Supplementary information

The synthesis of polydopamine nano- and microspheres in microdroplets

Jianze Zhang [a], Shufang Tian*[b], Chenghui Zhu [a], Lifeng Han*[c], and Xinxing Zhang*[a]

[a] College of Chemistry, Frontiers Science Center for New Organic Matter, State Key Laboratory of Advanced Chemical Power Sources, Key Laboratory of Advanced Energy Materials Chemistry (Ministry of Education), Tianjin Key Laboratory of Biosensing and Molecular Recognition, Renewable Energy Conversion and Storage Center (ReCAST), Nankai University, Tianjin, 300071, China

[b] School of Energy Science and Technology, Henan University, Zhengzhou, 450046, China

[c] State Key Laboratory of Component-Based Chinese Medicine, Haihe Laboratory of Modern Chinese Medicine, Tianjin University of Traditional Chinese Medicine, Tianjin 301617, China

* Corresponding author

E-mail address: zhangxx@nankai.edu.cn; hanlifeng@tjutcm.edu.cn; tianshufang@henu.edu.cn

Experimental methods

Chemicals

Dopamine (DA) was purchased from Shanghai Macklin Biochemical Co., Ltd and was used directly without purification. Milli-Q water (18.2 MΩ cm^{-1}) used for all experiments was obtained from a Purelab Quest system (ELGA LabWater, UK). Different concentrations of DA solutions were prepared just before spraying.

Generation of microdroplets and mass spectrometric analyses

Solutions of DA were sprayed to generate microdroplets by using a syringe pump at 15 μL min^{-1} flow rate with high purity nitrogen at a varied high pressure as the nebulizing gas. The inner diameter (I.D.) of the silica capillary used for spraying is 100 μm. Unlike electrospray ionization, no voltage was applied to the solutions. The distance between the tip of the silica capillary and the mass spectrometer inlet could be changed and was defined as the reaction distance. The products were detected and analyzed by an LTQ-XL mass spectrometer (Thermo-Fisher, Waltham, MA). **The tube lens voltage of the mass spectrometer was set as 0 V in all of the experiments to avoid fragmentation of the ions, and this is very important because fragments resulting from the acceleration and collision caused by the tube lens voltage could sometimes be mistaken as the microdroplet reaction products.** Changing the reaction distance can effectively rule out this mistake. Collision-induced dissociation (MS^n) was also performed for the structural analysis of the products. All these experiments were carried out in the atmosphere.

Collection of PDA microspheres

The tip of the silica capillary was extended into the mouth of a glass bottle and microdroplets were sprayed vertically downward. PDA samples were collected and loaded onto support films for TEM characterization.

Morphology Characterization

The morphologies of polydopamine (PDA) microspheres were investigated by transmission electron microscopy (TEM, JEOL JEM 1400-Flash).

