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Supporting Information

Vapor generation of mercury and methylmercury in aqueous microdroplets produced by pneumatic nebulization

Qian He,[1,2]* Ningxin Zhang,[2] Yifan Qiao,[2] Chenchen Li,[2] Jing Zhang[3,4]*

[1] *Frontiers Science Center for Deep Ocean Multispheres and Earth System, and Key Laboratory of Marine Chemistry Theory and Technology, Ministry of Education, Ocean University of China, Qingdao 266100, China*

[2]*College of Chemistry and Chemical Engineering, Ocean University of China, Qingdao 266100, China*

[3]*Faculty of Science, University of Toyama, Toyama 930-8555, Japan*

[4]*Laboratory for Marine Ecology and Environmental Science, Qingdao National Laboratory for Marine Science and Technology, Qingdao 266237, China*

**Corresponding author email: heqian@ouc.edu.cn; jzhang@sci.u-toyama.ac.jp*

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Fig. S7 Comparison of FI-$SnCl_2$/HCl-CVAFS system and FI-PN-CVAFS system for Hg^{2+} (10 μg L^{-1}) determination. (FI-$SnCl_2$/HCl-CVAFS conditions: $SnCl_2$, 5% (m/v); HCl, 5% (v/v); sample solution flow rate, 200 μL min^{-1}; Ar gas flow rate, 300 mL min^{-1}. FI-PN-CVAFS conditions: Nebulizing Ar gas pressure, 0.1 MPa (i.e. Ar gas flow rate, 300 mL min^{-1}); sample solution flow rate, 200 μL min^{-1}; solution pH, 11)

Preparation of CuI particles on the copper wire. The preparation of CuI particles on the copper wire was similar to the literature 1. Iodine (s) was sublimed in a container with a water bath at 60 °C. Then the sublimed I_2 (g) was introduced into the dielectric barrier discharge (DBD) reactor by the Ar carrier gas. The DBD discharge reactor consisted of a quartz tube (110 mm length, i.d. 10 mm, and o.d.12 mm) and a copper foil (40 mm length) wrapped on its outside surface as the outer electrode. Another straight copper wire (i.d. 2 mm) served as the inner electrode. A compact AC ozone generation power supply with a maximal power output of 65 W (Anhui Tianze Electronic Technology Co. Ltd., China) was connected to the electrodes to provide high voltage for generation of the DBD plasma. After 10 mins reaction with DBD plasma on, the white CuI particles were observed covering the copper wire surface.

Microscopy imaging for microdroplet diameter analysis. Microdroplets imaging study was performed with a zoom-stereo microscope (ST-70, Beijing Changheng Rongchuang Technology Co., Ltd, China) equipped with 1X objective lens and WF10X/22 eyepiece. Aqueous solution containing 0.3% (m/v) methyl orange was sprayed on hydrophobic silane-treated glass slides at about 1.5 cm distance from the pneumatic nebulization spray source. The glass slide with microdroplets sprayed was mounted on the object stage equipped with a humidified chamber to prevent a rapid evaporation of sprayed microdroplets. Imaging was carried out within several seconds after spraying, before any significant evaporation occurred. The microdroplet diameter at different nebulizing gas pressure was calculated by the average droplets diameter in the image.

Comparision of vapor generation efficiency. To calculate the vapor generation efficiency of Hg^{2+} in microdroplets produced by PN, a comparison of this FI-PN-CVAFS system with the conventional FI-$SnCl_2$/HCl-CVAFS system for Hg^{2+} determination with the sample Ar gas flow rate was investigated. As shown in Fig. S7, the vapor generation efficiency of Hg^{2+} from microdroplets was estimated to be about 32.9% from $SnCl_2$-HCl system. Although this efficiency was not very satisfactory, it

was still comparable with plasma induced vapor generation systems for Hg^{2+} without formic acid.[2,3]

