Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Electronic Supplementary Information

Selenium in Nitrogen-Doped Microporous Carbon Spheres for High-Performance Lithium-Selenium Batteries

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SI-1: The synthetic details

Preparation of monodispersed Polypyrrole Nanospheres: In a typical synthesis, 2 mL pyrrole (99%, Aladdin) was dispersed in 120 mL deionized water firstly. After energetically stirring for 30 minutes, 0.2 g $FeCl_2{\cdot}4H_2O$ (Aladdin) was introduced and then 10 mL H_2O_2 (30 wt% in H_2O, Sinopharm Chemical Reagent) was added drop by drop. This mixture was kept stirring for 12 h under normal room temperature. The products were harvested after filtration, washed with abundant ultrapure water and freeze-dried for 24 h.

Preparation of N-MPCS: The above puce powder was carbonized at 700 ^oC for 2 h in Ar atmosphere. The obtained nitrogen doped carbon spheres (denoted as N-CS) were poured into KOH solution (N-CS:KOH=1:3, w/w) and kept stirring for 6 h. Then, the mixture was dried at 60 ^oC for three days. After being grinded enough in an agate mortar and heated at 650 ^oC for 0.5 h under the protection of argon, the mixture were immersed in 1 M HCl and stirred for 12 h. Finally, the activated carbon spheres were obtained after being washed with DI water thoroughly to wash away any inorganic ion and dried at 60 ^oC for 48 h.

Preparation of Se/N-MPCS: The mixture composed of N-MPCS and Se with a weight ratio of about 1:1 was dispersed in acetone. Thereafter, the mixture was ground together. After evaporating the solvent at 60 ^{o}C for one night, the mixture was sealed in a stainless steel autoclave and kept at 280 ^{o}C for 12 h in argon to melt selenium into the pores of nitrogen-doped carbon spheres to obtain the Se/N-MPCS product.

For comparison, the selenium was mixed with activated carbon with a weight ratio of 1:1 to prepare the Se/AC composite just as the preparation of Se/N-MPCS. TGA showed the selenium content was about 47% in the Se/AC.

SI-2: Theoretical Calculation

The density functional theory (DFT) is a powerful quantum chemical calculation tool due to its merits. The MPWB1K method as an excellent hybrid density functional theory model with performance for thermochemistry, weak interactions and hydrogen bonding,[1] has been widely applied to optimize the geometry.[2-4] In addition, the selection of basis sets, which requires a compromise between accuracy and computational time, is importance for getting accurate results.[5] In this paper, the geometrical parameters of the clusters were optimized at the MPWB1K/6-31+G (d, p) level. The vibrational frequencies have been calculated at same level in order to determine the nature of the clusters. All the works were performed using the Gaussian 03 programs and SGI workstation.[6]

References

1 Y. Zhao and D. G. Truhlar, *J. Phys. Chem. A*, 2004, **108**, 6908.

2 X. H. Qu, H. Wang, Q. Z. Zhang, X. Y. Shi, F. Xu and W. X. Wang, *Environ. Sci. Technol.*, 2009, **43**, 4068.

3 F. Xu, W.N. Yu, R. Gao, Q. Zhou, Q. Z. Zhang and W. X. Wang, *Environ. Sci. Technol.*, 2010, **44**, 6745.

4 F. Xu, Q.Z. Zhang, R.X. Zhang, X. Qu and W. X. Wang, *Environ. Sci. Technol.*, 2010, **44**, 1399.

5 R. L. Zhang, J. H. Huang and Y. X. Bu, et al. *Science in China (B)*., 2000, **43**, 375.

6 M.J. Frisch, G.W. Trucks, H.B. Schlegel, J.A. Pople, et al., 2003, Gaussian 03, Revision B. 03. Gaussian, Inc, Pittsburgh PA.

