Journal of Power Sources 364 (2017) 465-472

Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

High volumetric supercapacitor with a long life span based on polymer dots and graphene sheets



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HIGHLIGHTS

G R A P H I C A L A B S T R A C T

- Abundant functional groups from polymer dots (PDs) take part in faradic reactions.
- PDs can bind onto graphene sheets tightly through chemical bonds.
- PDs can effectively increase the surface areas and pore volumes of the composites.

ARTICLE INFO

Article history: Received 26 May 2017 Received in revised form 6 July 2017 Accepted 1 August 2017

Keywords: Polymer dots Graphene sheets Supercapacitor Volumetric capacitance Pseudocapacitance



ABSTRACT

A series of polymer dots/graphene sheets composites with high densities are prepared and tested for supercapacitors. Polymer dots (PDs) are synthesized by one-step method at room temperature. They can effectively increase surface areas of the composites (almost 10 times), and the functional groups from PDs produce high pseudocapacitance, so that the samples exhibit high specific capacitances (e. g., 364.2 F cm⁻³ at 1 A g⁻¹) and high cycling stability (e. g., more than 95% of the initial capacity retention over 10 000 cycles at different current densities). The optimal sample is employed to fabricate a symmetric supercapacitor, which exhibits an energy density up to 8 Wh L⁻¹ and a power density up to 11 800 W L⁻¹, respectively.

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1. Introduction

The concerns of electronic hazards and high cost of metallic materials let researchers keep on developing metal-free electrode for greener and more sustainable energy storage systems [1]. In a

http://dx.doi.org/10.1016/j.jpowsour.2017.08.002 0378-7753/© 2017 Elsevier B.V. All rights reserved. variety of nonmetallic materials, graphene has become a focus in the fundamental research of supercapacitors electrode materials regarding its unique properties in chemical stability, tunable structure, excellent electrical conductivity and high surface area [2]. However, capacitive performance of related nanomaterials like 2D graphene nanosheets (GS) tend to degrade after chemical processing, which mainly arises from fewer functional groups on the surface, nonporous structures and lower surface areas caused by aggregation [3]. And as for electrical double layer capacitance (EDLC), a key parameter of supercapacitor, specific surface areas



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(SSA) and pore size distributions (PSDs) of the electrode materials play the main roles in the influence of it [4]. In order to increase the SSA and pore volume of GS, hard templates, self-assembly and chemical activation agents (like KOH) have been employed to achieve above objectives [5,6]. Nevertheless, such methods mean complex processes or harsh conditions, which do not fit the concepts of green chemistry. On the other side, some other researchers have tried to introduce more functional groups through compositing graphene with pseudocapacitive materials like conducting polymer [7]. Polyaniline (PANI), as a typical example, has been widely studied as a supercapacitor material for its high capacitance, good conductivity in the doped state and fast redox reactions [7]. Although such composite could exhibit an outstanding specific capacitance, its cycle life was influenced heavily by the PANI dissolution from graphene layers during charge-discharge cycles. Therefore, it is still a challenge to find a better material, which can offer abundant organic groups for faradaic reactions, increase the surface area of graphene for electrical double layer capacitance and bind onto graphene layers tightly for stable combination.

In view of this, polymer dots (PDs) will be a better choice to meet above requirements. Typically, PDs are cross-linked polymers prepared from linear polymers (lower molecular weight) or monomers [8]. Similar to carbon quantum dots (CQDs) or graphene quantum dots (GQDs), PDs have advantages in small size (around 10 nm), good dispersion in many solvents, abundant surface groups and low production cost [8,9]. Yet due to these natural merits of PDs, they will have better prospects when taken as supercapacitors electrode materials. First, the functional groups on PDs are not only able to produce high pseudocapacitance, but also able to bind PDs onto graphene tightly through chemical bonds [10,11]. Thus, PDs could play their significant role continuously during the long cycle life. Moreover, quantum sizes make PDs an excellent filler for the graphene-based materials, which means it is possible to make full use of the limited space between layers. Therefore, the dense structure of GS will be protected and volumetric capacitance can be greatly improved accordingly. Finally, according to our and other previous works [12], such nano dots would have a positive effect on the morphologies, SSA and PSDs of matrix materials. Accordingly, it will provide some considerable benefits for the electrochemical performance. But so far, PDs were merely studied for fluorescence sensors and bioimaging probes [8,9], while their applications in the electrode materials have never been reported.

