Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supplementary Information

Facile surfactant-free synthesis of polybenzoxazine-based polymer and nitrogen-doped carbon nanospheres

Jianming Zhao,[ab] Muhammad Rehan Hasan Shah Gilani,[abcd] Zhongyuan Liu,[a] Rafael Luque,[aef] and Guobao Xu*[ag]

[a] State Key Laboratory of Electroanalytical Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun, Jilin 130022, People's Republic of China. E-mail: guobaoxu@ciac.ac.cn; Fax: +86-0431-85262747; Tel: +86-0431-85262747

[b] University of Chinese Academy of Sciences, Chinese Academy of Sciences, No. 19A Yuquanlu, Beijing 100049, People's Republic of China

[c] Department of Chemistry, the Islamia University of Bahawalpur, Bahawalpur, Pakistan

[d] Department of Chemistry, Government College University Faisalabad, Layyah Campus, Pakistan

[e] Departamento de Química Orgánica, Universidad de Córdoba Campus de Rabanales, Edificio Marie Curie (C-3), Ctra Nnal IV, Km 396, Córdoba, E-14014, Spain

[f] People's Friendship University of Russia (RUDN University), 6 Miklukho-Maklaya str., 117198, Moscow, Russia

[g] University of Science and Technology of China, Hefei, People's Republic of China

Table S1. Synthesis parameters of phloroglucinol, p-phenylenediamine, and formaldehyde polymer spheres (PPFSs-n) and carbon spheres (CPPFSs-n).

Sample	Water mL	Ethanol mL	Phloroglucinol mmol L^{-1}	*p*-Phenylenediamine mmol L^{-1}	Formaldehyde mmol L^{-1}	PPFSs Size nm	CPPFSs Size nm
1	**160**	**0**	**1.88**	**1.41**	**5.64**	**105 (±8)**	**79.2 (±7.7)**
2	**120**	**40**	**1.88**	**1.41**	**5.64**	**157 (±9)**	**113 (±7)**
3	**120**	**40**	**2.50**	**1.88**	**7.50**	**167 (±7)**	**121 (±6)**
4	**120**	**40**	**3.75**	**2.81**	**11.3**	**186 (±11)**	**137 (±9)**
5	**120**	**40**	**5.63**	**4.22**	**16.9**	**238**	**------**

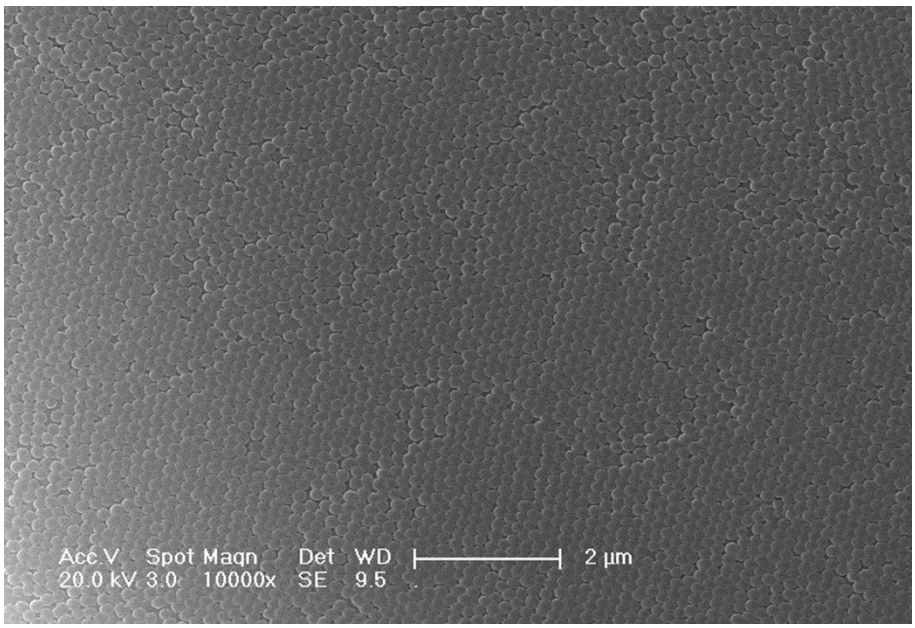

Fig. S1. A typical large scale SEM image of PPFSs-3.