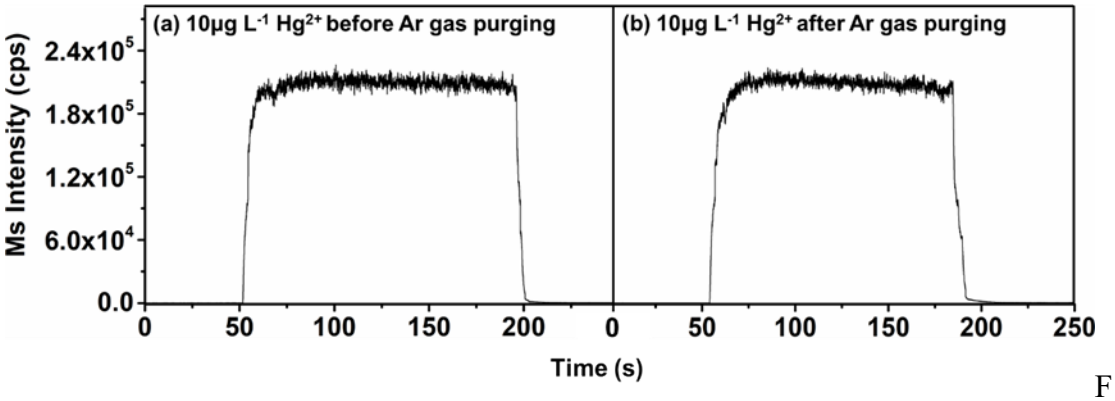


Fig. S1 Typical temporal profile of Hg signal intensity in 10 μg L^{-1} Hg^{2+} standard solution before (a) and after (b) Ar gas purging determined by ICP-MS.

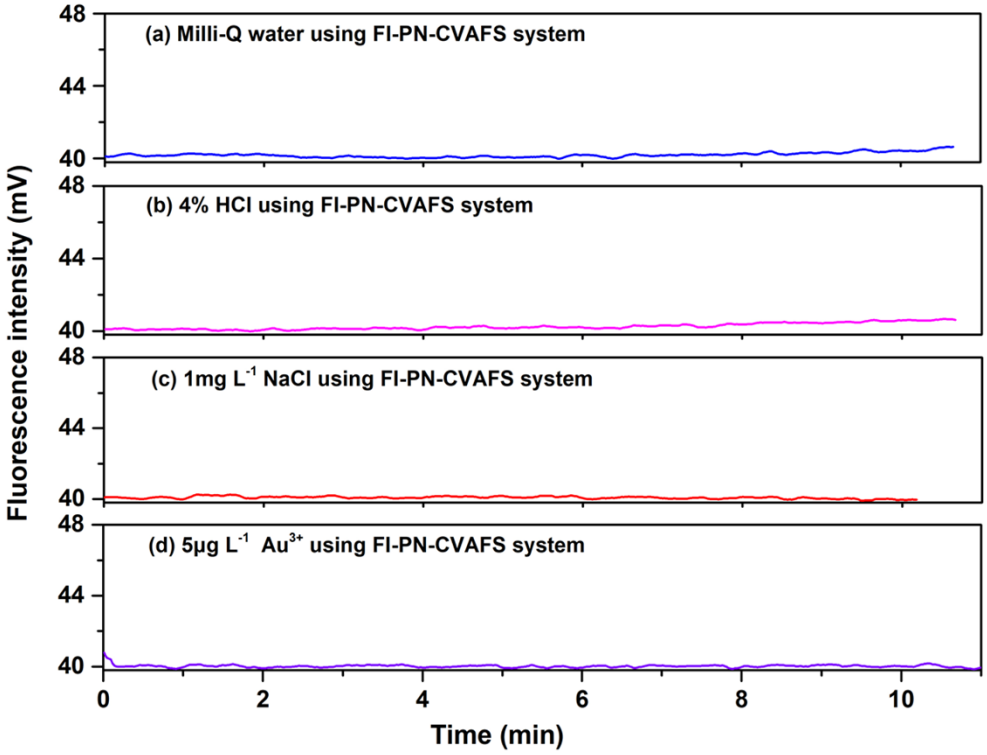
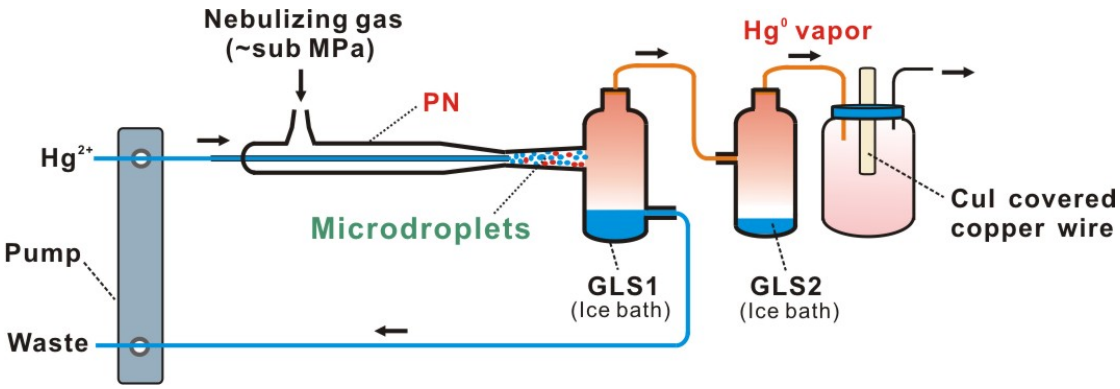