In the present research, we synthesized PDs from polyethylene imine (PEI) and prepared PDs/GS composites at room temperature in facile ways. Mild conditions enable the preservation of a large number of amino groups from PDs, which have a great contribution to pseudocapacitance. The introduction of PDs can improve the SSA of graphene sheets and contribute to a diversified distribution of pore sizes. More than that, reactions between surface groups from both PDs and GS will make such composites very stable. The optimal sample had a density of about 1.4 g cm⁻³ (compaction density, including binder), with its specific volumetric capacitances of 364.2 F cm⁻³. In comparison to graphene sheets, whose specific capacitance is only 193 F cm⁻³, the optimal result is nearly twice as much. The corresponding symmetric supercapacitor showed a volumetric energy density of 8 Wh L^{-1} and a volumetric power density of 11 800 W L⁻¹. Furthermore, almost 100% retention rates were observed at different current densities during long term cycling tests.

2. Experiment section

2.1. Synthesis of PDs

PEI (0.5 g, Aldrich) was dissolved in DI water (20 mL) and then

hydroquinone solution (0.5 mL, 1 mg mL⁻¹) was also added. After standing at room temperature for one day, the color of the mixed solution changed from colorless to clear yellow. Solid PDs were obtained by adding *N*,*N*-Dimethylformamide (DMF) into the solution and collecting the precipitate after centrifugation. The precipitate was washed by DMF and further dried in a vacuum oven at 40 °C for 48 h.

2.2. Preparation of GS and PDs/GS composites

GS colloidal suspension (5 mg mL⁻¹) was prepared by sonication of graphite oxide powder which has been synthesized from nano graphite powder (Aladdin) by a modified Hummers method. After that, PDs was added in the suspension with different mass ratios (1:10, 1:5, 1:2 and 1:1). After standing at room temperature for 12 h, the as-prepared hydrogels (PDs/GS composites) were freeze dried to remove adsorbed water for following experiments.

2.3. Characterizations

The data of X-ray diffraction (XRD) were collected at room temperature using a Bruker D4 Endeavor X-ray diffractometer with Cu K α radiation ($\lambda = 0.1541$ nm, 40 kV). Fourier transform infrared (FT-IR) spectra were recorded on a Thermo Fisher Nicolet 6700 FTIR spectrometer in a range of $4000-500 \text{ cm}^{-1}$, using the KBr pellet method. The UV-vis absorption spectra were measured on the Unico UV-2802 PC spectrometer. The fluorescence spectra were recorded using a Horiba Jobin Yvon FluoroMax-4 spectrofluorometer. Nitrogen adsorption-desorption measurements were performed at 77.3 K with a Quantachrome Autosorb IQ surface area analyzer to obtain the SSA. X-ray photoelectron spectroscopy (XPS) data were obtained by a Thermo ESCALAB 250 electron spectrometer using an Al Kα X-ray source (1486.6 eV). The morphologies of the samples were characterized via a fieldemission scanning electron microscopy (FESEM) under a JSM-6390 microscope (Zeiss, German), while the transmission electron microscopy (TEM) images of the samples were obtained by a high resolution transmission electron microscope (JEM-2010) at 200 kV.