SI-3: Supplementary Figures

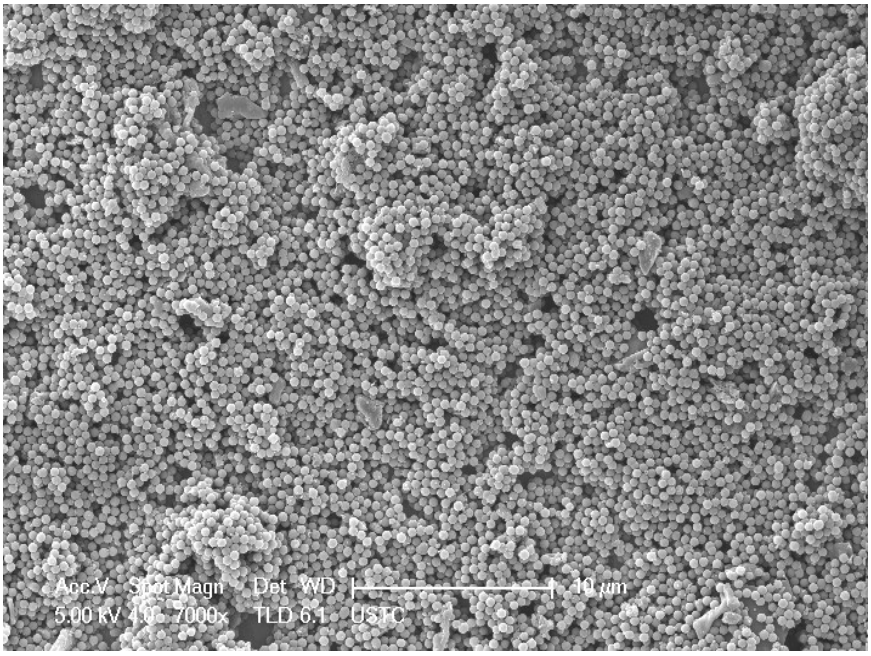

Figure S1. A panoramic view of the nitrogen doped microporous carbon spheres (N-MPCS).

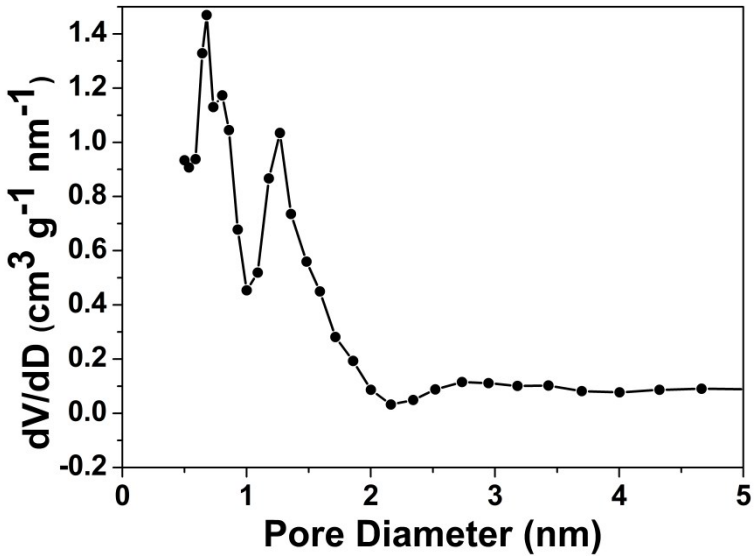

Figure S2. The corresponding micropore size distribution of N-MPCS.

