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A Free-standing Graphene-Polypyrrole Hybrid Paper via Electropolymerization with an Enhanced Areal Capacitance

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Abstract

Here we developed a free-standing reduced graphene oxide (rGO)-polypyrrole (PPy) hybrid paper via electropolymerization on a paper-like graphene gel. This flexible hybrid paper displayed a uniform layered structure with PPy coated onto the graphene layers. A high areal mass of 2.7 mg cm^{-2} could be obtained. It delivered a greatly enhanced areal capacitance of 440 mF cm^{-2} at 0.5 A g^{-1}, in contrast to that 151~198.5 mF cm^{-2} previously reported for graphene paper or polypyrrole-graphene paper. It can retain ~81% of the initial capacitance at a high current density of 6 A g^{-1}. The combined high flexibility with outstanding electrochemical performance, makes such novel hybrid paper a promising electrode for flexible supercapacitors.

Keywords: Graphene; Areal capacitance; Polypyrrole; Supercapacitor; Flexible hybrid paper electrode

1. Introduction

Recently, there is increasing interest in the development of wearable electronic devices, flexible displays and bendable television screens. Such devices require the development of flexible high efficiency energy storage devices [1-3]. Supercapacitors, due to the high power density attainable and excellent cycling stability, are an important class of energy storage devices [4, 5]. An ideal flexible supercapacitor should combine excellent mechanical strength and large electrochemical capacitance. Due to their excellent electrical conductivity, chemical stability and high specific surface area offered by graphene nanosheets, graphene based electrodes in the form of films or papers have shown remarkable flexibility with high gravimetric capacitances in the range of 138 to 210 F g^{-1} [6-8].

Although these graphene-based flexible electrodes present promising gravimetric capacitance, they normally deliver a very low areal capacitance in the range of 57 to 94.5 mF cm^{-2} due to the low areal mass loading (< 1 mg cm^{-2}) [9, 10]. For practical usage, it is suggested that the areal mass loading is at least 5 mg cm^{-2} and the electrode thickness is between 50-200 μm [11, 12]. One effective way to improve the areal capacitance is to incorporate metal oxides with high theoretical capacitances. However, graphene/metal oxide hybrid electrodes normally suffer from poor conductivity and excellent performance is only achieved at low scan rates/current densities. A MnO$_2$/carbon nanotube/textile nanostructure could deliver a large areal capacitance of 2.8 F cm^{-2} at a scan rate of 0.05 mV s^{-1}, but this dropped sharply to 120 mF cm^{-2} when the scan rate increased to 50 mV s^{-1} [13]. A rGO/MnO$_2$ film electrode showed a capacitance of 245 F g^{-1} (i.e. 196 mF cm^{-2}) at 2 mV s^{-1}. Approximately 58% of the capacitance was observed at 300 mV s^{-1} [14]. The use of a 3D graphene/MnO$_2$ electrode resulted in a large areal capacitance of ~600 mF cm^{-2} at 5 mA cm^{-2}, but showed a greatly decreased capacitance of 300 mF cm^{-2} at 20 mA cm^{-2} [15].

Integration of conducting polymers (CPs) with graphene may provide another route to achieve high areal capacitance. In CPs/graphene composites, CPs can provide high pseudocapacitance while graphene can provide a conductive network to overcome the poor cyclic stability of CPs, thus lead to enhanced gravimetric capacitance and good rate performance. Capacitance of 210 F g^{-1} (at 0.3 A g^{-1}) and 285 F g^{-1} (at 0.5 A g^{-1}) was obtained from polyaniline/graphene film and polypyrrole/sulfonated graphene film, respectively [16, 17]. Polypyrrole (PPy) is one of the most widely used CPs due to its good conductivity, low cost and high charge storage capability [8, 18]. Flexible electrodes based on graphene/PPy composites provide a high gravimetric capacitance ranging from 92 to 345 F g^{-1} [19-21] and an areal capacitance in the range of 152 to 175 mF cm^{-2} [22, 23].

In this work, a novel flexible reduced graphene oxide (rGO)-PPy hybrid paper with an enhanced areal capacitance was developed. PPy was incorporated into a paper-like graphene hydrogel via electropolymerization forming a layered structured rGO-PPy hybrid paper. The rGO-PPy paper with 3 times increased thickness can still keep an equivalent gravimetric capacitance compared to a neat rGO paper. It delivered a much higher areal capacitance of 440 mF cm^{-2} at 0.5 A g^{-1}, in sharp contrast to 185 mF cm^{-2} from a neat rGO paper. The capacitance decreased slightly to 356 mF cm^{-2} when the current density was increased to 6 A g^{-1}, indicating an excellent rate capability. Compared to the previously reported free-standing graphene-polypyrrole materials, our flexible free-standing rGO-PPy hybrid paper presents a higher areal capacitance and better rate performance.

2. Experimental

2.1 Material synthesis

Graphene oxide (GO) was synthesized from natural graphite flakes by the modified Hummers method. The reduced graphene oxide (rGO) aqueous solution was prepared by

reducing GO solution with hydrazine in the presence of ammonium solution [24]. Typically, ammonium solution (28 wt%, 350 μL) and hydrazine hydrate (92 μL) were added to GO dispersion (0.72 mg mL^{-1}, 100 mL), and stirred at 95°C for 1 h to complete the reduction. The resultant solution was then subjected to dialysis against a ~0.5 % ammonia solution to remove the excess hydrazine. Paper-like graphene gel was formed via vacuum filtration of rGO solution. This rGO wet gel was peeled off and immersed in water for 6h to remove the impurities.

Prior to PPy electropolymerization, rGO gel was immersed into the aqueous solution of 0.1 M pyrrole and 0.1 M sodium *p*-toluenesulfonate (pTS) overnight at 4 °C. PPy was electrodeposited galvanostatically onto rGO gel at a current density of 1 mA cm^{-2} for 20, 40 or 60 min. The obtained rGO-PPy hybrid papers were rinsed with deionized water for several times and then soaked in water overnight to remove the excess monomer or dopant.

