Supporting Information

Transition metal ions assisted photochemical vapor generation of niobium, and tantalum

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Liang Dong and Yongyan Ning made equal contributions to this work

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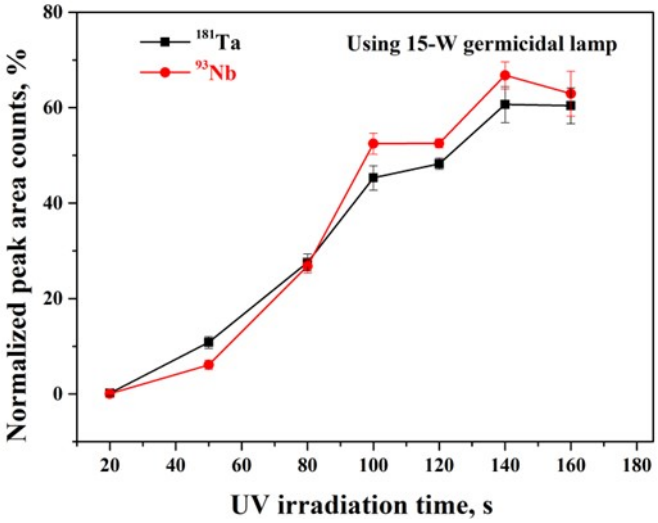

Figure S1. Effect of the irradiation time on $^{93}Nb/^{181}Ta$ response equipped with germicidal lamp: 10 µg L^{-1} Nb/Ta, 25% (v/v) FA and 20 mg L^{-1} Cu^{2+}.

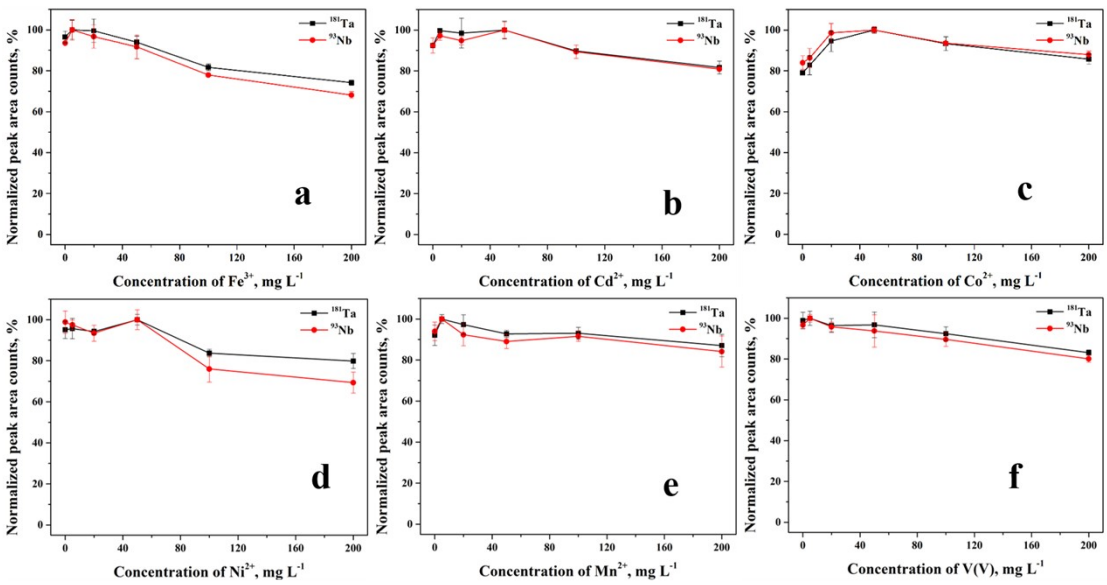

Figure S2. Effect of the concentration of Fe^{3+}, Cd^{2+}, Co^{2+}, Ni^{2+}, Mn^{2+}, and V(V) on $^{93}Nb/^{181}Ta$ response: 10 µg L^{-1} Nb/Ta, 25% (v/v) FA, 20 mg L^{-1} Cu^{2+} and 25 s irradiation time.