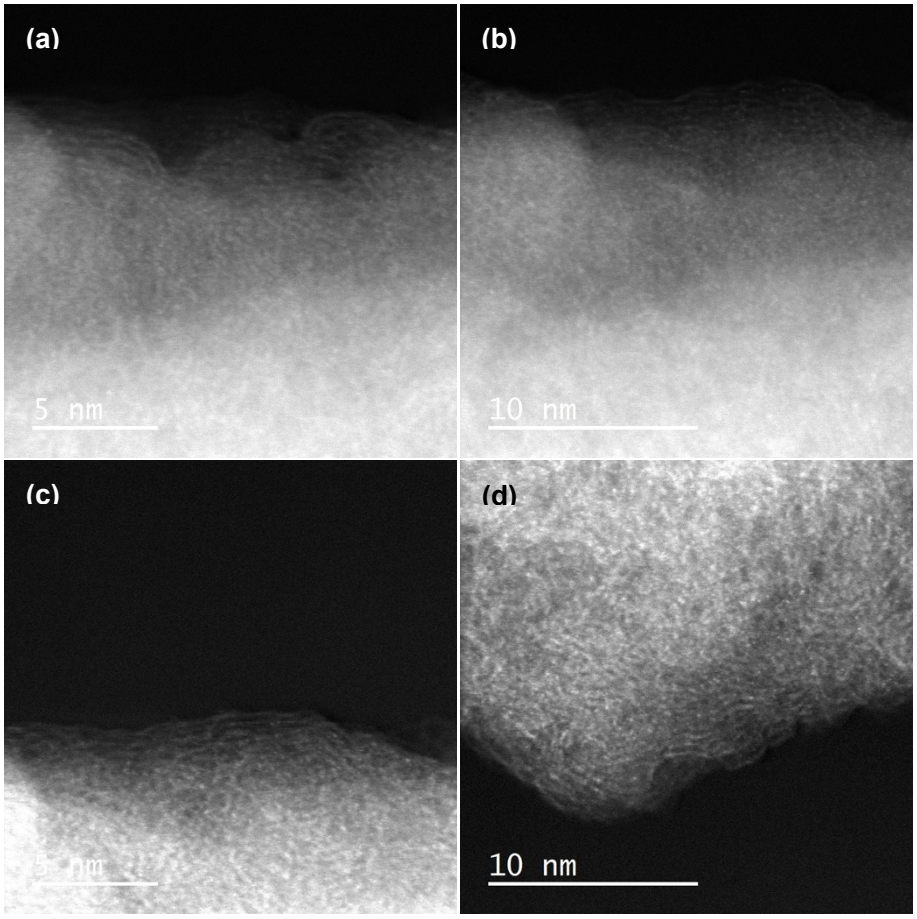

Figure S3. HAADF-STEM images taken from the Se/N-MPCS different fringe region.

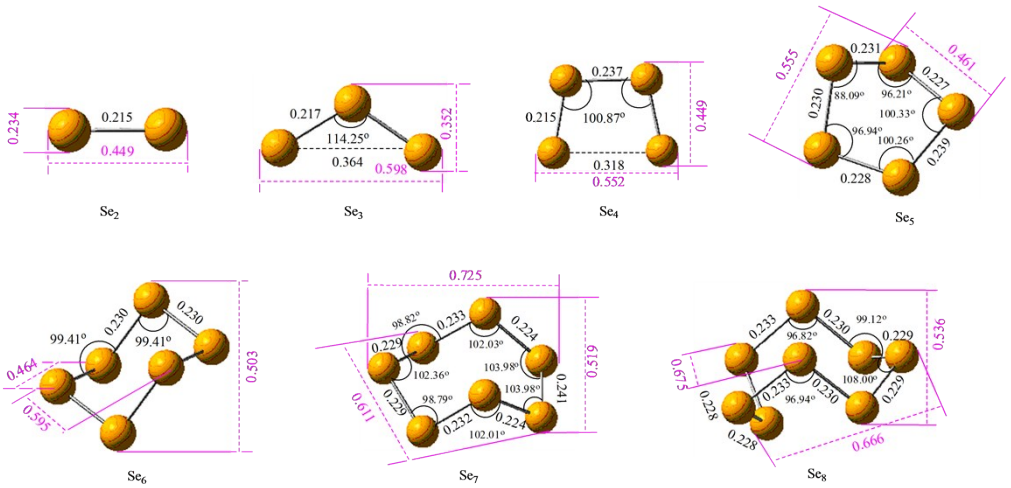

Figure S4. Theoretical calculation results of selenium allotropes from Se_2 to Se_8 (units of bond length: nm).

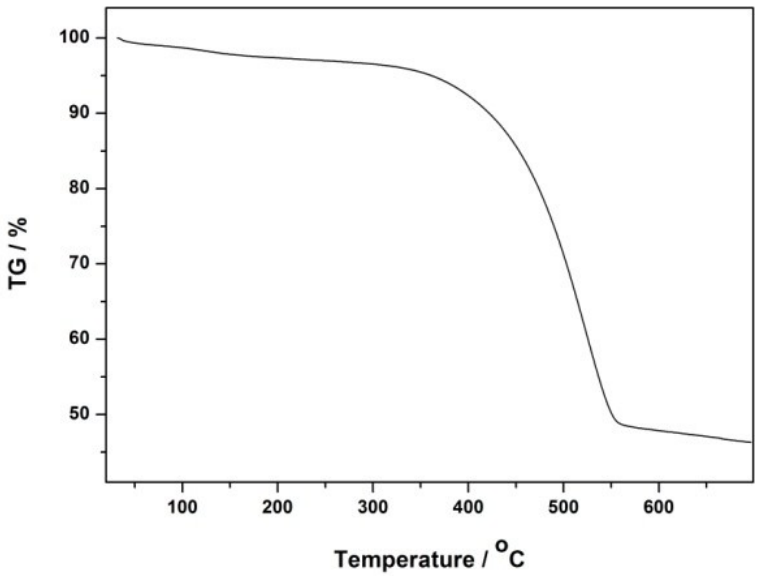

Figure S5. Thermogravimetric (TGA) analysis of Se/N-MPCS in nitrogen.