2.4. Electrochemical measurements

The electrochemical performance was determined using a three-electrode or two-electrode system (symmetric capacitor) in 1 mol L^{-1} H₂SO₄ aqueous solutions. For three-electrode system, cyclic voltammetry (CV) was recorded on a CH Instruments 660E electrochemical workstation at the potential range of -0.6 to +0.4 V vs. Hg/Hg₂SO₄ and the scan rate was set from 2 to 100 mV s⁻¹. Galvanostatic charge-discharge (GCD) tests were performed by a CT2001A Land cell tester at the same potential ranges, while the current densities varied from 1 to 30 A g^{-1} . Electrochemical impedance spectroscopy (EIS) measurements were also conducted on the electrochemical workstation and frequency limits were set at 100 kHz to 0.01 Hz with 5 mV of voltage amplitude at the open-circuit potential. In this system, the working electrode was prepared by pressing a mixture of the sample (95 wt %) and poly(tetrafluoroethylene) (PTFE) binder (5 wt %) onto a stainless steel grid with an area of 1 cm², followed by drying at 80 °C for 24 h, and the active material loading for each electrode was about 1.2 mg cm⁻². The counter electrode was prepared with activated carbon (commercial, surface area > 1200 m^2g^{-1}) and PTFE binder in the same proportion, but the area of the counter electrode was about 3 cm^2 (about 5 mg cm⁻²) in order to reduce the interference to working electrode.

Symmetric supercapacitors (two-electrode system) were assembled by using the optimal sample (PDs/GS-0.5) as positive



Scheme 1. Synthetic routes of PDs and PDs/GS composites.

and negative electrode materials. Potential range was set from 0 to 1 V, while the scan rate was set from 2 to 200 mV s⁻¹ and current density was set from 1 to 30 A g⁻¹.

Optimal materials (PDs/GS-0.5) were also used as the test sample to explore effect of a higher mass loading on capacitance as well as energy and power densities. For three-electrode system, mass loadings of working electrode were 2.5, 5, 10 mg cm⁻², respectively. For symmetric supercapacitors, mass loadings of positive or negative electrodes were 2.5, 5, 10 mg cm⁻², respectively.



Fig. 1. (A) FTIR spectra and (B) XRD patterns of PDs/GS composites.

For three-electrode system, C_s is the gravimetric-specific capacitance of the single electrode (working electrode, F g⁻¹).

$$C_{s}\left(F\,g^{-1}\right) = I \times \Delta t / (m \times \Delta V) \tag{1}$$

where I is the constant current applied, Δt is the discharge time, ΔV is the operating voltage and m is the net mass of the active material on working electrode. The volumetric-specific capacitance was calculated (three-electrode system) as:

$$C_{v} \left(F \, cm^{-3} \right) = \rho \times C_{s} \tag{2}$$

where ρ is the compaction density of electrode materials (prepared films, including active materials and binder).

For symmetric capacitors, gravimetric-specific capacitance (C_s total, F g⁻¹), volumetric-specific capacitance (C_v total, F cm⁻³), energy density (E) and power density (P) of capacitor are calculated according to the following equations:

$$C_{s \text{ total}} \left(F g^{-1} \right) = I \Delta t / M \Delta V \tag{3}$$

$$C_{v \text{ total}} \left(F \text{ cm}^{-3} \right) = \rho \times C_{s \text{ total}}$$
(4)

$$E\left(Wh L^{-1}\right) = 0.5 \times C_{v \text{ total}} \times \Delta V^2 / 3.6$$
(5)

$$P(W L^{-1}) = E \times 3600/\Delta t$$
 (6)

where I is the constant current applied, Δt is the discharge time, ΔV is the operating voltage of symmetric capacitor, M is total weight of positive and negative materials, ρ is same as above.

3. Results and discussion

Experimentally, PDs were synthesized by adding quinol into the PEI aqueous solution. Through electrostatic attraction and interaction between different functional groups, chain molecules of PEI chains were aggregated as zero-dimensional structures (See Scheme 1). The as-prepared PDs are characterized by TEM that shows the products are uniform and monodispersed with diameters of 6–10 nm (Fig. S1 A and B). The fluorescence spectra of the PDs exhibit optimal excitation and emission wavelengths at 410 nm and 527 nm respectively, and exhibit a chartreuse color under a UV lamp (inset of Fig. S1 B). The UV-Vis absorption curve of the PDs contains two typical absorption bands at 245 and 348 nm, corresponding to the electron transitions from the n orbital to the π orbital (Fig. S1 D) [13,14]. These optical features confirm that the asprepared PDs are similar to those typical PDs in previous works [8,9].