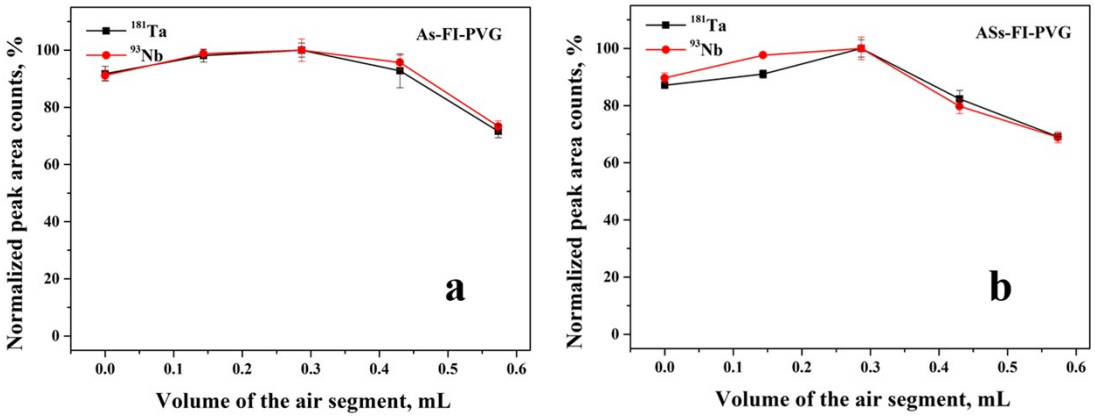

Figure S3. Effect of the volume of the air segment on $^{93}Nb/^{181}Ta$ responses: 10 µg L^{-1} Nb/Ta, 25% (v/v) FA, 20 mg L^{-1} Cu^{2+} and 25 s UV irradiation time.

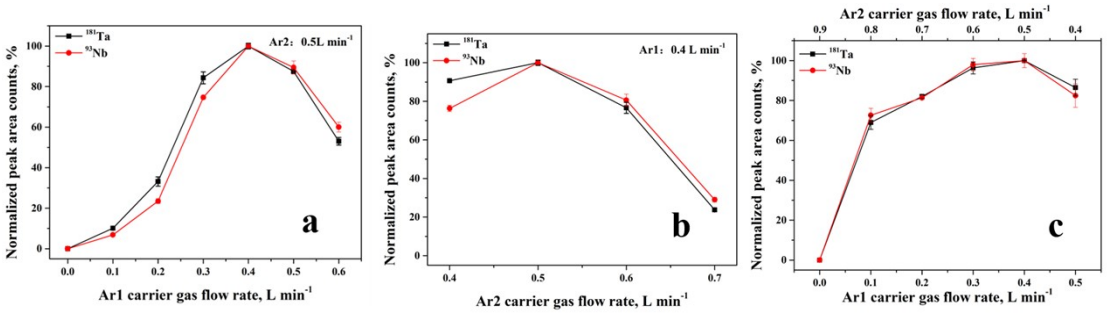

Figure S4. Effect of Ar flow rate on the separation of volatile Nb/Ta from sample solution: 10 μg L^{-1} Nb/Ta, 25% (v/v) FA, 20 mg L^{-1} Cu^{2+} and 25 s irradiation time.

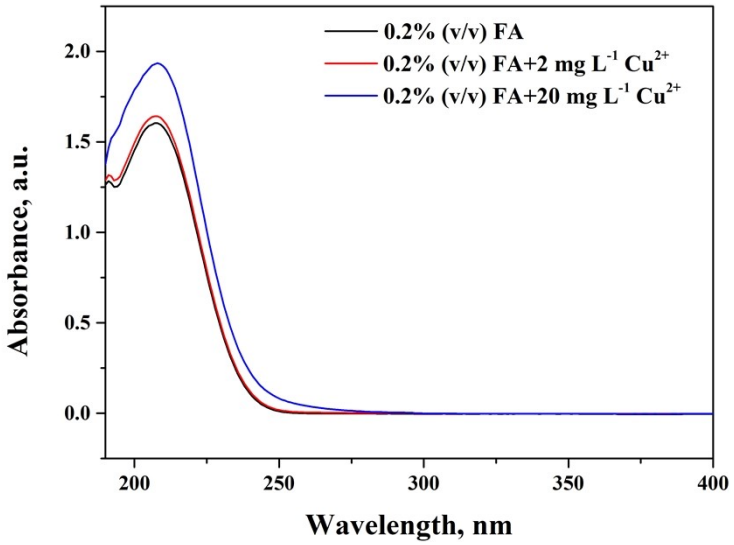

Figure S5. UV−vis spectra of the PVG medium.