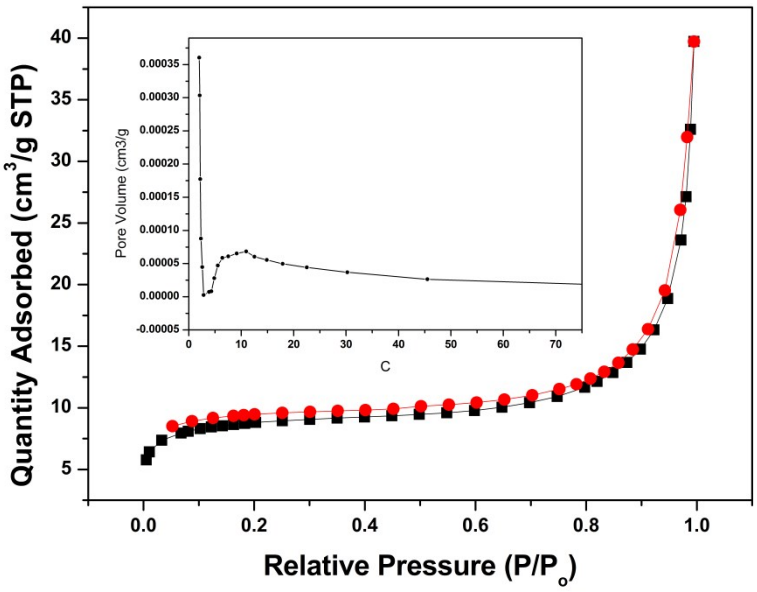

Figure S6. Pore size distribution of Se/N-MPCS (BET surface area = 30.1 m^2/g, pore volume = 0.036 cm^3/g).

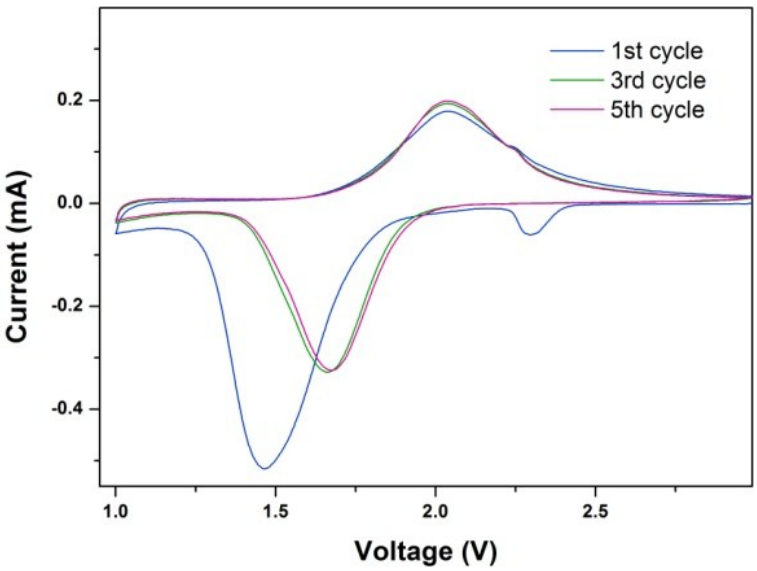

Figure S7. Cyclic voltammograms of Se/AC at 0.1 mV s^{-1}.

