEM images depict the structure of self-assembled \( \{\text{Fe}_2\text{O}_3^{\text{NS}_x-(\text{SG SnO}_2)}\}_n \) multilayers. As shown in these figures, multilayer structures can be found between the layers after 10 cycles. However, there are a few agglomerations after 20 cycles of deposition. A possible hypothesis is that it is due to the precipitation, as previously described. Therefore, further study for stable suspension for \( \text{Fe}_2\text{O}_3^{\text{NS}_x} \) is needed. Moreover, the growth rate is calculated to be \(~43\) nm/cycle based on its thickness of \(~860\) nm at 20 cycles deposition (figure 20).
Figure 19. Cross-sectional SEM images of \( \{ \text{Fe}_2\text{O}_3^{\text{NS}}_{x-\text{SG SnO}_2} \} \) multilayers after (a) 10 and (b) 20 cycles deposition.
Figure 20. The relationship between the \( \{\text{Fe}_2\text{O}_3^{\text{NS}}_x(\text{SnO}_2)^n\} \) multilayer thickness and number of deposition cycles.
4.2.5. \( \{\text{CuO}^{\text{NP}}_x(\text{SG SnO}_2)\}_n \) multilayers

\( \{\text{CuO}^{\text{NP}}_x(\text{SG SnO}_2)\}_n \) multilayers provide multiple stacking film structures as shown in Figure 21. This film has a very uniform film, but the multilayer structure cannot be observed. The possible reason for more agglomerated layers is that the CuO NPs formed self-aggregated clusters to reduce their high surface energy and affect the multilayer’ stacking behavior. This phenomenon is well known in the nanoparticle formations. Additional surface treatment with special functional groups or coating onto the surface of CuO NPs can help to prevent their self-aggregating behaviors. This will give the uniform bilayer to the LbL structure and further studies are required in the future [45].

As-prepared \( \{\text{CuO}^{\text{NP}}_x(\text{SG SnO}_2)\}_n \) multilayers had \( \sim 330 \) nm of thickness after 20 cycles of deposition, as shown in Figure 22.
Figure 21. Cross-sectional SEM images of \{\text{CuO}^{\text{NP}}_x - (\text{SG SnO}_2)\}_a\ multilayers after (a) 10 and (b) 20 cycles deposition.
Figure 22. The relationship between the \( \{\text{CuO}^{\text{NP}}_{x-\text{SG SnO}_2}\}\_s \) multilayer thickness and number of deposition cycles.
4.2.6. $\{r^-G_{x-(SG \;SnO_2)}\}_n$ multilayers

Cross-sectional SEM images of $\{r^-G_{x-(SG \;SnO_2)}\}_n$ multilayers were given in Figure 23. As shown in the figures, it has very uniform films and the film thickness lineally increases with the number of deposition cycles. Although there is some agglomeration, layers can also be observed. It can be explained that these samples demonstrate higher adhesion behavior from each other among very thick and homogeneous layers. Therefore, further study is required to provide a clear multilayer.
Figure 23. Cross-sectional SEM images of $r$-GNS$_x$-($^{SG}$SnO$_2$)$_n$ multilayers after (a) 10 and (b) 20 cycles deposition.
Figure 24. The relationship between the \( r^{-G^{NS_x-(SG \text{ SnO}_2)}}_n \) multilayer thickness and number of deposition cycles.
4.3. Electrochemical Characterization

Cyclic Voltammetry (CV) was used in order to evaluate the feasibility of using these self-assembled LbL multilayer films as electrodes for electrochemical capacitor (EC) applications. Every sample is coated for 20 cycles.

4.3.1 \{r-G^{NS}_{x-(SG\,ZrO_2)}\}_{20} multilayers

Figure 25 shows the CV plots of \{r-G^{NS}_{x-(SG\,ZrO_2)}\}_n multilayers at different scan rates ranging from 5-100 mV/s. Two broad peaks were observed during the cathodic and anodic scans. This indicates that the various redox reactions are taking place through the system rather than electrostatic attractions. According to the shape of the CVs, it can be noted that the \{r-G^{NS}_{x-(SG\,ZrO_2)}\}_{20} multilayer behaves similarly to the pseudocapacitor.