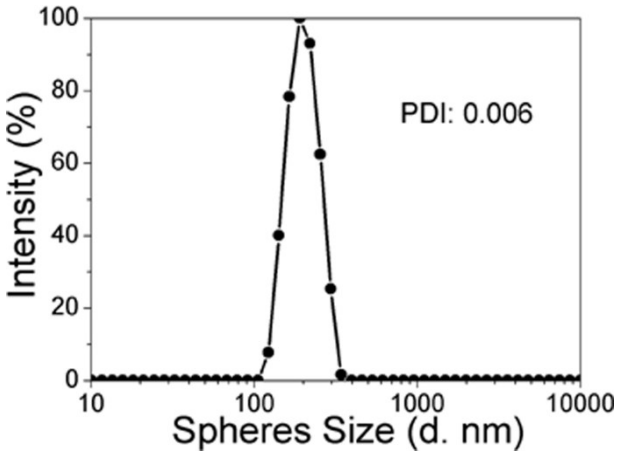

Fig. S2. DLS of PPFSs-3.

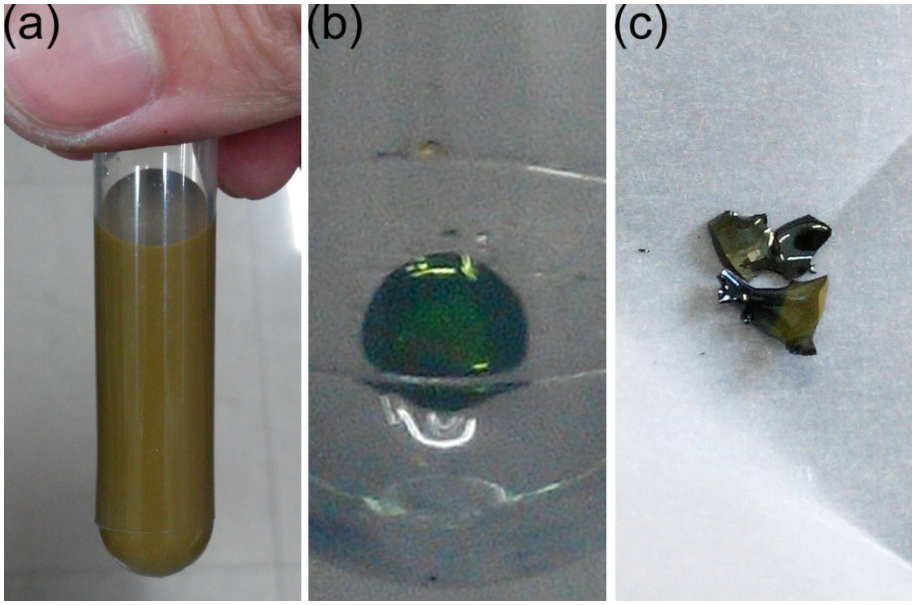

Fig. S3. Photographs of PPFSs-3 sample: (a) solution, after (b) centrifugation and (c) dry. Photograph (b) and (c) show bright shiny green.