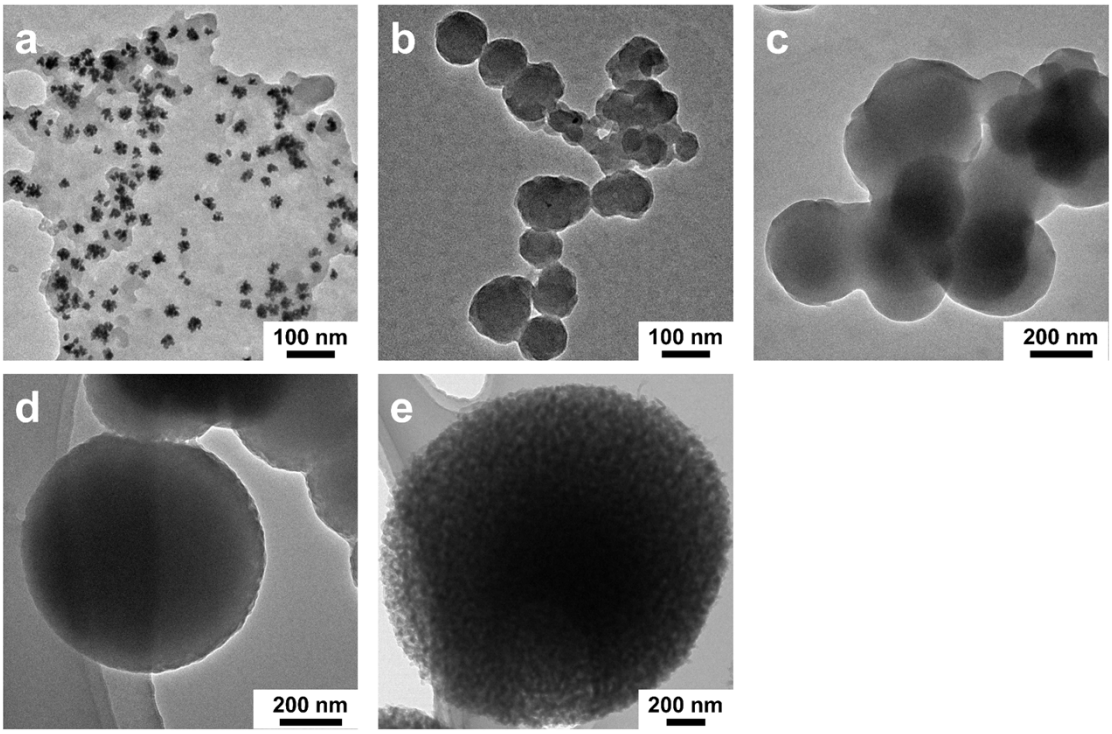

Fig. S1 TEM images with higher magnification of PDA microspheres prepared with (a) 0.5, (b) 1, (c) 5, (d) 10, and (e) 20 mM DA solutions in microdroplets. From (a) to (e), the sizes of the spheres increased from nanoscale to microscale, and the PDA film only existed in (a) and (b), but disappeared in (c) to (e).

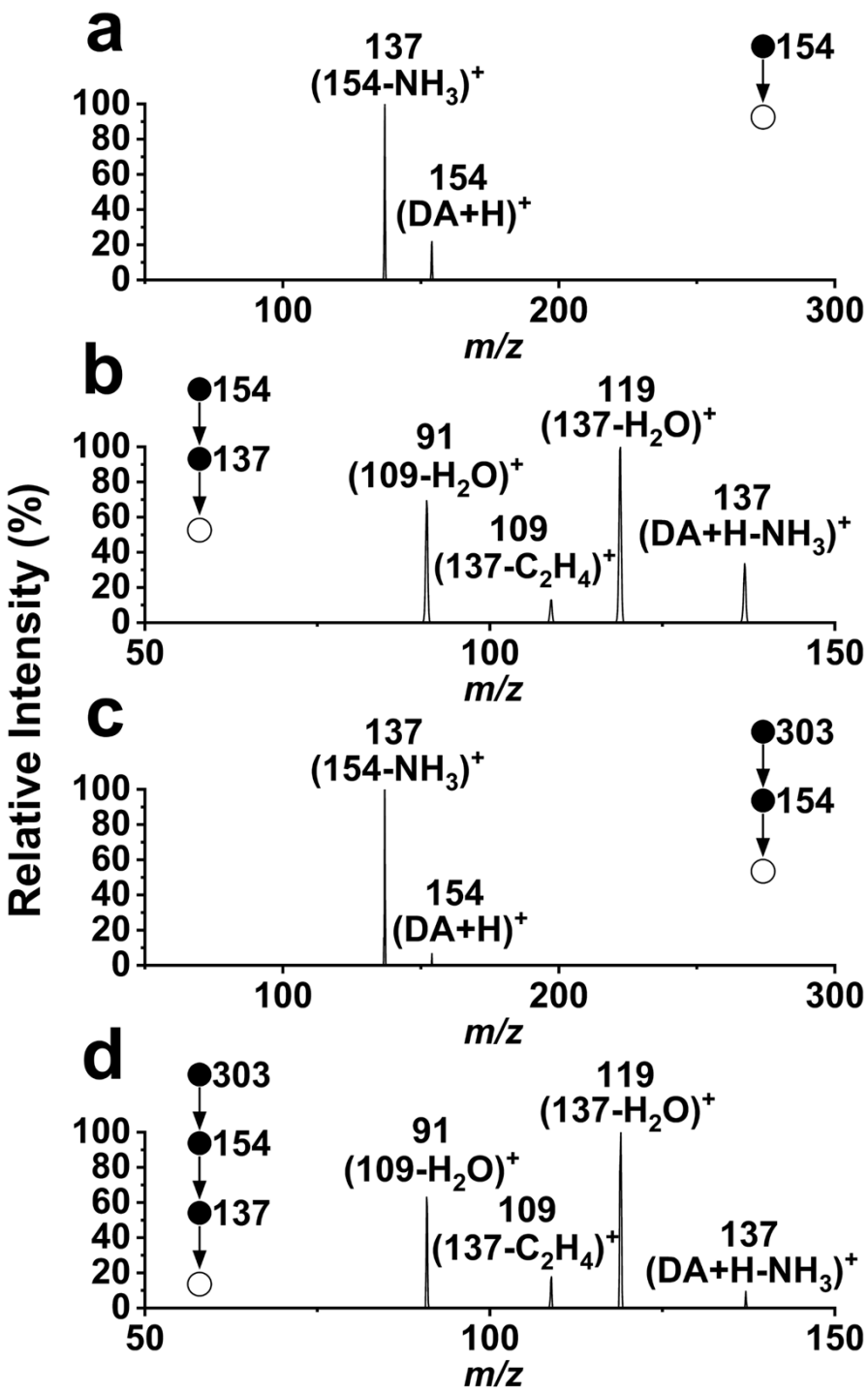

Fig. S2 The (a) MS^2 and (b) MS^3 spectra of the peak at *m/z* 154 (protonated DA). The (c) MS^3 and (d) MS^4 spectra of the peak at *m/z* 303 (protonated DA+AC dimer), confirming that this species at *m/z* 303 indeed contains the DA moiety.