2.2 Characterization and electrochemical properties

The surface morphology and cross-sectional view were observed by a field-emission scanning electron microscope (FESEM, JEOL JSM7500FA). The elemental analysis and mapping of the materials were conducted by Bruker X-Flash 4010 energy dispersive X-ray (EDX) detector on FESEM. Raman measurements were performed on a confocal Raman spectrometer (Jobin Yvon HR800, Horiba) utilizing 632.8 nm diode laser. FT-IR spectra were recorded on a FT-IR spectrometer (IRpretige-21, Shimadzu) over the range from 700 to 2000 cm^{-1}. The thermal stability was characterized by TGA (Q500, TA instruments), and the measurements were tested under nitrogen at a ramp rate of 5° min^{-1}. X-ray photoelectron spectroscopy (XPS) was conducted using XPS system equipped with a hemispherical energy PHOIBOS100/150 analyzer.

The rGO or rGO-PPy paper was assembled into Swagelok-type cell (X2 Labwares Pte Ltd.) to construct symmetric supercapacitor device. The electrolyte used was 1 M H_2SO_4. An all solid state supercapacitor was fabricated using PVA-H_3PO_4 polymer electrolyte following the procedure reported previously [8]. Cyclic voltammetry of the cells was tested using a CHI 650D (CH Instruments, Inc.) and scanned over a range of 0.0 to 1.0 V. Galvanostatic charge/discharge tests were performed using a BTS3000 battery test system (Neware Electronic Co.) over a potential range of 0.005-1.0 V. Electrochemical impedance spectroscopy (EIS) measurements were performed using a Gamry EIS 3000 system, and the frequency range was spanned from 100 kHz to 0.01 Hz with an amplitude of 10 mV at open circuit potential.

3. Results and discussion

The procedure used to prepare rGO-PPy paper is summarized in Figure 1a. With the assistance of vacuum filtration, the self-gelation of rGO occurs due to the intersheet π-π attractions, forming a lamellar structured graphene wet gel [25]. This gel was then soaked in a pyrrole solution overnight to allow the monomer and dopant to infiltrate into the gel. The polymerization of PPy occurred both on the surface and throughout the gel interior, creating a layered graphene-PPy hybrid structure. The rGO-PPy hybrid papers were named as rGO-PPy20, rGO-PPy40 and rGO-PPy60 according to the deposition time of 20, 40 or 60 min. Their areal mass was 1.80, 2.36 and 2.70 mg cm^{-2}, respectively. It was 1.13 mg cm^{-2} for the control sample, an unmodified pure rGO paper. The estimated PPy content in rGO-PPy20, rGO-PPy40 and rGO-PPy60 ratio was 37%, 52% and 58%, respectively. Longer deposition time was not necessary since PPy growth tended to saturate after 60 min. The rGO-PPy was flexible, as demonstrated in Figure 1b and can be used directly as binder-free electrode.

The cross-sectional view of rGO paper and rGO-PPy hybrid papers are shown in Figure 2a-c. The rGO paper presents a typical compact layered structure with a thickness of ~3.7 μm, due to the strong π-π interaction between graphene sheets (Figure 2a). In contrast, rGO-PPy paper displays an expanded layered structure (Figure 2b, 2c, 2d). PPy acts as spacer between rGO sheets, leading to an enlarged thickness in the range of 12 to 15 μm. All the rGO-PPy papers display similar structure, taking rGO-PPy40 as an example, it clearly shows a lamellar structure with nodule-like PPy on the graphene layers at higher magnification (Figure 2f). An rGO-PPy paper displays a surface morphology with more wrinkles, lumps or islands (Figure 2h) compared to a smoother feature for an rGO paper (Figure 2g).

The elemental analysis of rGO-PPy40 paper surface was detected by EDX module associated with SEM and shown in Figure 3. Only carbon and oxygen elements can be detected on the surface of rGO paper (Figure 3a, b, c). The existence of sulphur and nitrogen elements (originated from PPy/pTS) apart from C and O proves the existence of PPy on the hybrid paper surface (Figure 3d, e, f). The distribution of sulphur element in the cross section of neat rGO or rGO-PPy40 paper was also compared. Very weak sulphur element signal was detected for rGO paper, and it was distributed discretely even at the sample-free area (Figure 3j). Thus the existence of S can be excluded. In contrast, rGO-PPy40 paper displays a clear distribution of sulphur element, evidence of the existence of S (Figure 3l). These results prove that PPy was successfully grown not only on the surface but also the interior of graphene layers. We cannot get a clear mapping image of nitrogen, which may be due to the weak signal of N element.

The successful deposition of PPy can also be confirmed by Raman spectra (Figure 4a). There are only two peaks in the range of 1000-2000 cm^{-1} for neat rGO paper. The peak at around 1333 cm^{-1} (D band) is related to the defects and disorder structure in graphene. The peak at 1593 cm^{-1} (G band) is ascribed to the doubly degenerate zone centre E$_{2g}$ mode [26,

27]. Three new peaks can be observed for rGO-PPy paper. The peaks at 928 cm^{-1} and 971 cm^{-1} can be assigned to C-H out of plane deformation and PPy ring deformation, respectively. The tiny peak at 1047 cm^{-1} represents C-H in plane deformation. PPy has characteristic peaks at 1335 cm^{-1}, 1372 cm^{-1} and 1590 cm^{-1}, which reflect the ring stretching and C=C backbone stretching [28]. Similar to the previously reported graphene/polypyrrole composite materials, they are overlapped with the D-band and G-band of graphene [29]. Since these rGO-PPy samples present similar IR spectra, only the IR spectroscopy from rGO-PPy40 paper are shown (Figure 4c). No obvious peaks were observed for neat rGO paper over the range of 700-2000 cm^{-1} in the IR spectroscopy (Figure 4c). The rGO-PPy40 paper exhibits the characteristic adsorption bands of PPy and pTS dopant. The peaks at 1535 and 1446 cm^{-1} are assigned to C=C and C-C stretching of PPy backbone. The band at 1288 cm^{-1} and 1026 cm^{-1} corresponds to C-N stretching vibration and C-H, N-H in-plane deformation vibrations, respectively [30, 31]. The band at 1150 cm^{-1} is due to the stretching vibration of the sulfonate group in pTS [32].