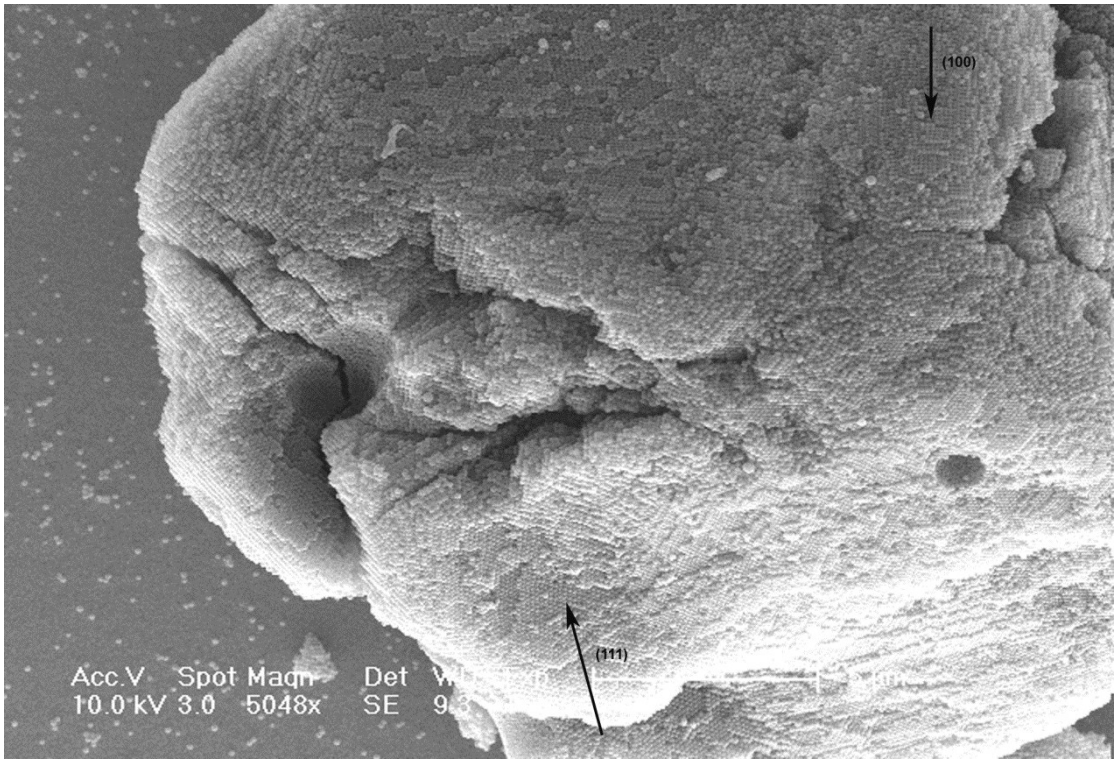

Fig. S4. SEM micrograph of CPPFSs-3. Different planes occurring in the sample can be seen. Facets corresponding to the (111) and (100) set of planes of an fcc structure can be observed. The relative orientation of the mentioned planes can be seen as well.

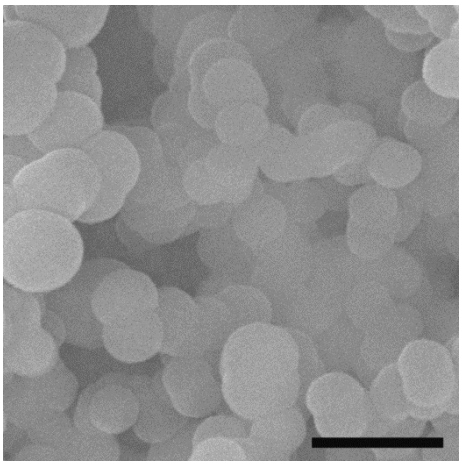

Fig. S5. SEM image of the polymer spheres PPFSs-5 prepared at the phloroglucinol concentration of 5.63 mmol L^{-1}, p-phenylenediamine concentration of 4.22 mmol L^{-1}, formaldehyde concentration of 16.9 mmol L^{-1} ethanol/water volume ratio of 1/3. The scale bar is 500 nm.

Detailed description of TGA spectrum of PPFSs-3:

The weight loss from 40 to 315 °C relates to the evaporation of the physical adsorbed water and solvent present in PPFSs-3, and then the condensation and volatilization of unreacted oligomers. The next mass loss from 315 to 1000 °C corresponds to the elimination of various volatiles, including N oxides, H_2O, CO_2, CO, C_2H_6, H_2, CH_4, and their methyl derivatives as well as some condensed hydrocarbons.

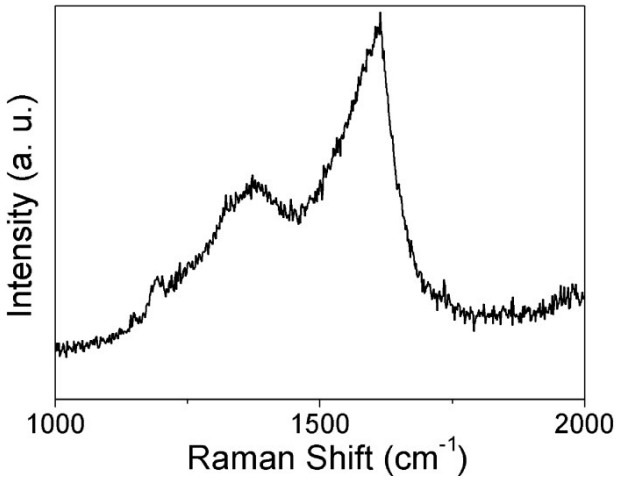

Fig. S6 Raman spectrum of PPFSs-3.

FTIR spectrum:

The characteristic spectral peaks at 1513, 1580, and 1615 cm^{-1} are due to the C=C stretching in the aromatic rings in the condensed PPFSs-3. But the peak at 1513 cm^{-1} may associate with aromatic amine. The C-H stretching vibrations of -CH_2- appeared at 2925 and 2859 cm^{-1}, while stretching vibrations of aromatic bonds Ar-H are present at 3035 and 3056 cm^{-1}.