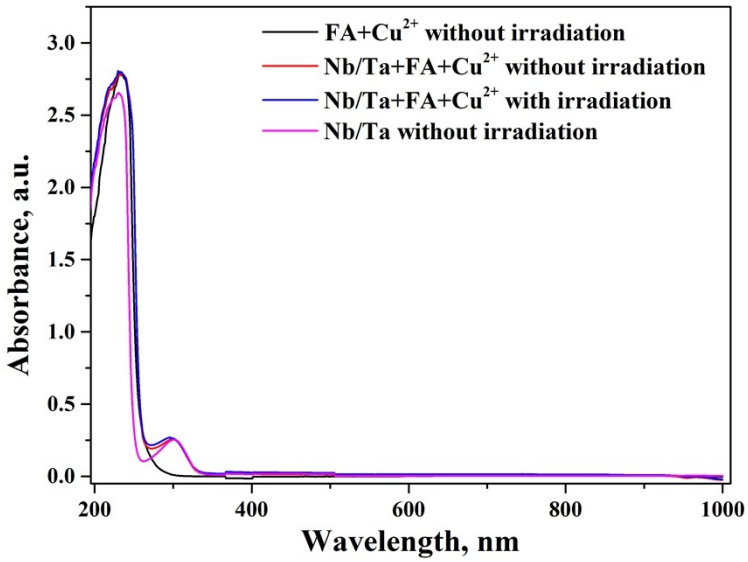

Figure S6. UV−vis spectra of Nb and Ta in the media: 50 mg L^{-1} Nb/Ta, 25% (v/v) FA, 20 mg L^{-1} Cu^{2+} and 25 s irradiation time.

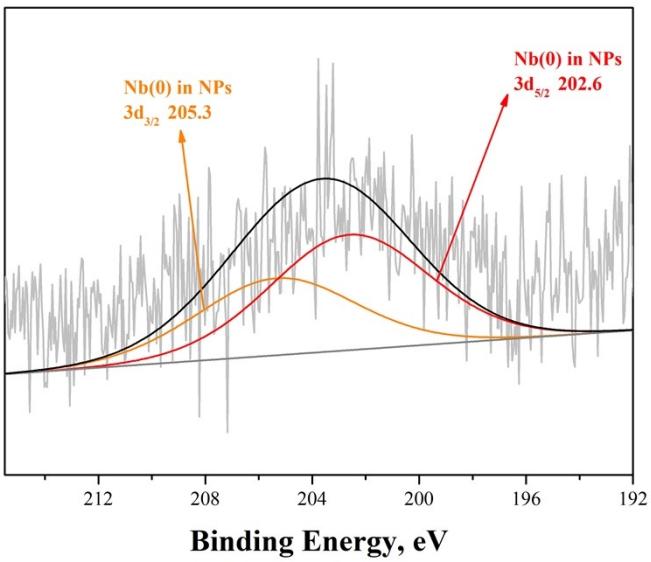

Figure S7. XPS spectra of the generated Nb species collected from the gas phase: 50 mg L^{-1} Nb, 25% (v/v) FA, 20 mg L^{-1} Cu^{2+} and 25 s irradiation time.