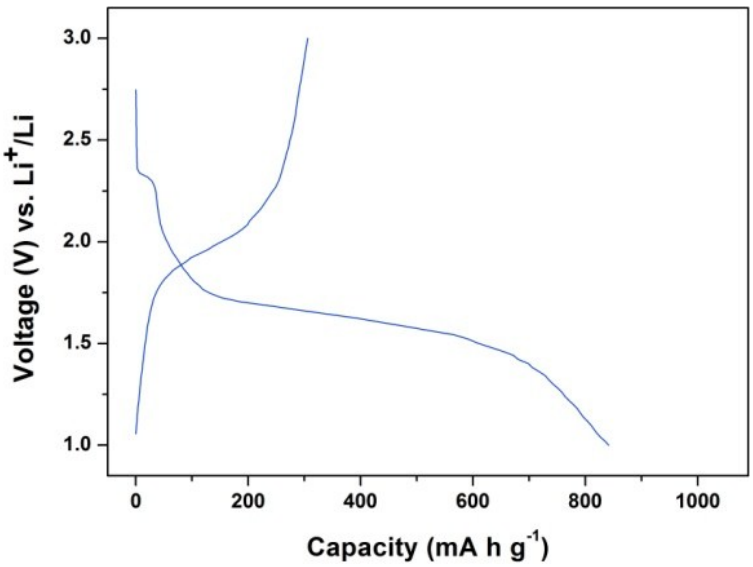

Figure S8. Discharge and voltage profiles for the Se/AC.

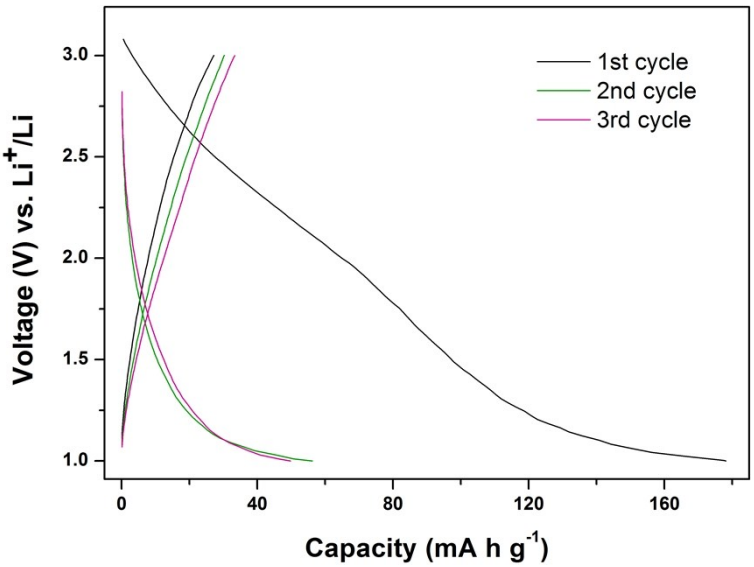

Figure S9. The discharge and charge profiles for the N-MPCS.

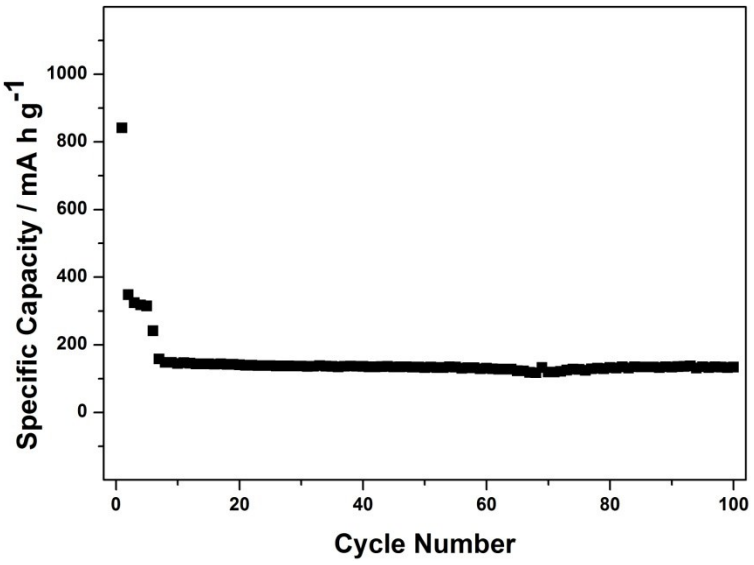

Figure S10. Cycling performance for the Se/AC at about 2 C.