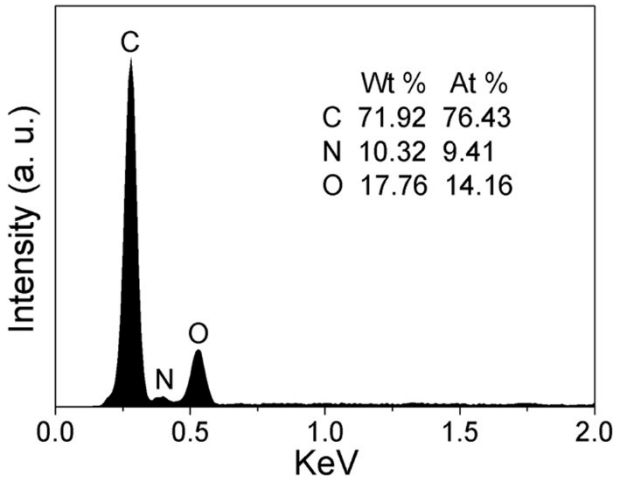

Fig. S7 EDX of PPFSs-3.

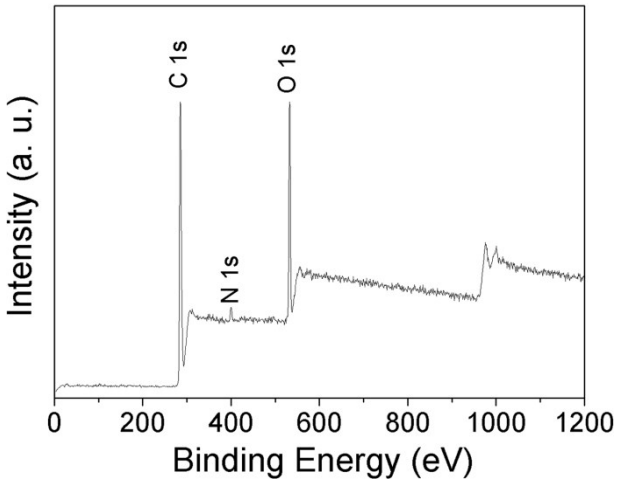

Fig. S8 Full scanned XPS spectrum of PPFSs-3.

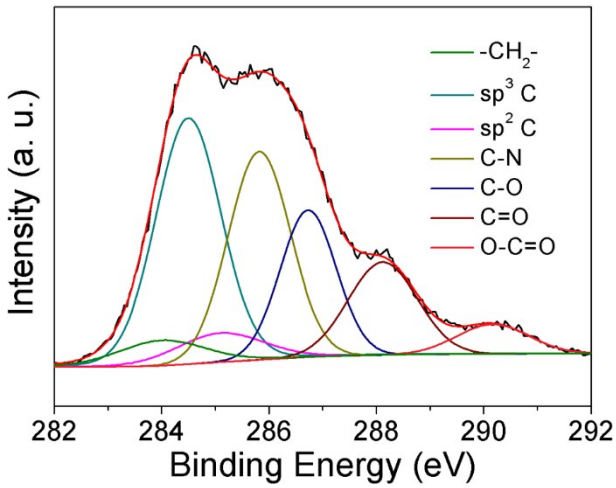

Fig. S9 C1s high-resolution XPS spectrum of PPFSs-3.

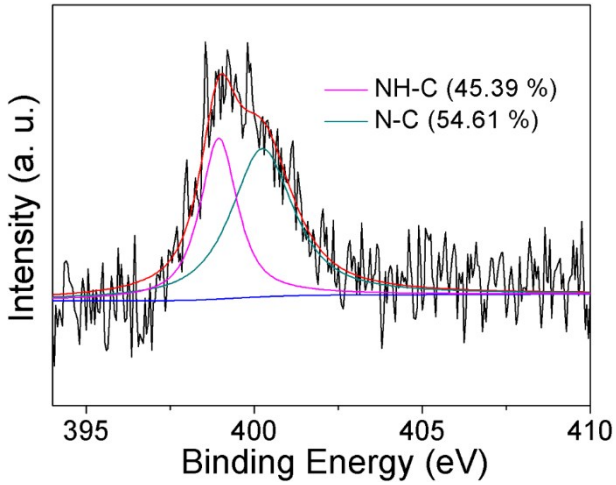

Fig. S10 N1s high-resolution XPS spectrum of PPFSs-3.

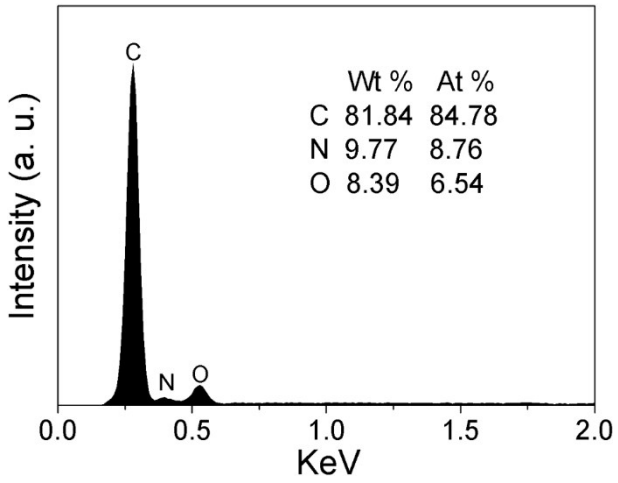

Fig S11. EDX spectrum of CPPFSs-3.