Figure 26 depicts the specific capacitance values at different scan rates based on the total mass of active materials (multilayer film). The specific capacitance decreases by increasing the scan rate. At 5 mV/s, the specific capacitance is 340 F/g while the specific capacitance decreases to 33 F/g at 100 mV/s. Giri et al. reported a specific capacitance of 317.5 F/g for graphene/zirconium oxide nanocomposite at a scan rate of 1 mV/s. Compared with the previous report, it seems that it is possible to use this multilayer film as an electrode for electrochemical applications [46].
Figure 25. Cyclic voltammograms for \( r\text{-G}^{\text{NS}}_{x}(\text{SG ZrO}_2)_{20} \) multilayers at different scan rates.
Figure 26. Specific capacitance values of \( \{r\text{-G}^{NS} \text{,} \text{ZrO}_2\}_{20} \) multilayers at different scan rates.
4.3.2. \( \{ \text{BN}^{\text{NS}}_{x}(\text{SG} \text{ ZrO}_2) \}_{20} \) multilayers

\( \{ \text{BN}^{\text{NS}}_{x}(\text{SG} \text{ ZrO}_2) \}_{20} \) multilayers’ CVs show rectangular shapes without resolved cathodic and anodic peak voltages, the CVs are shown in Figure 27. It has been asserted that if the material is an ideal capacitor, it will exhibit a rectangular form of the voltammogram. Its CVs indicate a nearly ideal supercapacitor behavior. However, the calculated specific capacitance was very low (~ 0.05 F/g at scan rate of 100 mV) while ZrO\(_2\) films have ~ 60.2 F/g of reported capacitance at a scan rate of 100 mV. These results imply that the insertion of the BN nanosheet lowered its specific capacitance. It is possible to be affected by the non-uniform surface of multilayers and impeded by precipitates [35]. Therefore, further studies should focus on having stable suspensions and forming uniform bilayers to improve the specific capacitance.
Figure 27. Cyclic voltammograms for \( \text{BN}^{\text{NS}}_x (\text{SGZrO}_2)_{20} \) multilayers at different scan rates.
Figure 28. Specific capacitance values of $\text{BN}^{\text{NS}}_x(\text{SG ZrO}_2)_{30}$ multilayers at different scan rates.
4.3.3. $\{\text{BN}^{\text{NS}}_{x-\text{SG} \text{SnO}_2}\}_{20}$ multilayers

In Figure 29, CVs for $\{\text{BN}^{\text{NS}}_{x-\text{SG} \text{SnO}_2}\}_{20}$ multilayers are shown with different scan rates. As-prepared $\{\text{BN}^{\text{NS}}_{x-\text{SG} \text{SnO}_2}\}_{20}$ multilayers show relatively rectangular CV curves for scan rates up to 25 mV/s indicating a nearly ideal supercapacitor behavior similar to the previous results of $\{\text{BN}^{\text{NS}}_{x-\text{SG} \text{ZrO}_2}\}_{20}$ multilayers. However, as the scan rate increases (50, 75, and 100 mV/s), the peak current increases and the shape of CV curves show some distortions from an ideal shape, possibly due to the increasing overpotentials from ion transport at the interface or solid electrolyte interphase (SEI) formation. These $\{\text{BN}^{\text{NS}}_{x-\text{SG} \text{SnO}_2}\}_{20}$ multilayers also showed very low capacitance of ~0.05 F/g at a scan rate of 100 mV/s. It can be noted that the addition of BN to the LbL assemblies represents the possibility that can be applicable to the supercapacitor, but the very low specific capacitance should be resolved first.
Figure 29. Cyclic voltammograms for \{(BN^{NS_x} \cdot (SnO_2))_{20}\} multilayers at different scan rates.
Figure 30. Specific capacitance values of \( \text{BN}^{\text{NS}}_x(\text{SnO}_2)_{20} \) multilayers at different scan rates.
4.3.4. \(\{\text{Fe}_2\text{O}_3^{NS_{x-(SG SnO_2)}}\}_{20}\) multilayers

Figure 31 represents the CVs for \(\{\text{Fe}_2\text{O}_3^{NS_{x-(SG SnO_2)}}\}_{20}\) multilayers. The nearly linear shape of CV curves can be observed over a range of scan rates of 5 \(-\) 100 mV/s. The linear CV curves indicate poor capacitance, therefore the self-assembled sample does not have charge/discharge behavior. Recently, it has been shown that carbon coated SG SnO\(_2\)-Fe\(_2\)O\(_3\) thin film shows a specific capacitance of 78 F/g at scan rate of 200 mV/s, which is much higher than our result (~0.05 F/g at scan rate of 100 mV/s). It is believed that the use of carbon facilitates ion mobility to provide higher capacitance [47,48].
Figure 31. Cyclic voltammograms for \( \{\text{Fe}_2\text{O}_3^{NS-x}(^SG\text{SnO}_2)\}_{20} \) multilayers at different scan rates.
Figure 32. Specific capacitance values of $\{\text{Fe}_2\text{O}_3^{\text{NS}} x - (\text{SG SnO}_2)\}_{20}$ multilayers at different scan rates.
4.3.5. \( \{\text{CuO}^{\text{NP}}_x (\text{SG SnO}_2)\}_{20} \) multilayers