X-ray photoelectron spectroscopy was performed to further investigate the structure of rGO-PPy paper. Figure 4d and 4e show the deconvoluted C$_{1s}$ spectra of neat rGO and rGO-PPy 40. The C$_{1s}$ of neat rGO (Figure 4d) can fit into four component peaks, corresponding to different chemical states of carbon. The dominant peak at 284.7 eV is attributed to the collective effect of sp2 and sp3 hybridized carbon [33]. Peaks at 287.9 eV and 291.0 eV are assigned to oxygen bonded carbon species, C=O and O-C=O [34]. The peak at around 286 eV in rGO-PPy C$_{1s}$ (Figure 4e) corresponds to C-N, C-S and C-O [33]. The intensity of the peak at 286 eV for rGO-PPy increased remarkably compared to that for neat rGO. It may be ascribed to C-N backbone bonding in polypyrrole. The N$_{1s}$ core level spectra of rGO-PPy (Figure 4f) was dominated by a main peak at 399.6 eV, which is assigned to the quinoid imine (=N-) in polypyrrole. The peak at a higher binding energy of 401.1 eV can be

ascribed to the positively charged protonated nitrogen species [33, 35]. In addition, a S_{2p} peak arises at 168 eV, which corresponds to sulfonated group in dopant pTS (Figure 4g) [33].

The thermal stability of these papers was investigated using thermal gravimetric analysis (Figure 4h). The weight loss of neat rGO paper over 25-600 °C is about ~10 %, which can be attributed to the decomposition of residual oxygen-containing groups [36]. For pure PPy/pTS film, the major weight loss (45%) occurred at the temperature range of 200~600 °C, which is mainly due to the removal of counter ion pTS [37, 38]. A total weight loss of 19%, 24% and 28% was displayed for rGO-PPy20, rGO-PPy40 and rGO-PPy60, respectively, which is related to the increase amount of PPy.

The capacitive performance of rGO or rGO-PPy paper electrode was studied using cyclic voltammetry (CV) in a three electrode system (Figure 5). No obvious redox peaks were observed for the rGO paper over the potential range -0.5~ 0.5 V (vs. Ag/AgCl) (Figure 5a). The rectangular CV shape indicates a nearly ideal electric double-layer capacitive behaviour. The rGO-PPy electrodes presented features of a pseudocapacitive activity which combining faradic and non-faradic responses. The redox peak of PPy can be observed at around -0.2 V and 0.2 V (Figure 5b, c, d) [39]. This pseudocapacitive behaviour became more significant with the increase amount of PPy.

The paper electrodes were then assembled into symmetric supercapacitors for evaluation. Different form the three electrode system, the rGO-PPy paper based symmetric supercapacitor did not show the remarkable redox peaks of PPy (Figure 6). It is typical for a two-electrode cell system since one electrode was oxidized while its symmetric electrode was reduced, resulting in negligible redox peaks [11, 40]. Over the scan rate range from 20 to 100 mV s^{-1}, all the rGO-PPy papers displayed nearly rectangular CVs even for that with a high areal mass loading of 2.7 mg cm^{-2}. All these reveal their ideal capacitive behaviour. This result is in sharp contrast to that of MnO$_2$-graphene paper electrode with similar areal mass

loading but presented highly distorted a CV curve at 20 mV s^{-1} [41, 42]. The areal capacitance at 20 mV s^{-1} was 298, 349 and 410 mF cm^{-2} for rGO-PPy20, rGO-PPy40 and rGO-PPy60, respectively. The rGO-PPy60 paper delivered the highest capacitance, which is over 2 times than that of the neat rGO paper (174 mF cm^{-2} at 20 mV s^{-1}). Our rGO-PPy papers offer much higher areal capacitance than those of the previously reported graphene-PPy film/membrane electrodes, which delivered a lower capacitance (151~175 mF cm^{-2}) even at a scan rate of 10 mV s^{-1} [22, 23, 43].

The charge/discharge tests were performed and the results are shown in Figure 7. Neat rGO delivered a gravimetric capacitance of 164 F g^{-1} at 0.5 A g^{-1}. It slightly decreased to 156 F g^{-1} at 2 A g^{-1}. The rGO-PPy20 paper showed the highest gravimetric capacitance among these hybrid papers, 190 F g^{-1} at 0.5 A g^{-1} and 165 F g^{-1} at 2 A g^{-1}. The rGO-PPy 40 and rGO-PPy 60 paper delivered a slightly decreased gravimetric capacitance of 163 F g^{-1} and 161 F g^{-1} at 0.5 A g^{-1}, but still comparable to the rGO papers in this work or the previously reported [6, 7, 18]. Benefited from the unique layered structure, rGO-PPy paper with 3 times thickness and much higher mass loading still keeps the similar gravimetric capacitance compared to neat rGO paper.

The areal capacitance of neat rGO and rGO-PPy hybrid papers can be calculated from their gravimetric capacitance and areal mass. The areal capacitance of rGO-PPy hybrid paper increases with the prolonged electrodeposition time. The rGO-PPy 60 paper gave the highest areal capacitance of 440 mF cm^{-2} at 0.5 A g^{-1}, which was 2.4 times higher than that 185 mF cm^{-2} of rGO paper. Meanwhile, rGO-PPy40 and rGO-PPy20 papers showed an areal capacitance of 380 and 342 mF cm^{-2}, respectively. It should be pointed out that the current 0.5 A g^{-1} was equal to that of 1.35, 1.18, 0.9, 0.57 mA cm^{-2} in an areal unit for rGO-PPy60, rGO-PPy40, rGO-PPy20 and rGO paper, respectively. The areal capacitance delivered from our rGO-PPy paper is higher than that from the flexible graphene/PPy fibre electrode (107

mF cm^{-2} at 0.24 mA cm^{-2}) [44] and carbon fibre/PPy paper electrode (198.5 mF cm^{-2} at 1 mA cm^{-2}) [45]. At a high current density of 6 A g^{-1} (~16 mA cm^{-2}), over 300 mF cm^{-2} was retained for rGO-PPy60 paper, 81 % of that obtained at 0.5 A g^{-1} (Figure 7e). Our rGO-PPy papers present better rate capability compared to the carbon fibre/PPy paper electrode, which demonstrated a capacity retention of only 66% when the current density increased from 1 to 10 mA cm^{-2} [45]. This unique PPy coated graphene layered structure ensured excellent rate performance of the rGO-PPy hybrid paper.

The cycle stability of rGO-PPy hybrid papers or neat rGO paper was tested at a current density of 2 A g^{-1} (Figure 7f). A capacitance retention of 75%, 78%, 85% and 92% was shown during the first 1000 cycles for rGO-PPy60, rGO-PPy40, rGO-PPy20 and rGO, respectively. A lower retention rate with the increased PPy ratio may be attributed to the decreased pseudocapacitance contribution from PPy. PPy suffers from physical changes associated with the doping/de-doping of ions during cycling [46, 47]. The repeated redox cycles can damage PPy molecule structure and promote PPy degradation, leading to the capacitance decay. It should be pointed out that these rGO-PPy hybrid papers can still retain 71-80 % of the initial capacitance after 5000 cycles, comparable to or higher than that 56~87% retention of the previously reported results for PPy or carbon-PPy based electrodes [48-51].