Fig. S2 The blank peak signal of Hg^0 in the microdroplets of milli-Q water (a), 4% (v/v) HCl solution (b), 1 mg L^{-1} NaCl solution (c) and 5 μg L^{-1} Au^{3+} solution (d) using FI-PN-CVAFS system with three injections. (Nebulizing Ar gas pressure, 0.2 MPa; sample solution flow rate, 200 μL min^{-1})



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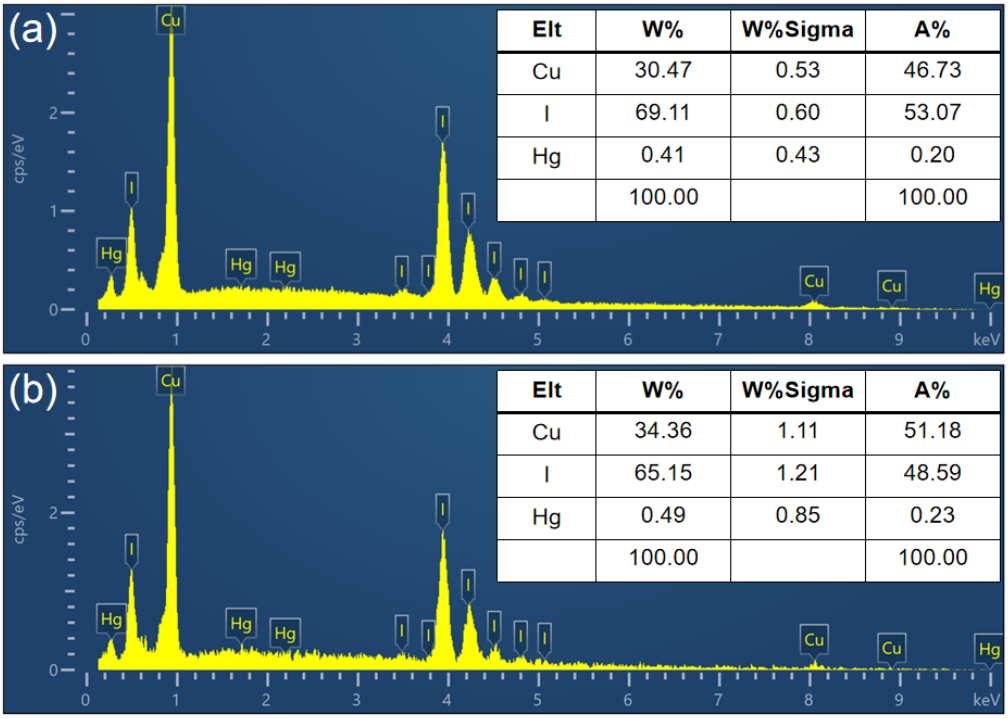
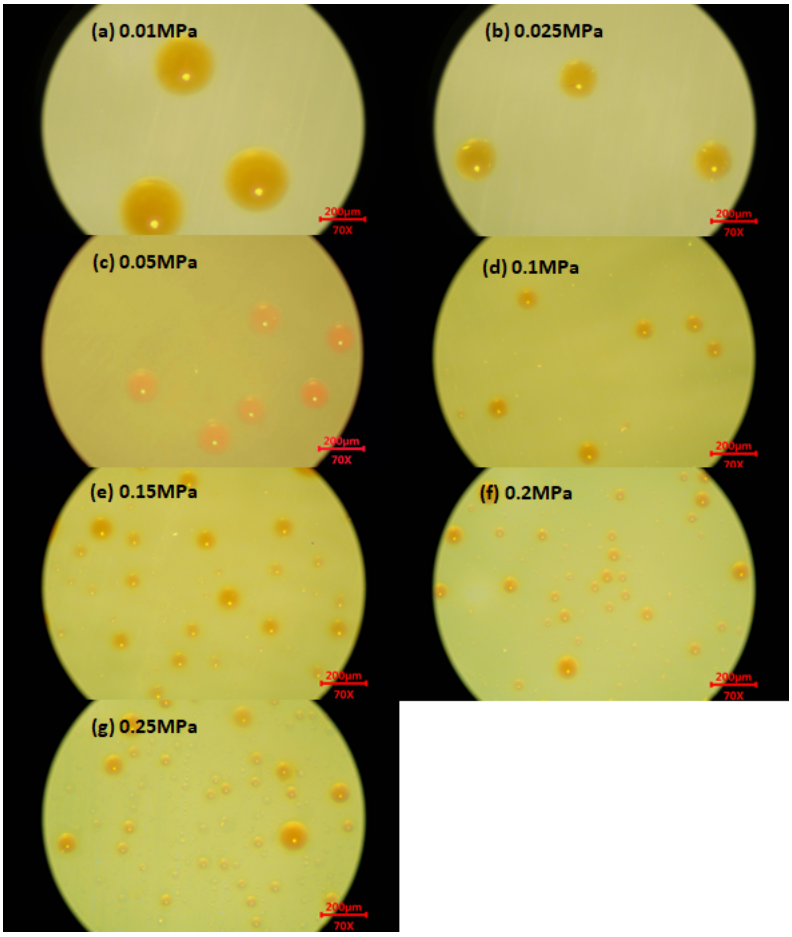