The compositions and structures of composites or PDs are characterized by FTIR, XRD, XPS and other measurements respectively. The FTIR spectra of different samples are compared in Fig. 1 A. For these composites, a broad band at 3450 cm⁻¹, indicating that the *N*-H and O-H stretching peaks cannot be distinguished in these composites. -NH- or NH₂- stretching vibrations are observed at 850 cm⁻¹ which relate to nitrogen-containing groups from PDs. Except that, C=O stretching bands are found at 1640 cm⁻¹ which different to C=O bands from –COOH groups (1690-1720 cm⁻¹) [4,15,16]. Such phenomena are caused by reactions between -NH₂ from PDs and -COOH from GS and the combination between C=O and *N*-H will decrease the strength of C=O band. As a result, their absorption frequency will move to a lower wavenumber. Compared



Fig. 2. FESEM of (A) GS and (B) PDs/GS-0.5; HRTEM of (C) GS and (D) PDs/GS-0.5.



Fig. 3. (A) Nitrogen adsorption-desorption isotherms and (B) PSDs calculated by the SF method of PDs/GS composites and GS.

to that, the most obvious differences between PDs and composites are C-H stretching and bending bands at 2950 cm⁻¹/2850 cm⁻¹ and 1550 cm⁻¹/1470 cm⁻¹ which are caused by methylene from chain of PDs. More importantly, the wave numbers of C-N bonds between PDs and four composite materials also exist a significant difference. The former one is 1330 cm⁻¹ and the latter four are 1400 cm⁻¹. Such phenomenon is mainly due to conjugated structures from amide bonds [8], which are able to make C-N bonds have a red shift. Accordingly, it also suggests $-NH_2$ groups belong to PDs could have reactions with -COOH from GS. In the same way, N-H bands of PDs and composites at 820 and 860 cm⁻¹ respectively also arise from the same reason. As a conclusion, FTIR data could be the useful evidence that PDs have effectively combined with the GS layers.

XRD patterns are shown in Fig. 1B, which consist of three broad diffraction peaks with 2 θ values of about 23.5° and 43.5° corresponding to the (002) and (101) planes of graphitic materials [4], respectively. It is easy to find that the width of the peaks has a positive correlation with adding the amount of PDs. It is due to the non-conjugated PDs could destroy the structure of GS, which decreases the structural order of the samples.

In order to observe in surface morphologies and structures between GS and composite more intuitively, FESEM and HRTEM images were recorded. Fig. 2A-B and Fig. S2 clearly illustrate that surface of pure GS is comparatively smooth [4]. In contrast, the morphology of the composite exhibits that the layered carbon sheets are sticking out from the fractured surface and forming a relatively well-developed highly porous structure. Comparing Fig. 2C and D, it can be found that PDs (marked with white circles, Fig. 2 D) are effectively combined with GS to form the composite structure. Moreover, it can also be clearly observed that each sheet of the composites is stacked one on top of another while layers of GS (Fig. 2C) have a flat structure, which is corresponding to the results of SEM. Thus, we can conclude that PDs can effectively bind onto layers and change the roughness of GS, so as to form a porous structure.

Surface areas and porous features of products are evaluated by nitrogen physisorption measurements at 77.3 K, and specific results are shown in Fig. 3 and Table 1. With the ratio of PDs to GS growing from 0 to 1, SSA and pore volume of the composites increase significantly, almost 10 times. Besides, adequate PSDs in the electrode materials also play an important role for obtaining high capacitance, which includes a balance between the micro- and meso-porosities as well as a match between the sizes of pores and diameters of hydrated electrolyte ions. In the present samples, PDs/GS-0.5 and PDs/GS-1 have pores with diameters in the range of

Table 1 Porosity properties and specific capacitance of different samples in 1 mol L^{-1} of H₂SO₄ at current density of 1.0 A g⁻¹.