The areal energy density and power density in the Ragone plot (Figure 8) are calculated using the following equations: $E = C_s \Delta V^2 / 7200$, $P = 3600E/t$. The rGO-PPy60 paper presented a maximum energy density of 61.3 μWh cm^{-2} at a power density of 1.2 mW cm^{-2}, while it maintained 49.5 μWh cm^{-2} at 14.2 mW cm^{-2}. Our rGO-PPy paper displayed higher energy density compared to the reported results for graphene paper [10], graphene-polypyrrole film [23], graphene-PANI paper [52], or even graphene-MnO$_2$ electrode [41] especially at high power density.

The Nyquist plots of a neat rGO or rGO-PPy paper-based electrode were obtained in the frequency range between 0.01 and 100 kHz, and are shown in Figure 9a. An equivalent circuit model is used to fit the impedance spectra (Figure 8a inset). The equivalent series resistance (ESR) includes solution resistance R_s, electrode-electrolyte interfacial double layer resistance R_{dl} and charge transfer resistance R_{ct} [46, 53]. The semi-circle portion in the high frequency region represents two constant phase elements CPE_{dl} and CPE_f, accounting for imperfect double layer capacitance and faradic pseudocapacitance. The ESR of our RGO-PPy papers was around 3.5~5.5 Ω, close to that 2.2 Ω for the rGO paper. At low frequency region, more vertical plot at low frequency region indicates more ideal capacitive performance [54]. All the rGO and rGO-PPy papers showed nearly vertical line in this region, indicating their good capacitive performances. The rGO paper gave the most vertical plot among those papers, which can be ascribed to the fastest ion and electron transportation due to the lowest layer thickness.

Dynamic electrosorption analysis (DEA) is an effective electrochemical method used to study ion adsorption and transport behaviour in bulk graphene based materials [55]. The relative ion-transport rate within a porous electrode can be implied from a characteristic relaxation time constant τ_0, the reciprocal of the frequency where the capacitance is 50% of its maximum value [56, 57]. The increase of τ_0 is largely attributed to the reduced average pore size. The τ_0 of rGO-PPy papers was around 1.8 to 2.5 s, slightly higher than that of a neat rGO paper (1.25 s) (Figure 9b). Nevertheless, the τ_0 offered by rGO-PPy paper based device is comparable to that 0.92-2.27 s for graphene paper based supercapacitors [55], indicating a good porosity for electrolyte to access.

The performance of an all solid-state supercapacitor based on rGO-PPy40 electrodes using polymer electrolyte PVA-H_3PO_4 was also investigated. Nearly triangular charge/discharge curves at the unbent state with a slightly lower gravimetric capacitance

compared with that with liquid electrolyte (Figure 10a), 140, 118, 96 F g^{-1} at 0.5, 1 and 2 A g^{-1}, respectively were obtained. That may be ascribed to the deceased ion diffusion or transport within the polymer electrolyte. The capacitive behavior at the bent state was nearly the same as that at the relaxed state (Figure 10b). It can retain 99% and 97% of its capacitance when it was bent 90° and 180°, indicating the robustness of this flexible supercapacitor.

4. Conclusion

Wet graphene gel was used to prepare free standing graphene/PPy hybrid papers via electropolymerization. PPy was uniformly coated onto the surface and interior of the graphene gel, creating a layered graphene/PPy structure with an increased thickness. The areal mass loading of the hybrid paper can be easily controlled by adjusting the electrodeposition time. Benefiting from this unique structure, these hybrid papers with enlarged thickness showed a gravimetric capacitance comparable to the graphene paper yet with a much higher areal capacitance. This hybrid paper also exhibited excellent rate performance. The high areal-normalized power density and high energy density make such flexible hybrid papers promising materials for the application in flexible energy storage devices.

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Captions for Figures

Figure 1 (a) Schematic procedures to fabricate a rGO-PPy paper include the following steps: formation of a wet rGO paper via filtration, soaking the wet paper in pyrrole monomer solution, PPy electropolymerization followed by drying. (b) Digital image of a rGO-PPy40 paper

Figure 2 SEM images of the cross section of a neat rGO (a), rGO-PPy20 (b), rGO-PPy40 (c) and rGO-PPy60 paper (d); Surface morphology and cross-sectional view of a neat rGO (e, g) and rGO-PPy40 paper (f, h) at higher magnification.

Figure 3 Element analysis of a neat rGO (a, b surface; g, h cross section) and rGO-PPy40 paper (d, e surface; j, k cross section). Element mapping of the surface of neat rGO (c), rGO-PPy40 (f), and the cross section of rGO (i) and rGO-PPy40 (l).

Figure 4 Raman spectra of a neat rGO or rGO-PPy40 paper (a) and the expanded view over $500 \sim 1200$ cm^{-1} (b); IR spectra of a neat rGO or rGO-PPy40 paper (c); XPS spectra of C_{1s} in neat rGO (d), C_{1s} in rGO-PPy (e), N_{1s} in rGO-PPy40 (f) and S_{2p} in rGO-PPy (g) (black line, experimental data; colour line: fitting line); TGA curves of neat rGO and rGO-PPy papers (h)

Figure 5 Cyclic voltammograms of a rGO (a), rGO-PPy20 (b), rGO-PPy40 (c) or rGO-PPy60 (d) paper in 1 M H_2SO_4 between -0.5 to 0.5 V (vs. Ag/AgCl) at scan rates of 20, 50, 100 mV s^{-1}.

Figure 6 Cyclic voltammograms of a rGO (a), rGO-PPy20 (b), rGO-PPy40 (c) or rGO-PPy60 (d) paper based supercapacitors in 1 M H_2SO_4 at scan rates of 20, 50, 100 mV s^{-1}.

Figure 7 Electrochemical performance of the symmetric supercapacitors using rGO, rGO-PPy 20, rGO-PPy40 or rGO-PPy60 paper electrodes in 1M H_2SO_4. (a-d) Charge/discharge curves; (e) Areal capacitance versus current densities; (f) Cycle stability at a current density of 2 A g^{-1}.

Figure 8 Ragone plot of rGO-PPy hybrid papers in comparison to the reported graphene-based paper materials.

