

SUPPORTING INFORMATION

Al₂O₃-supported transition metals for plasma-catalytic NH₃ synthesis in a DBD plasma: Metal activity and insights into mechanisms

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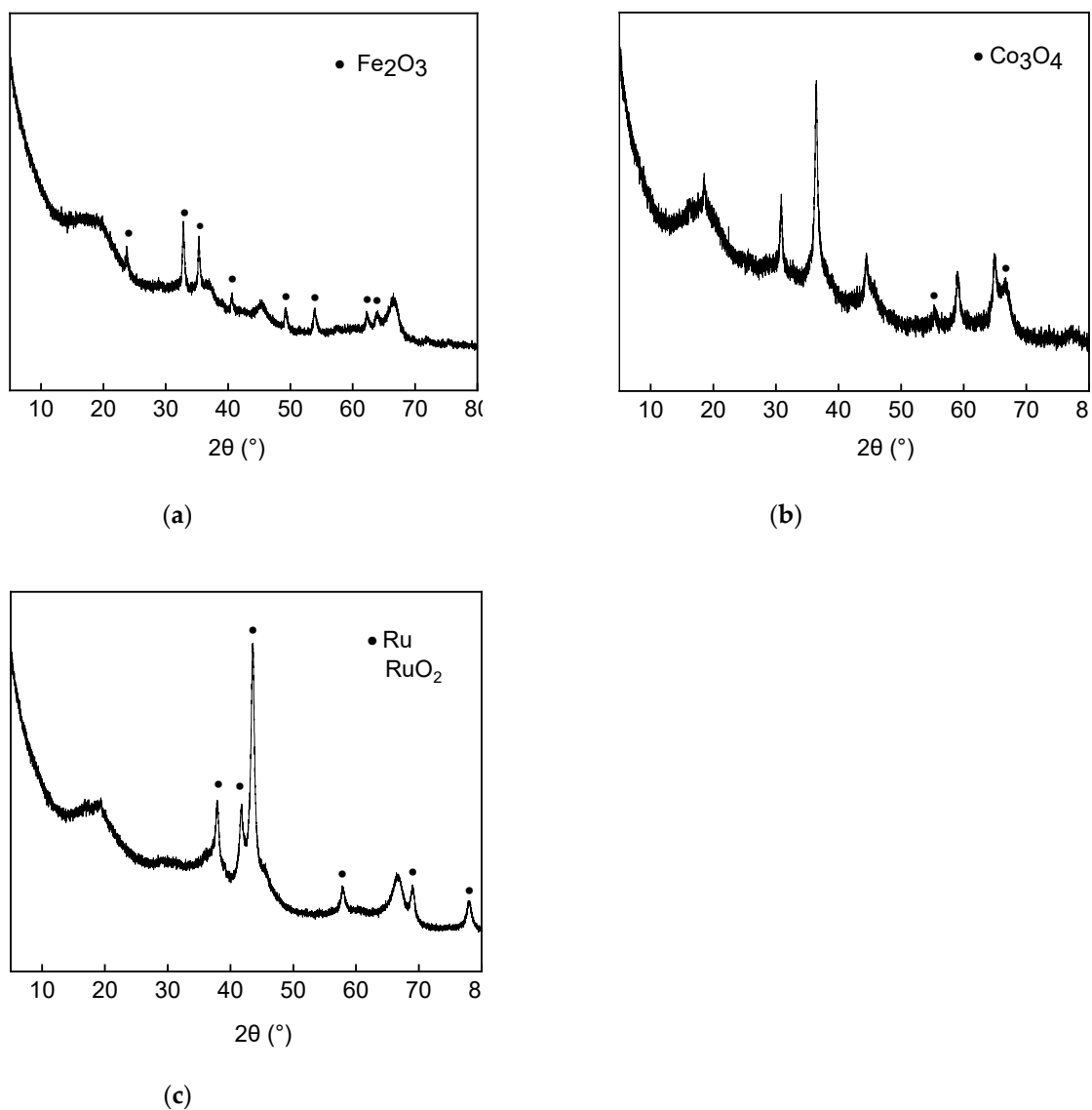


Figure S1. XRPD diffractograms of the catalysts used in our work. (a) Fe₂O₃/Al₂O₃ (after calcination, before reduction); (b) Co₃O₄/Al₂O₃ (after calcination, before reduction); (c) Ru/Al₂O₃ (after calcination, after reduction).

Table S1. Measured active surface area (S_{BET}) and pore volume (V) for the 10 wt% Co/Al₂O₃ catalyst before (fresh) and after (spent) the plasma-catalytic NH₃ synthesis experiments, showing no difference before and after the plasma experiments. The other catalysts showed similar behaviour.