Sample	$\stackrel{S_{BET}}{(m^2g^{-1})}$	$\stackrel{S_{micro}}{(m^2 \ g^{-1})}$	V_{tot} (cm ³ g ⁻¹)	V_{micro} (cm ³ g ⁻¹)	$\begin{array}{c} C_g \\ (F \ g^{-1}) \end{array}$	C _s (F cm ⁻³)
GS	40.3	0	0.041	0	110	193.6
PDs/GS-0.1	87.4	0.1	0.092	0.0002	163	252.7
PDs/GS-0.2	101.6	0.2	0.115	0.0005	223	323.4
PDs/GS-0.5	182.8	5.0	0.223	0.0036	262	364.2
PDs/GS-1.0	407.2	173.8	0.351	0.0791	251	271.1

1–2 nm and 2–5 nm, corresponding to the micropores and mesopores respectively. Compared to that, GS and other two composites just possess mesoporous structures. Some classical researches indicate that micropores could contribute greatly to the specific capacitance and mesopores would exhibit excellent ion accessibility. Therefore, such hierarchical porous structures will be of great benefit to the capacitive performance of the materials [4].

Characterization of by XPS is shown in Fig. 4. Fig. S4 and Table S1. which confirms the presence of carbon, nitrogen, and oxygen in PDs/GS composites. The comparison of different samples, N 1s spectra can all be deconvoluted into two peaks corresponding to N-5 (pyrrolic and pyridonictype nitrogen; BE = 400.7 - 402.6 eV) and $H_2N=C$ (amine moieties; BE = 399.5-401 eV) [4,16]. While the atomic proportions of nitrogen show an obvious upward trend, from 2.86% to 5.14%, with the addition of PDs. More specifically, contents of amine moieties between different composites are similar, while the percent of pyrrolic nitrogen (N-5) has a significant change from 0.76% to 2.77% with the increase of PDs. And according to the wide recognition, N-5 species benefits to the pseudocapacitance. Different from the results about nitrogen, atomic proportions of oxygen in different composites always maintain at 16%–17%. At the same time, there are only three species of O1s, denoted as COOH (BE = 535-536.6), C-O-C (BE = 533.6-535), and C-OH (BE = 532.1-533 eV), respectively [4,16]. For C1s, existences of O=C-O (carboxyl groups, BE = 287.5-288.8 eV), C-O/C-N and C=C/C-H are consistent with the results of N1s and O1s. In the view of pseudocapacitance, N-5, H₂N=C, COOH and C-OH are all contributive to faradaic reactions, which have a huge profit to holistic capacitance. Moreover, plentiful organic functional groups will also facilitate the ion diffusion and decrease interface resistance.

Cyclic Voltammetry (CV) experiments are carried out at different sweep rates to examine the electrode reactions of materials (See Fig. 5 A and Fig. S5). The shape of the CV curves is almost square, indicating an ideal capacitance behavior based on electrostatic attraction. Pairs of symmetrical, wide-redox peaks are observed in these curves, which is the character of the faradaic pseudo capacitance [4]. According to the results of FTIR and XPS tests, oxygen-containing groups and nitrogen-containing groups consist of carbonyl oxygen, hydroxyl oxygen, amino nitrogen and pyridine nitrogen. So the related faradaic reactions can be considered as following processes [4] (See Scheme 2).

Electrochemical impedance spectroscopy (EIS) is another way to study the capacitive behavior of these samples. In a typical Nyquist impedance plot like Fig. 5B, the semicircles at the high-frequency region represent the conductivity of the electrode materials and electrolyte. Curves in the high-tomedium-frequency region show the charge transfer resistances which relate to the nature of the materials. At the high- and medium-frequency region, as shown in the inset, after the semicircles are extended to intersect with the X axis to obtain the fitted radius of the semicircles [4,17]. And they are regarded as the internal contact resistance of the electrode (R_{ct}). The specific values are 1.6, 2.8, 3.0, 6.6, 13.8 Ω for GS, PDs/GS-0.1, PDs/GS-0.2, PDs/GS-0.5 and PDs/GS-1, respectively.