Figure 9 Nyquist plots (a) (scatter: experimental plots, line: fitting plots), and frequency response (b) of neat rGO or rGO-PPy papers based supercapacitor. (a inset: equivalent circuit model)

Figure 10 (a) Charge discharge curves of rGO-PPy40 based flexible supercapacitor. (b) CVs of rGO-PPy40 based flexible supercapacitor (bending and relaxation state) at a scan rate of 20 mV s^{-1}.

Figure 1
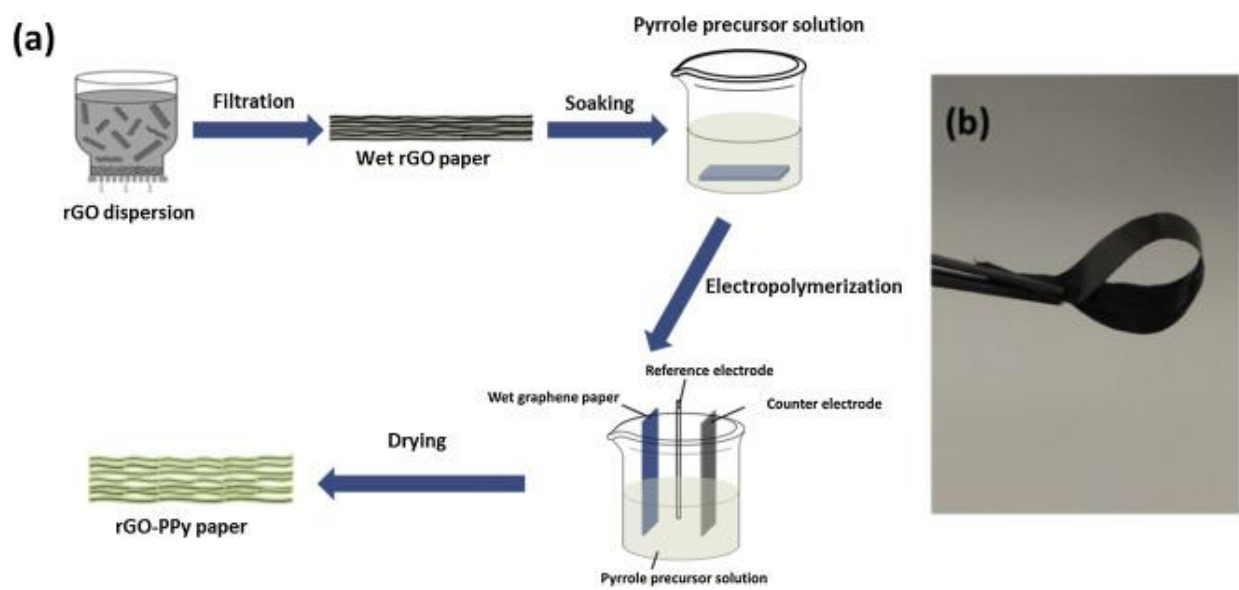
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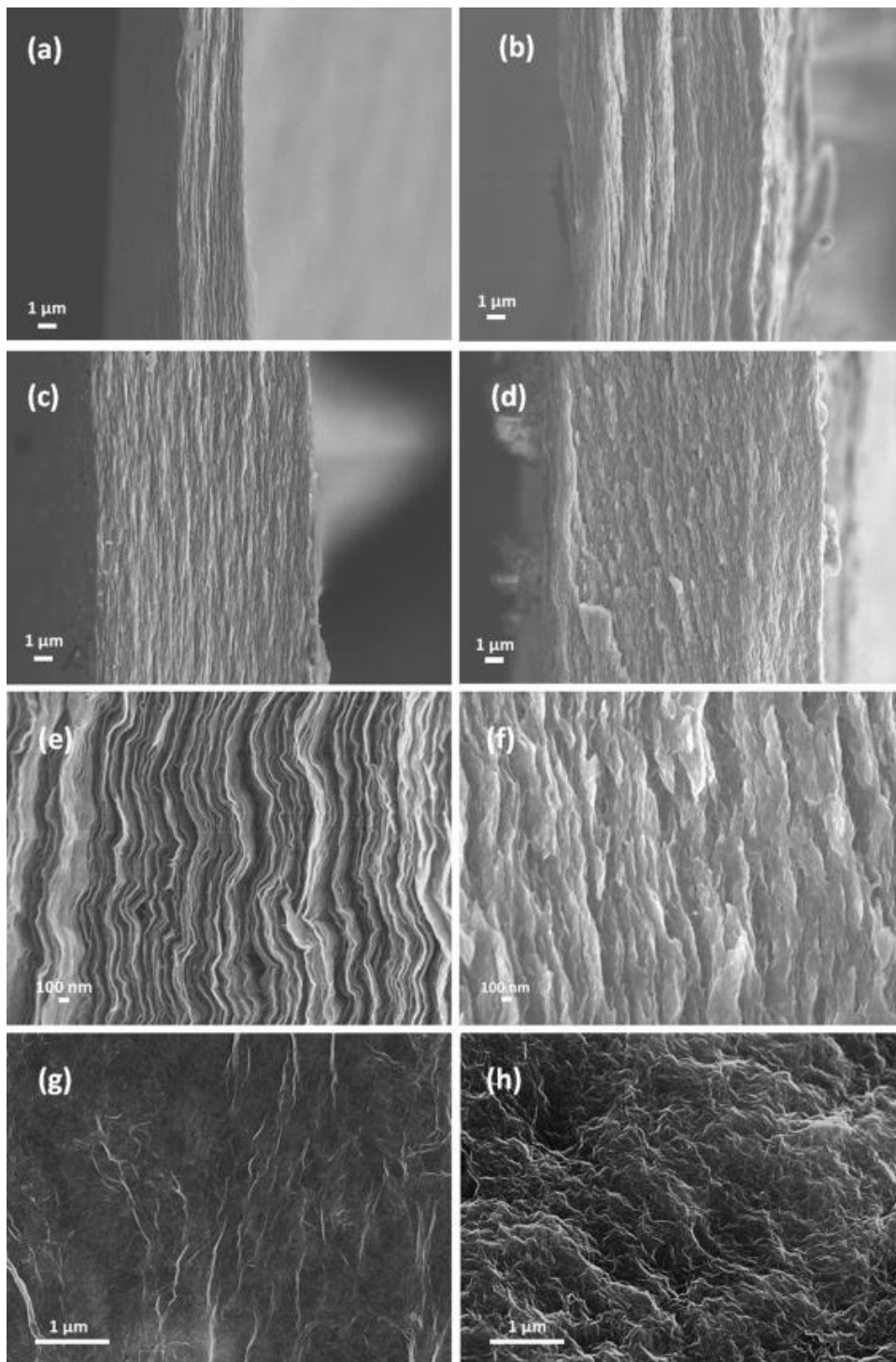
