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Simple *in situ* analysis of metal halide perovskite-based sensor materials using micro X-ray fluorescence and inductively coupled plasma mass spectrometry

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1. Micro-XRF measurements

A high-resolution M4 Tornado Plus micro-X-ray spectrometer (Bruker Nano GmbH, Germany) with a resolution of 145 eV was used for the purpose of quantitative determination of the content of elements and examination of the spatial distribution of $CsPbHal_3$ on the sensor surface. Rh K-L_3 line was used for excitation of the X-ray fluorescence; the anode (the tube voltage and current of the X-ray were 50 kV and 600 µA, respectively) was equipped with a polycapillary lens, focal spot – 20 µm. The spectrum acquisition time was 60 s for each pixel. The following lines were used: Cs, Pb, I – L_3-M_5, Br, Zn – K-L_3. The results of bulk analysis of samples were obtained after the mapping of the surface by summing the points measurements results with a scan step of 20 µm. No vacuum was used. The scanning area of each sample was 3.2 × 3.2 mm^2.

2. ICP-MS measurements

Measurements were performed using a mass spectrometer with inductively coupled plasma Agilent 7500C (Japan), quadruple mass analyzer. Measurements of analytical signals and data processing were performed via the PC software ChemStation (version G1834B) software package (Agilent Technologies). To prepare working and standard solutions concentrated nitric acid (65%) of the ‘Suprapure’ grade (Merck, Germany), deionized water Milli-Q (18.2 MΩ/cm, Millipore, Bedford, USA), 0.4% NaOH (Shijiazhuang Xinlongwei Chemical Co, Ltd., China) and 2% tetramethylammonium hydroxide (TMAH, Tama Chemical Co, Japan) solutions of the ‘Suprapure’ grade were used. To prepare the standard solutions and model mixtures monoelement Cs, Pb, Br, and I with concentration of 1 mg/L (High Purity Standards, USA) were used. The following isotopes were used: ^{133}Cs, ^{206}Pb, ^{208}Pb, ^{79}Br, ^{81}Br, ^{127}I, ^{66}Zn, ^{68}Zn. After the sample dissolution (scanning area of each sample), the obtained solution was diluted to 2% HNO_3 or 2% TMAH to avoid contamination of the sample input system and of ion optics.

3. Synthesis

Nanocrystalline zinc oxide was prepared by two-step synthesis as follows:

1) 0.893 M solution of $Zn(CH_3COO)_2{\cdot}2H_2O$ (ACS reagent, ≥98%) was slowly added to 1.5 M solution of NH_4HCO_3 (ReagentPlus®, ≥99.0%) under intensive stirring at 20 ºC. Deionized water was used to prepare precursors solutions. The resulting white precipitate of basic zinc carbonate $Zn_x(OH)_y(CO_3)_z$ was filtered under vacuum, washed several times with water and ethanol, and dried at 70 ºC.

2) The synthesized powder of basic zinc carbonates was annealed at 300 ºC in air for 24 h to form nanocrystalline ZnO powder.

The colloidal perovskite $CsPbBr_3$ and $CsPbI_3$ NCs were synthesized by the hot-injection method using the Schlenk line[1–2]. First, a 0.125 M solution of cesium oleate in octadecene was prepared as follows: cesium carbonate (407 mg, Alfa Aesar™, Puratronic™, 99.994%), 1-octadecene (ODE, 20 ml, Sigma Aldrich, 90%) and oleic acid (OA, 5 ml, Sigma Aldrich, 90%) were loaded in 25-ml 3-neck flask and heated up to 120 ºC under vacuum with vigorous stirring until the reaction of Cs_2CO_3 with OA is complete. Since the cesium oleate is precipitated out of the ODE solution at room temperature, the heating up to 100–120 ºC is needed before using. Next, the required lead halide ($PbBr_2$, 138 mg, 99,999%, Sigma-Aldrich or PbI_2, 174 mg, 99.999%, Alfa Aesar™) and 10 ml of ODE were loaded in 25-ml 3-neck flask and degassed at 120 ºC under vacuum (10^{-2} torr) for 30 min. Then dried OA (1 ml) and oleylamine (OAm, 1 ml, Sigma Aldrich, 70%) were injected into the flask under the Ar flow. The reaction mixture was kept under vigorous stirring until lead halides are completely dissolved. Finally, the temperature was raised to 170 ºC and 0.8 ml of cesium oleate solution was rapidly injected in the flask under the Ar flow. After 5 s, the flask was cooled using an ice bath. The crude solution was centrifuged at 10000 rpm for 10 min, and the precipitate of lead halide perovskite NCs was carefully separated from the supernatant. For optical measurements and ZnO sensitization, $CsPbBr_3$ NCs were redispersed in hexane immediately before use. The approximate thickness of the active layer is 50 µm.