Comparing with the volumetric and gravimetric capacitances between five samples in Fig. 5C, PDs/GS-0.5 shows the favorable results. The capacitances are 262 F g⁻¹ and 364.2 F cm⁻³, which are almost two times higher than that of GS. Therefore, these results fully reflect the remarkable contributions of pseudocapacitance, which is mainly generated by PDs. It should also be noticed that PDs



Fig. 4. (A) XPS survey spectra of PDs/GS composites. High-resolution XPS of (B) C 1s, (C) N 1s and (D) O 1s of PDs/GS-0.5.



Fig. 5. Electrochemical performance of PDs/GS composites and GS (three-electrode system). (A) CV curves at a scan rate of 10 mV s⁻¹. (B) Nyquist impedance plots. (C) Comparison of the volumetric and gravimetric capacitances of the optimal composite with other similar materials in the aqueous electrolyte.

$$\sim C=O + H^{+} + e^{-} \iff \sim CH-O$$

$$\sim C-NH_{2} + H_{2}O \iff \sim C-NHOH + 2H^{+} + 2e^{-}$$

$$\swarrow N + e^{-} + H^{+} \iff \swarrow N H$$

Scheme 2. Related faradaic reactions.

will also be the obstacle when too much of them are composite with GS. Just like PDs/GS-1, whose mass ratio of PDs to GS is 1:1, show lower capacitances. According to the results of EIS, its internal contact resistance is the maximum among five samples and it will affect the electronic transmission. Therefore, the capacitances may also be restrained by this shortcoming. Generally speaking, porous carbon based materials usually have lower compact densities, $0.5-1 \text{ g cm}^{-3}$ as examples. While the density of the optimal sample (PDs/GS-0.5) reaches to 1.4 g cm^{-3} , which guarantees the ability of compact energy storage. Taking this sample to compare with different graphene based materials like porous graphene particles, RGO/CNTs or RGO/ γ -Fe₂O₃ composite, it also shows a decent performance (See Fig. 5D and Table S2) [18–24]. More than that, PDs/ GS composites also have good cycling stability. In Fig. S8, after 10 000 cycles at different current densities, capacity decay rates of all samples are less than 5%. And it provides a direct proof that PDs could stably combine with GS during charging-discharging cycles, which mainly depends on tight chemical bonds between surfaces of PDs and graphene layers.

Two-electrode symmetric supercapacitor is assembled to evaluate the as-prepared PDs/GS materials for practical applications by using PDs/GS-0.5 as the positive electrode and negative electrode. As shown in Fig. 6A and B, CV curves and GCD curves of the symmetric supercapacitor at various scan rates or current densities in a potential range of 0–1.0 V. There were no obvious peaks about pseudocapacitance of the CV curves can be observed, showing a typical capacitor behavior. More than that, highly symmetrical charge-discharge curves also imply the same characteristic and a good coulombic efficiency. The specific capacitance ($C_{s tot}$) based on the total mass of the active materials of the two electrodes is 56.6 F cm⁻³ (40.5 F g⁻¹) at a current density of 1 A g⁻¹ (formulae (3) and (4)). Cycling stability is also an important factor to evaluate its performance. Owing to firm bonds between PDs and GS layers, these active sites could be intact during cycling tests. Closing to or reaching 100% retain rate at different current densities is shown in Fig. 6C just perfectly confirms this.

Power density and energy density are also key parameters to judge the performance and predict the application of a supercapacitor. According to the formulae (5) (6), this symmetric supercapacitor delivers an energy density of 8 Wh L⁻¹ at a power density of 356 W L⁻¹, and it still delivers an energy density of 6.4 Wh L⁻¹ even at a high power density of 11 800 W L⁻¹. Such performances are superior over many other graphene based materials like reduced graphene oxide hydrogels (6 Wh L⁻¹, 5400 W L⁻¹) [20], carbon-graphene composite (5 Wh L⁻¹, 500 W L⁻¹) [21], graphene macro-assembly electrode (5 Wh L⁻¹, 6000 W L⁻¹) [25] and other aqueous supercapacitors under the similar conditions [26].