Elt	W%	W%Sigma	A%
Cu	30.47	0.53	46.73
I	69.11	0.60	53.07
Hg	0.41	0.43	0.20
	100.00		100.00

Elt	W%	W%Sigma	A%
Cu	34.36	1.11	51.18
I	65.15	1.21	48.59
Hg	0.49	0.85	0.23
	100.00		100.00

Fig. S4 EDS spectrum of the final products covered on the copper wire surface prepared by PN system (a) and $SnCl_2$/HCl vapor generation system (b).



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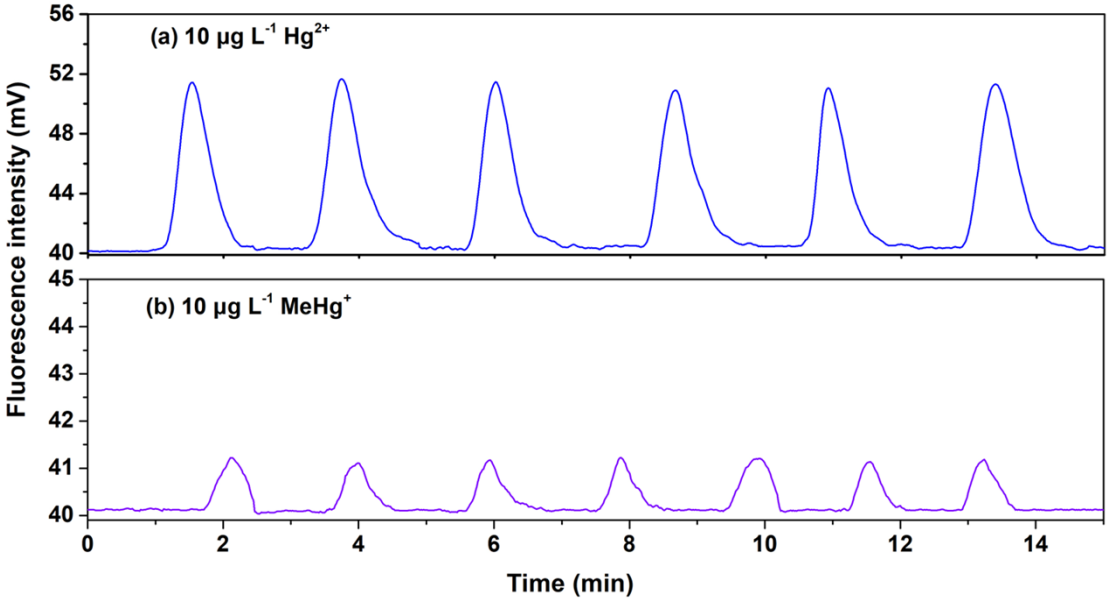

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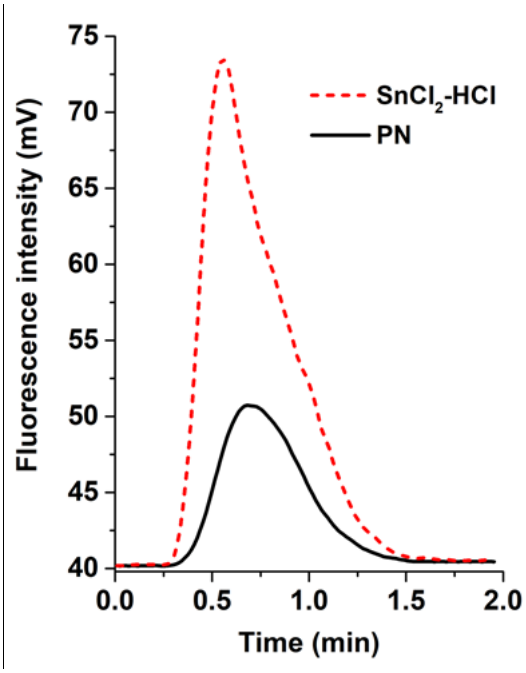

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