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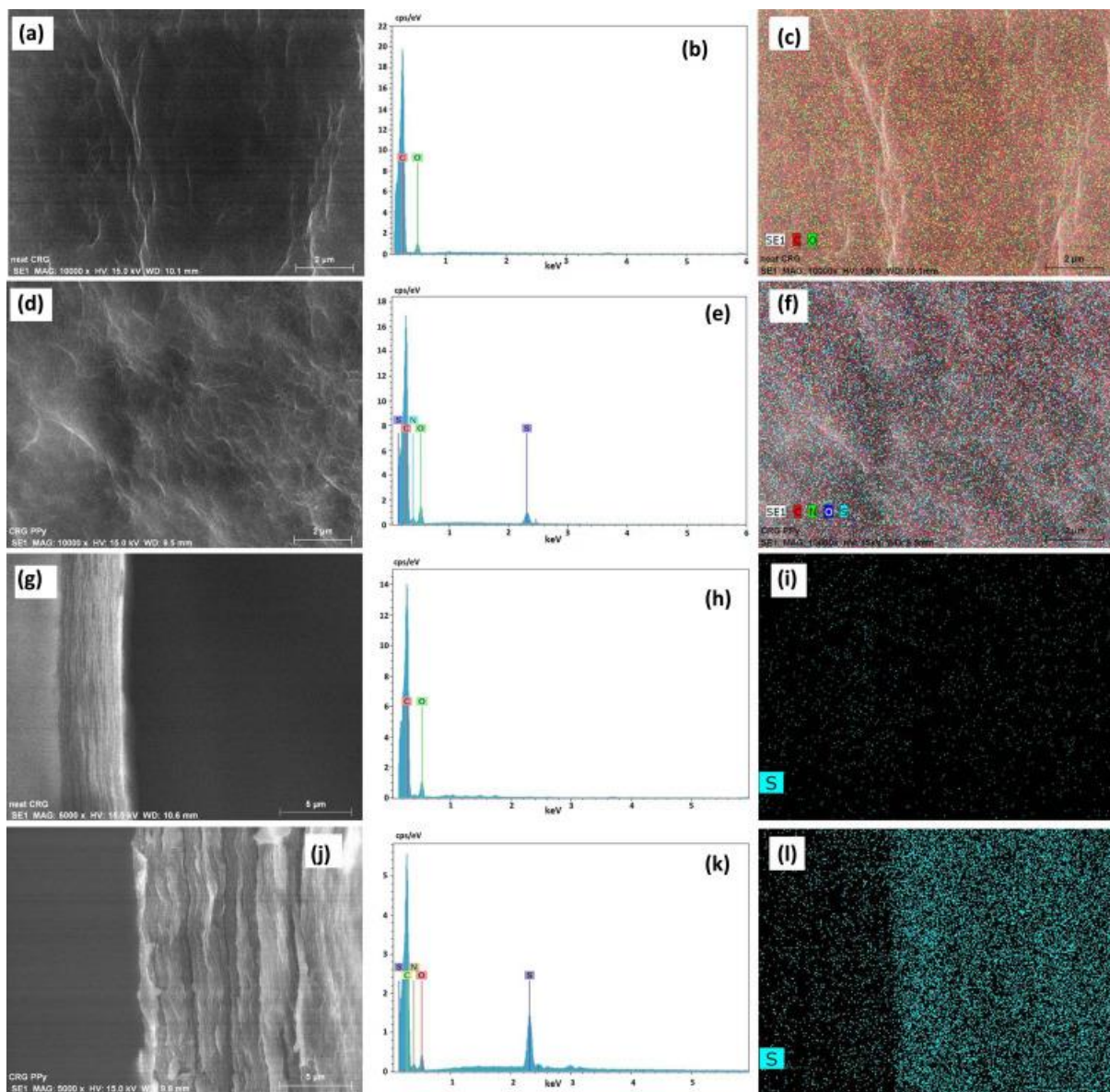
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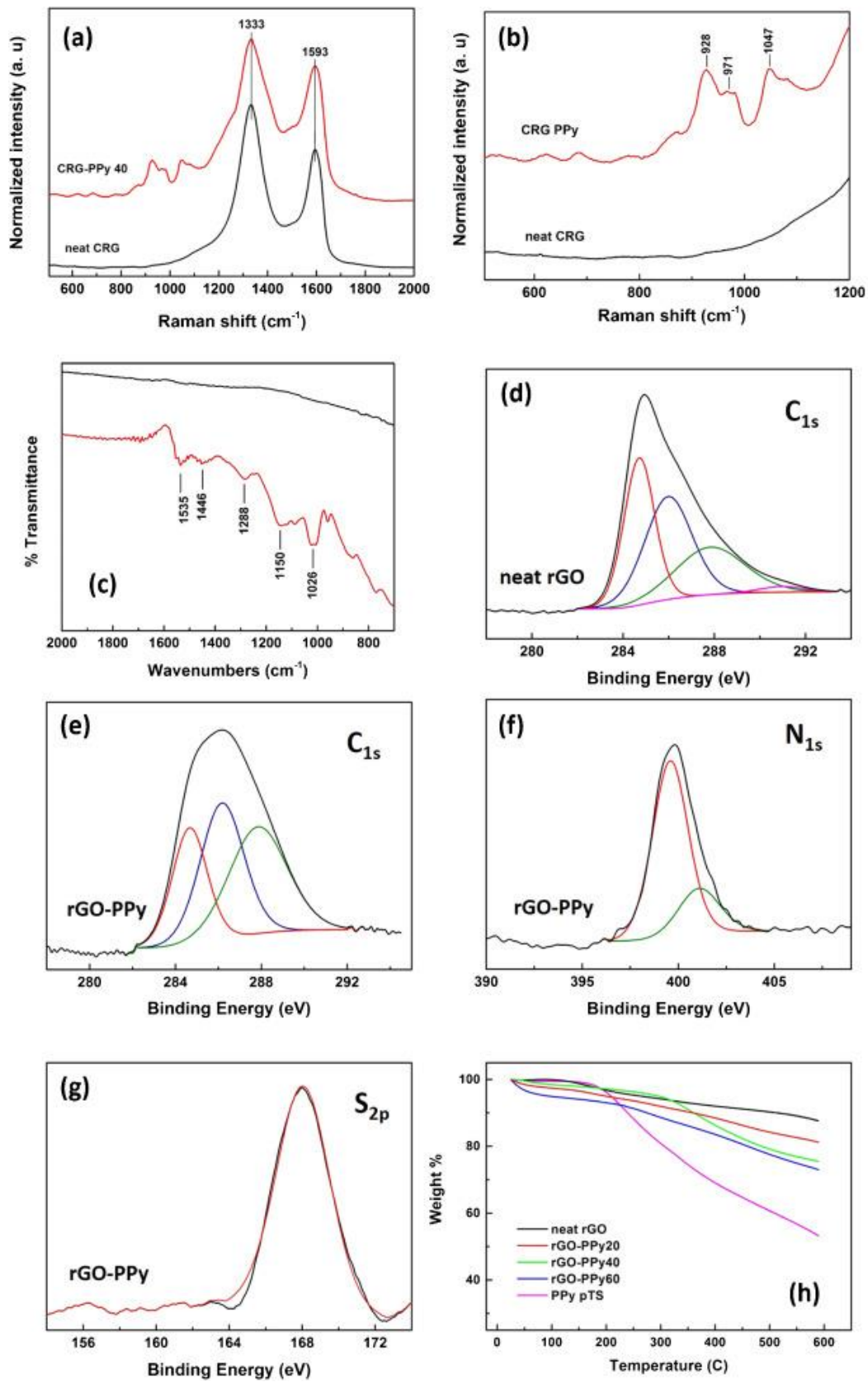
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