To better understand the electrochemical properties of the PDs/ GS composites for practical applications, the optimal sample (PDs/ GS-0.5) was also used as electrode material for effects of massloading on the specific capacitance as well as energy and power densities. As shown in Fig. 7(A) and (B), specific capacitance



Fig. 6. Electrochemical performance of symmetric supercapacitor. (A) CV curves at scan rates of 2–100 mV s⁻¹ (B) GCD curves at current densities of 1–30 A g⁻¹. (C) Cycle stability at various current densities. (D) Ragone plots of our device and other graphene based aqueous symmetric supercapacitors reported previously.



Fig. 7. For three-electrode system (A) specific capacitance vs. current density for electrodes with different mass loading. (B) specific capacitance vs. mass loading at different scan rates. For symmetric supercapacitor (C) specific capacitance vs. current density for electrodes with different mass loading. (D) Reagon plot for electrodes with different mass loading.

decreases at first with the increasing mass loading from 1.2 to 5 mg cm⁻² (thickness of ~50 μ m–~210 μ m). And it maintains at 292 F cm⁻³ (1 A g⁻¹) with a larger mass loading (10 mg cm⁻², thickness of ~430 μ m). When the current density increased 30-times from 1 to 30 A g⁻¹, 73% of the initial capacitance is retained for electrode with mass loading of 1.2 mg cm⁻². In comparison,

these values are 69%, 68% and 68% with mass loading of 2.5, 5 and 10 mg cm⁻², respectively. This result shows a good rate capability of the electrode with higher mass loadings. For symmetric super-capacitor, shown in Fig. 7(C), the specific capacitance maintains at first with the increasing mass loading from 1.2 to 2.5 mg cm⁻² (~56 F cm⁻³, 1 A g⁻¹). As for large mass loading (5 and 10 mg cm⁻²),

the specific capacitances are 43 and 42 F cm⁻³, respectively. Power densities and energy densities (Fig. 7(D)) also show similar trends. It (mass loading of 10 mg cm⁻²) can deliver an energy density of 6 Wh L⁻¹ at a power density of 352 W L⁻¹, and it still delivers an energy density of 4.55 Wh L⁻¹ even at a high power density of 10 656 W L⁻¹. Above results suggest that with the increasing of mass loading, the electrochemical performance of optimal material is still well, and it reflects the potential in practical application.

4. Conclusion

In summary, PDs/GS nano composites are successfully prepared by facile one-step mixing route. Through changing the mass ratio of PDs to GS, a serious of hierarchical porous GS based composites were prepared. The optimal material PDs/GS-0.5 exhibits distinguished electrochemical performance, including capacitances up to 262 F g⁻¹ or 364.2 F cm⁻³ at 1 A g⁻¹ and a capacitance retention over 98% after 10 000 cycles. Additionally, the symmetric supercapacitor based on optimal sample has both a high energy density $(8 \text{ Wh } \text{L}^{-1})$ and a high power density (11.8 kW L⁻¹), and exceeding cycling stability over 10 000 cycles at different current densities. These outstanding performances are credited to the introduction of PDs, which are the key part of the electrode materials. First, abundant nitrogen-containing groups from PDs will bring faradaic reactions, thereby raising the holistic capacitance and energy density. At the same time, amide bonds between PDs and conductive GS substrate can effectively increase cycling stability. And nearly 100% retention rates of symmetric supercapacitors just prove it well. Furthermore, PDs will effectively increase specific area and enlarge pore size distribution of original GS, which will greatly improve the EDLC and offer adequate ion channels. Therefore, with the development of microelectronic devices, supercapacitor with a higher volumetric capacity will emerge as the requirement, such 0D nano-materials will also be a promising choice.

Acknowledgements

This work was supported by the National Major Basic Research Program of China (Grant 2013CB934101), the National Natural Science Foundation of China (Grant 21771039), Shanghai Science and Technology Committee (No. 16DZ2270100) and Grant NCET-11-0115.

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jpowsour.2017.08.002.

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