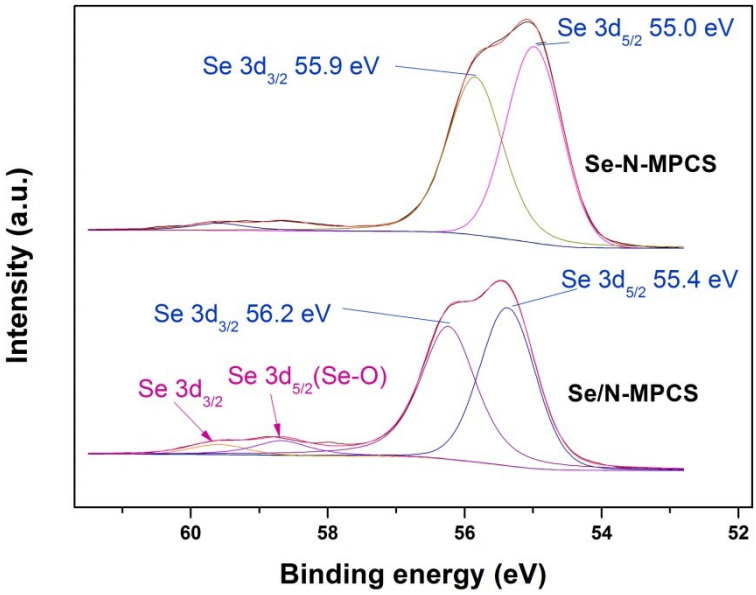

Figure S11. XPS spectra of Se 3d in Se/N-MPCS and Se-N-MPCS.

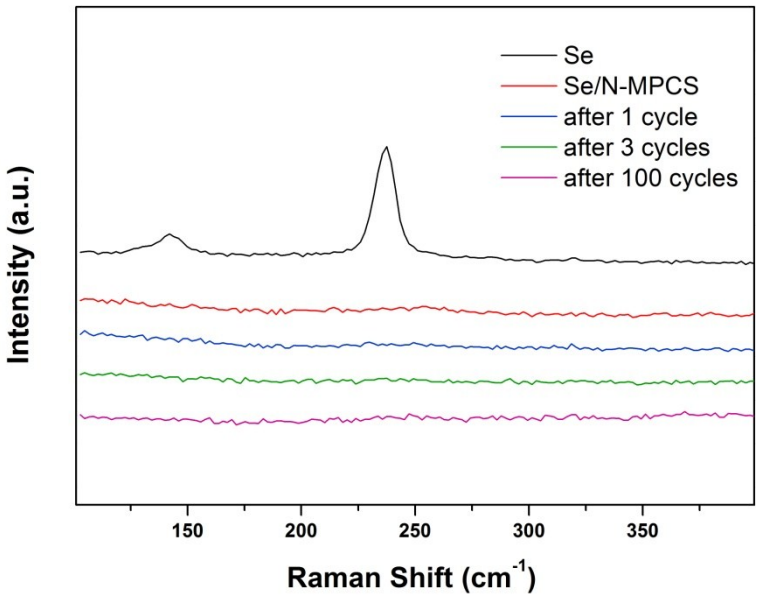

Figure S12. Raman spectra of selenium, Se/N-MPCS, and the Se/N-MPCS after 1 cycle, 3 cycles, and 100 cycles.

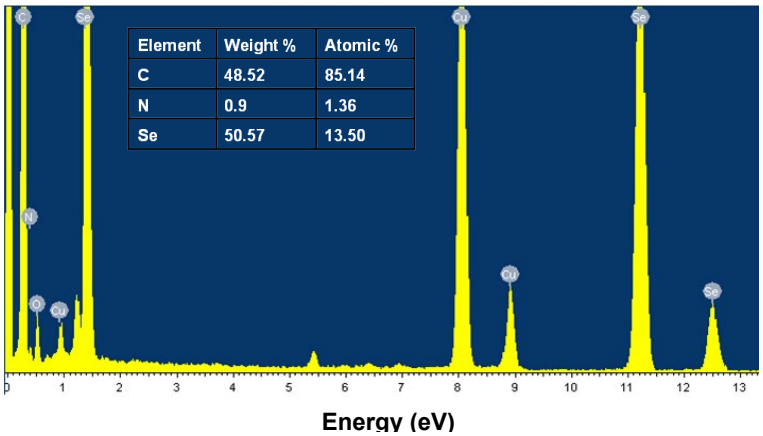

Figure S13. The energy dispersive X-ray spectroscopy (EDX) analysis of the Se/N-MPCS after 300 cycle.