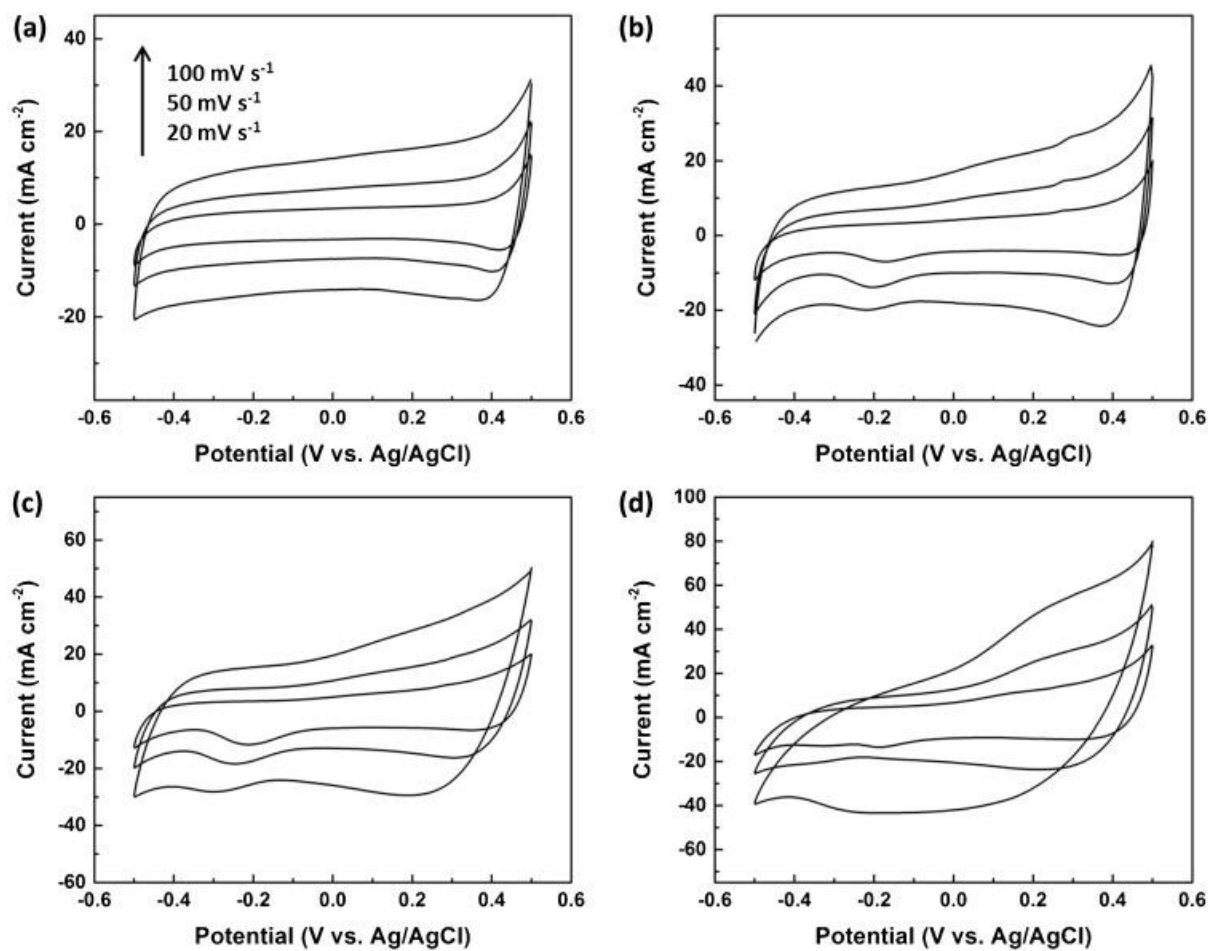
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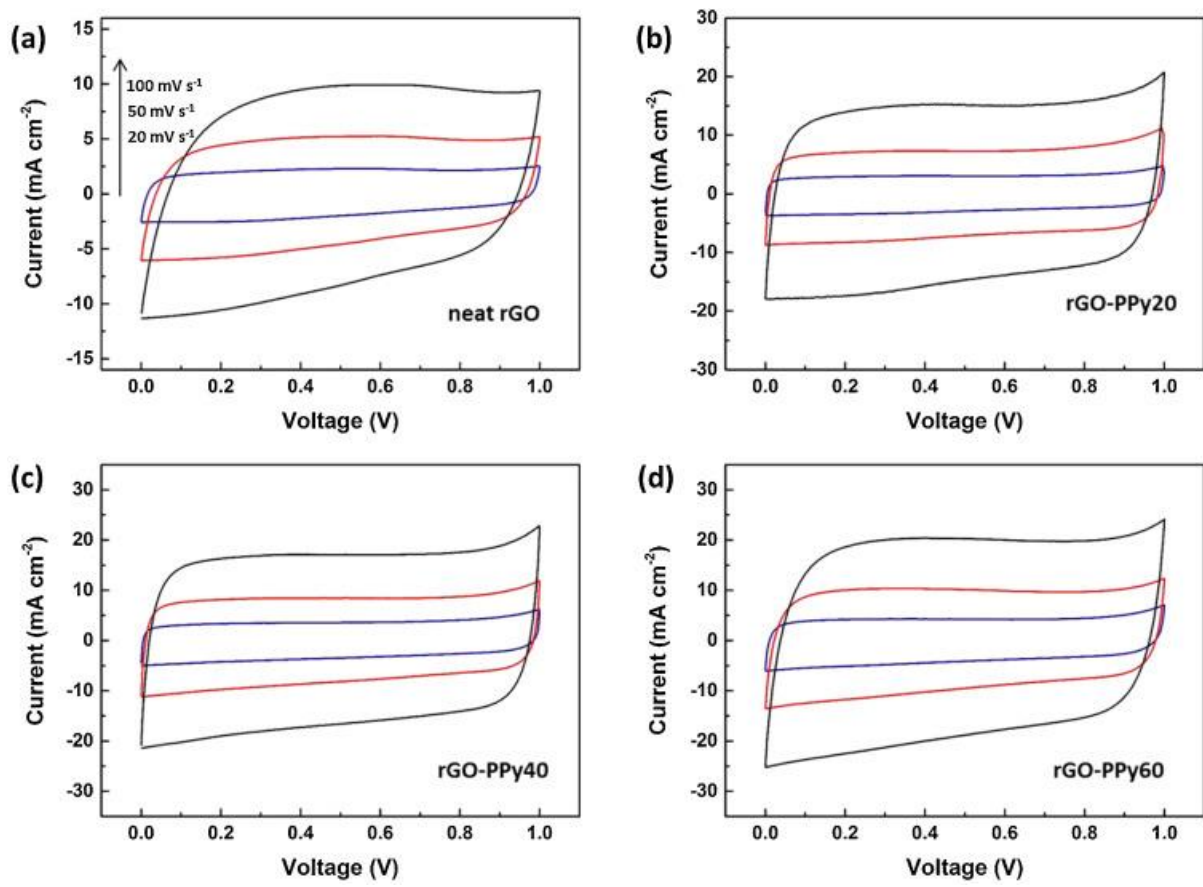
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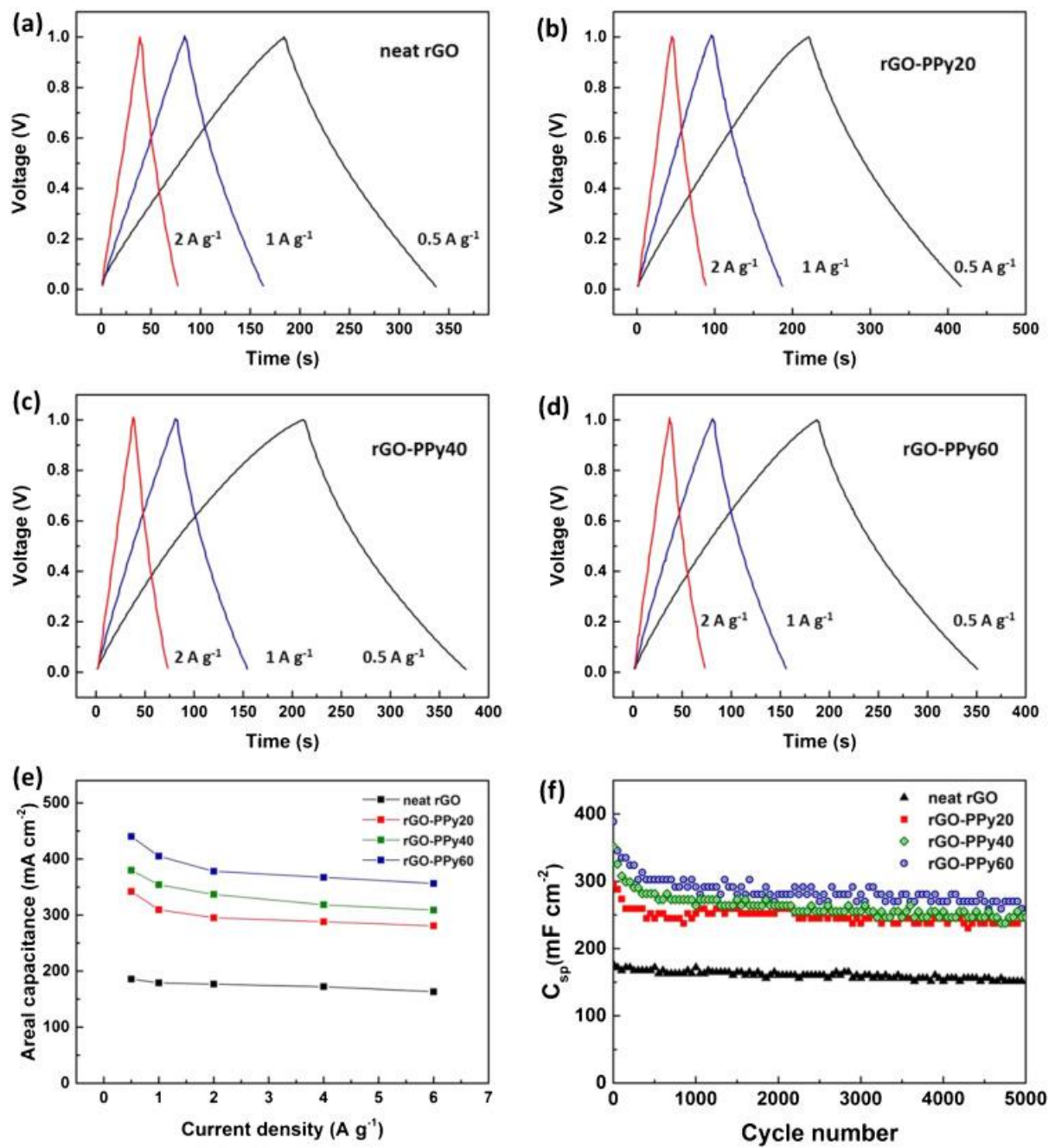
Figure 8

Figure 9

Figure 10