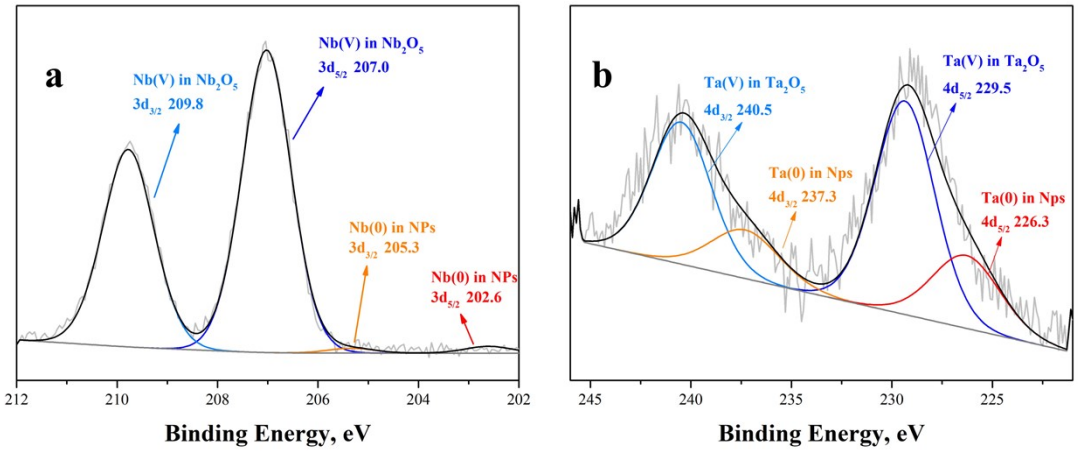

Figure S8. XPS spectra of the generated (a) Nb and (b) Ta species collected from the test solution outflowing the PVG reactor: 50 mg L^{-1} Nb/Ta, 25% (v/v) FA, 20 mg L^{-1} Cu^{2+} and 25 s irradiation time.

Table S1. ICP-MS operating parameters.

Instrument Settings	Value
auxiliary Ar gas flow rate	1.2 L min^{-1}
plasma Ar gas flow rate	15 L min^{-1}
sample flow rate	4.3 mL min^{-1}
RF power	1175 W
Resolution	0.7 amu
dwell time	30 ms
dead time	50 ns
Sweeps per reading	1
Readings per replicate	1
number of replicates	1000
scanning mode	peak hopping
isotope monitored	^{93}Nb, ^{181}Ta

Reagents

All reagents used in this work were of analytical grade or better. Deionized water (DIW) was used throughout. Formic acid (FA), acetic acid (AA), NH_4VO_3, $(CH_3COO)_2Co•4H_2O$, $(CH_3COO)_2Cu$ $•H_2O$, $FeCl_3•6H_2O$, $NiCl_2•6H_2O$, $ZnSO_4•7H_2O$, $MnSO_4•H_2O$, $CdCl_2$ were purchased from Aladdin Industrial Corporation (Shanghai, China). Standard solutions of Nb and Ta containing 2% (v/v) HNO_3 and 0.5% (v/v) HF with concentration of 1000 mg L^{-1} were obtained from National Research Center for standard materials. H_2SO_4, HNO_3, HF, and HCl were purchased from KESHI corporation (Chengdu, China). For the preparation of sample solution for PVG, FA was suggested to be the last reagent added to prevent the hydrolysis of Nb and Ta.

TEM and XPS analysis

To minimize the suppression of HNO_3 and HF on PVG performance, appropriate amounts of tantalum chloride and niobium oxalate were dissolved with diluted HNO_3 and HF to yield a standard solution containing 100 mg L^{-1} of Ta/Nb, 0.01% (v/v) of HNO_3 and 0.0025% (v/v) HF.

Since the reduced Ta/Nb species were chemically active and susceptible to oxidation, the whole PVG sampling apparatus was placed into a glove box degassed with high-purity argon, to facilitate the sample preparation for TEM and XPS characterization. Specifically, copper mesh (for TEM) or glass slides (for XPS) were positioned at the exit of the first GLS to trap the Ta/Nb volatiles. Meanwhile, test solutions of Ta/Nb outflowing the PVG reactor were also collected and dropped onto a copper mesh or glass slide, which were further dried under an infrared oven. Note that this drop-and-dry process was repeated six times to improve the detectability of TEM or XPS. In this vein, the gaseous and liquid PVG products were well isolated from air before TEM and XPS analysis.