Figure 33 shows the CV plots of \( \{\text{CuO}^{\text{NP}}_x (\text{SG SnO}_2)\}_n \) multilayers at different scan rates. The small integrated area of CV plots indicates poor capacitance of assembled LbL multilayer film. During the cathodic scan, a broad peak at \( \sim 0.1 \) V can be seen. This corresponds to the existence of some redox reactions within this system. Figure 34 shows the specific capacitance values versus scan rates based on the total mass of active electrode materials. The highest calculated capacitance is \( \sim 0.08 \) F/g at a scan rate of 50 mV/s. Some reported studies represent the capacitance for the mixture of SnO\(_2\)-CuO to be \( \sim 3.2 \) F/g at a scan rate of 50 mV/s. [48]. Compared with the pristine SnO\(_2\) and CuO values, 32 and 17.4 F/g at scan rate of 50 mV/s respectively, this assembled compositions seems unstable, so they reduce their capacitance. This can occur due to the fact that the CuO layer cannot be directly deposited onto the SnO\(_2\) layer [49]. Therefore, it is suggested that further study apply different assembled compositions with \( \text{SG SnO}_2 \) to explore supercapacitor behaviors.
Figure 33. Cyclic voltammograms for \( \{\text{CuO}^{\text{NP}}_x (\text{SnO}_2)\}_{20} \) multilayers at different scan rates.
Figure 34. Specific capacitance values of $\{\text{CuO}_{x}^{NP}(\text{SnO}_2)\}_{20}$ multilayers at different scan rates.
4.3.6. $\{r$-$G^{NS}_{x-}(^{SG} \text{SnO}_2)\}_{20}$ multilayers

Figure 35 depicts the CVs for $\{r$-$G^{NS}_{x-}(^{SG} \text{SnO}_2)\}_{20}$ multilayers over a range of scan rates of $5 - 100$ mV/s. Their curves represent relatively stable and rectangular shapes only except at a low scan rate of $5$ mV/s. However, their absolute area of the rectangular curve was very small which indicates low capacitance. Since $r$-GO is reported to have high capacitance, the LbL structure of $\{r$-$G^{NS}_{x-}(^{SG} \text{SnO}_2)\}_{20}$ was expected to show good supercapacitor behavior. As shown in Figure 36, the specific capacitance shows very low specific capacitance of $\sim 0.08$ F/g at scan rate of 100 mV/s while reported value for their mixed suspension is $\sim 35$ F/g at the same scan rate [49]. This result can be supported by its morphologies. Our results already confirmed that the r-GNS cannot be continuously grown with a deposition of SnO$_2$ layers via SEM micrographs; therefore, it is difficult to integrate the advantage of r-GO to the LbL structure. To increase their capacitance, better conversion of r-GO and adhesion between the layers are needed [50].
Figure 35. Cyclic voltammograms for \( \{r^{-G_{NS}}x^{-SG_{SnO_2}}\}_{20} \) multilayers at different scan rates.
Figure 36. Specific capacitance values of \( r\-G^{NS}_x\-(SG\ \text{SnO}_2)_{20} \) multilayers at different scan rate.
Chapter 5. Conclusion

In this study, two sol-gel oxide materials (ZrO₂ and SnO₂) and four nanomaterials were examined by applying into the LbL assembly for 6 different compositions which are \{r-G^{NS}_{x-(SG\ ZrO_2)}\}_n, \{BN^{NS}_{x-(SG\ ZrO_2)}\}_n, \{BN^{NS}_{x-(SG\ SnO_2)}\}_n, \{Fe_2O_3^{NS}_{x-(SG\ SnO_2)}\}_n, 
{CuO^{NP}_{x-(SG\ SnO_2)}\}_n, \{r-G^{NS}_{x-(SG\ SnO_2)}\}_n. \text{A stable multilayer structure is shown in}
{r-G^{NS}_{x-(SG\ ZrO_2)}\}_n, {r-G^{NS}_{x-(SG\ SnO_2)}\}_n \text{and } {Fe_2O_3^{NS}_{x-(SG\ SnO_2)}\}_n. \text{The relationship between their thickness and the number of deposition cycles are also plotted.}

The electrochemical characterizations for the 6 compositions of LbL assembly were also tested by CV plot. The samples of BN^{NS}_{x-(SG\ ZrO_2)}\}_20, \{BN^{NS}_{x-(SG\ SnO_2)}\}_20,
{Fe_2O_3^{NS}_{x-(SG\ SnO_2)}\}_20, \{CuO^{NP}_{x-(SG\ SnO_2)}\}_20, \text{and } {r-G^{NS}_{x-(SG\ SnO_2)}\}_20 \text{were not suitable for EC applications due to their low capacitance. However, the results of } {r-G^{NS}_{x-(SG\ ZrO_2)}\}_20 \text{imply strong feasibility for supercapacitor applications. In order to improve and explore in-depth electrochemical properties of } {r-G^{NS}_{x-(SG\ ZrO_2)}\}_20 \text{further studies are required.}
References


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