Table S1 The results of Cs, Pb, Br determination in model HNO_3 solution of $CsPbBr_3$ by 'introduced-found' method (1-α = 0.95, n = 5).

	Cs		Pb		Br	
	introduced, ppb	found, ppb	introduced, ppb	found, ppb	introduced, ppb	found, ppb
Sample 1	100	100 ± 2	100	99 ± 3	300	290 ± 15
Sample 2	200	200 ± 4	200	195 ± 6	500	480 ± 35

Table S2 The results of Cs, Pb, Br determination in $CsPbBr_x$ NCs sample and sensitive sensor layer by ICP-MS (1-α = 0.95, n = 5).

	Found, ppb				Ratio %, at. Cs:Pb:Br(:Zn)
	Cs	Pb	Br	Zn	
$CsPbBr_x$	710 ± 60	1290 ± 90	1800 ± 180	–	1.0: 1.2 : 4.3
$CsPbBr_x$ (after additional purification)	110 ± 10	180 ± 20	188 ± 20	–	1.0 :1.0 : 2.8
Sensitive ZnO/$CsPbBr_x$ sensor layer	340 ± 20	500 ± 20	560 ± 30	1570 ± 80	1 : 0.9 : 2.8 : (9.7)

Table S3 The results of Cs, Pb, I determination in model NaOH and TMAH solutions by 'introduced -found' method.

	Cs		Pb		I	
	introduced, ppb	found, ppb	introduced, ppb	found, ppb	introduced, ppb	found, ppb
NaOH, 0,4%	200	190 ± 6	200	175 ± 6	200	180 ± 12
TMAH, 2%	100	100 ± 3	100	95 ± 5	100	96 ± 6

Table S4 The results of Cs, Pb, I determination in $CsPbI_x$ NCs sample and sensitive sensor layer in 2% TMAH solution by ICP-MS (1-α = 0.95, n = 5).

	Found, ppb				Ratio %, at.
	Cs	Pb	I	Zn	Cs:Pb:I(:Zn)
$CsPbI_x$	180 ± 20	280 ± 20	580 ± 60	–	1.0 :1.0 : 3.3
Sensitive ZnO/$CsPbI_x$ sensor layer	120 ± 7	190 ± 8	380 ± 30	580 ± 40	1.0 : 1.0 : 3.3 : (8).

Table S5 The results of Cs, Pb, Br, Zn determination in sensitive sensor layer by micro-XRF.

	k × 10^{-2}	Calculated, atomic mole × 10^{-2}				
sample		1	2	3	4	5
Cs	2.55	1.3	2.7	3.5	3.5	4.8
Pb	1.5	1.2	2.6	3.4	4,2	4.9
Br	2.25	4.3	8	12	16	14.3
Zn	5.5	18	20	16.2	18	19

The conversion factor for iodine was 1.9×10^{-2}.

References

S1 L. Protesescu, S. Yakunin, M. I. Bodnarchuk, F. Krieg, R. Caputo, C. H. Hendon, R. X. Yang, A. Walsh and M. V. Kovalenko, *Nano Lett.*, 2015, **15**, 3692.

S2 K. A. Drozdov, I. V. Krylov, A. S. Chizhov, M. N. Rumyantseva, L. I. Ryabova and D. R. Khokhlov, *Semiconductors*, 2019, **53**, 814 (*Fiz. Tekh. Poluprovodn.*, 2019, **53**, 824).