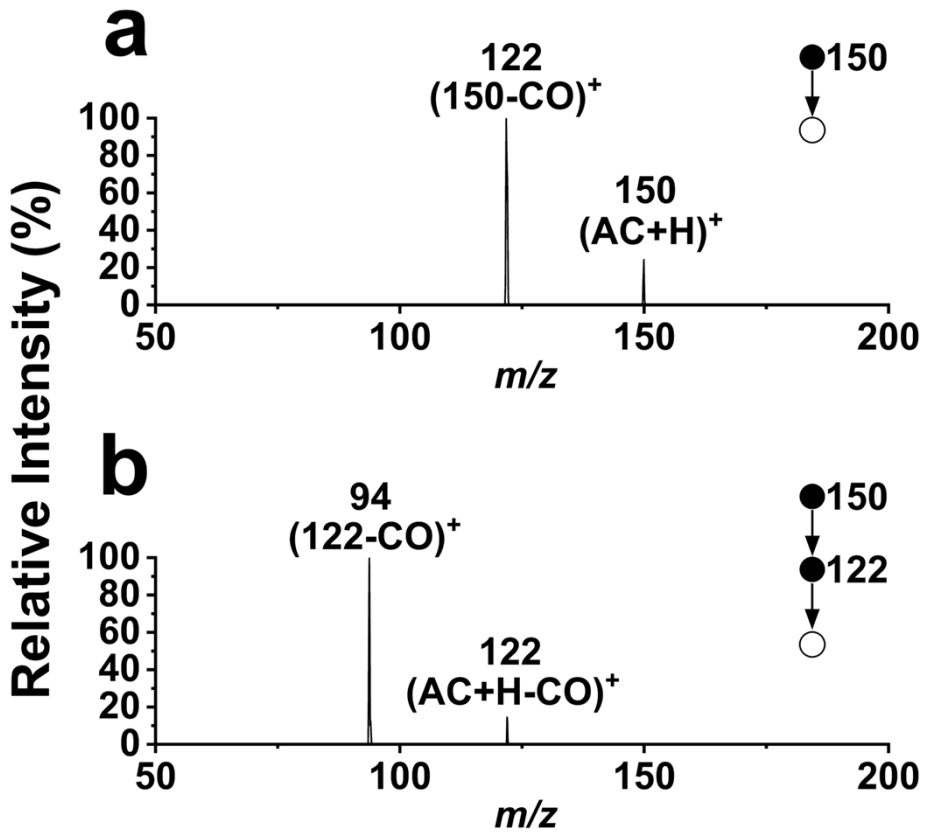

Fig. S3 The (a) MS^2 and (b) MS^3 spectra of the product peak at *m/z* 150, and the consecutive losses of two CO fragments confirms the structure of aminochrome.