Raman spectrum of CPPFSs-3:

The G band characteristic of the in-plane vibration from a layer of sp^2-hybridized carbon atoms provides the formation of graphitic carbon in CPPFSs-3, while the D band could be attributed to the defects or imperfections, reflecting the presence of disorder and the edges and the boundaries of the graphene domains.

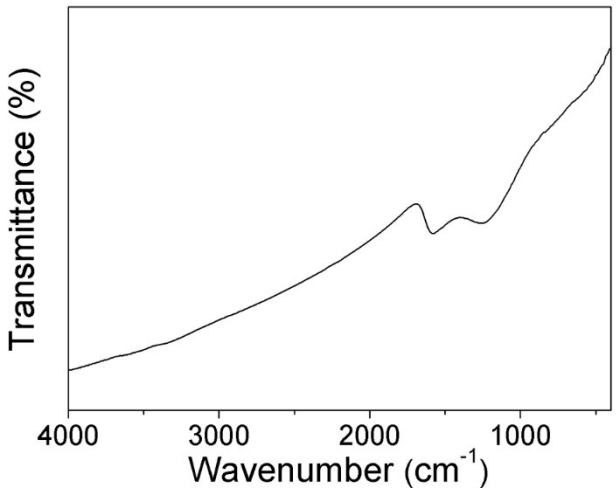

Fig S12. FTIR spectrum of CPPFSs-3.

Table S2. Comparison of nitrogen content of CPPFSs with that of other reported carbon spheres.

Corresponding carbon precursors	Temperature of pyrolysis	Nitrogen content (wt %)	Reference
resorcinol/1,6-diaminohexane/formaldehyde resins polymer spheres	660 °C	~ 2.2 %	[1]
melamine/formaldehyde/resins polymer spheres	800 °C	~ 6.02 %	[2]
polypyrrole	1300 °C	~ 4.3 %	[3]
resorcinol/ethylenediamine/formaldehyde resins polymer spheres	850 °C	~ 7.2 %	[4]
phloroglucinol/p-phenylenediamine/formaldehyde resin polymer spheres	900 °C	~9.77 %	This work

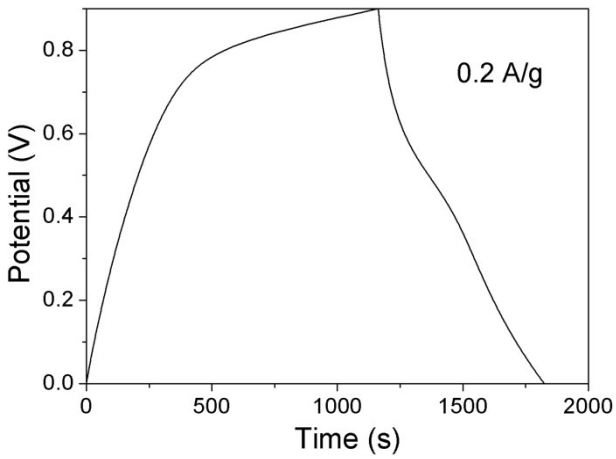

Fig. S13 Galvanostatic charge/discharge curve of CPPFSs electrode by two-electrode testing method with current density 0.2 A/g in 1.0 M H_2SO_4.

Table S3. Comparison of capacitance of CPPFSs with that of other reported carbon spheres.

Corresponding carbon precursors	Current density or scan rate	Specific capacitance values	Reference
resorcinol/1,6-diaminohexane/formaldehyde resins polymer spheres	0.1 A g^{-1}	306 F g^{-1}	[2]
polypyrrole	100 mV s^{-1}	237.9 F g^{-1}	[3]
Fructose	0.1 A g^{-1}	170 F g^{-1}	[5]
Melamine-doped polystyrene spheres	0.2 A g^{-1}	< 140 F g^{-1}	[6]
Mesoporous aminophenol/resorcinol /formaldehyde resins polymer spheres	10 mV s^{-1}	159 F g^{-1}	[7]
Phloroglucinol/p-phenylenediamine/formaldehyde resin polymer spheres	0.2 A g^{-1}	293.8 F g^{-1}	This work

References

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