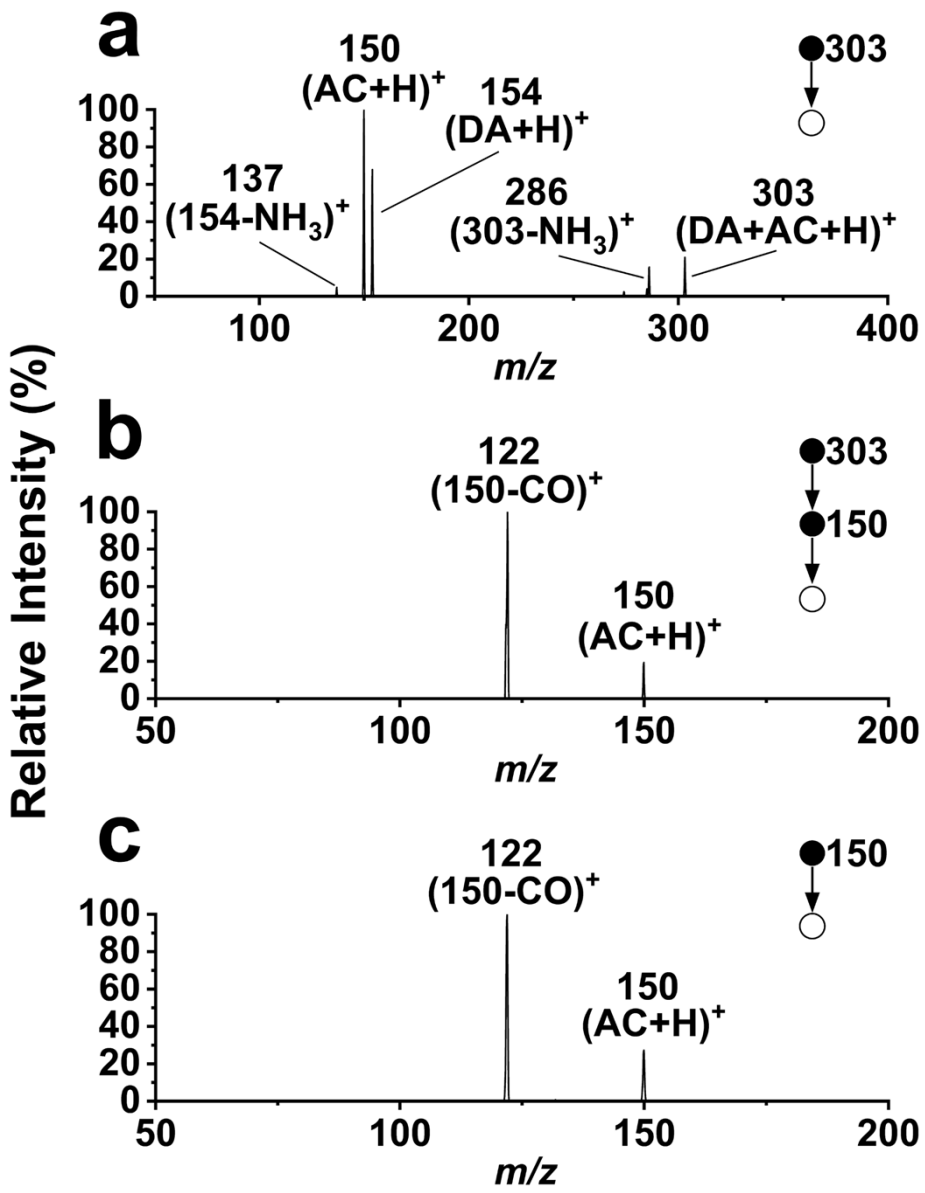

Fig. S4 The MS^n spectra of the peak at *m/z* (a, b) 303 and (c) 150 after the DA solution was aged for 15 min, suggesting that the oxidation products were the same both in the bulk and in microdroplets.

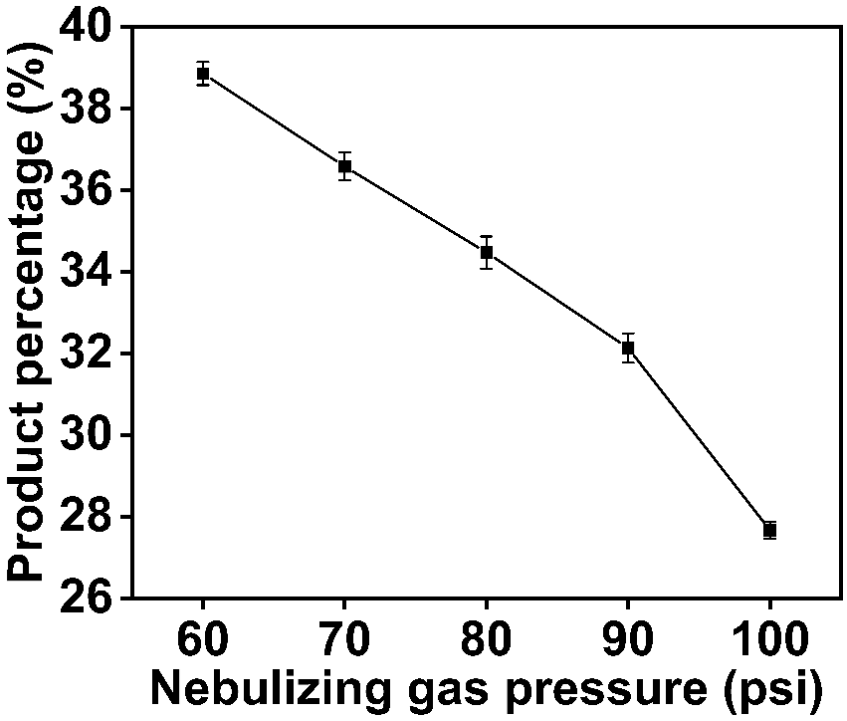

Fig. S5 Product percentage as a function of sheath gas pressure when the reaction distance was 10 mm and the DA concentration was 0.1 mM.