Material	S_{BET} (m ² /g)	V (cm ³ /g)
10 wt% Co/Al ₂ O ₃ (fresh)	175	0.37
10 wt% Co/Al ₂ O ₃ (spent)	177	0.37

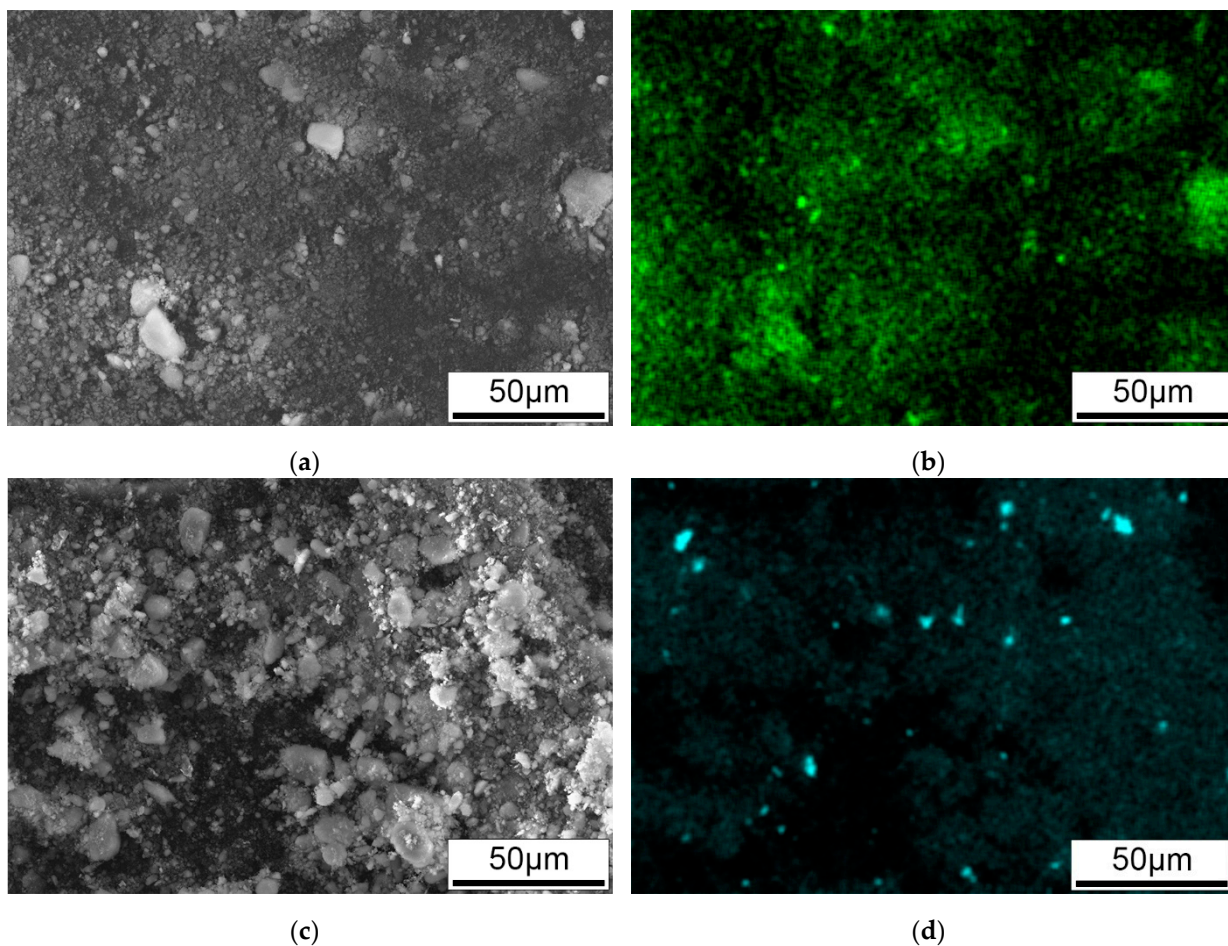


Figure S2. Typical SEM-EDX images of the catalysts, for the example of 10 wt% Co and Cu/Al₂O₃ catalysts with EDX maps applied for visualisation of the respective metals. (a) SEM image of the 10 wt% Co/Al₂O₃; (b) SEM EDX map of Co on the surface of the 10 wt% Co/Al₂O₃; (c) SEM image of the 10 wt% Cu/Al₂O₃; (d) SEM EDX map of Cu on the surface of the 10 wt% Cu/Al₂O₃. Green and cyan colours indicate the particles of the respective metal on the surface of Al₂O₃.

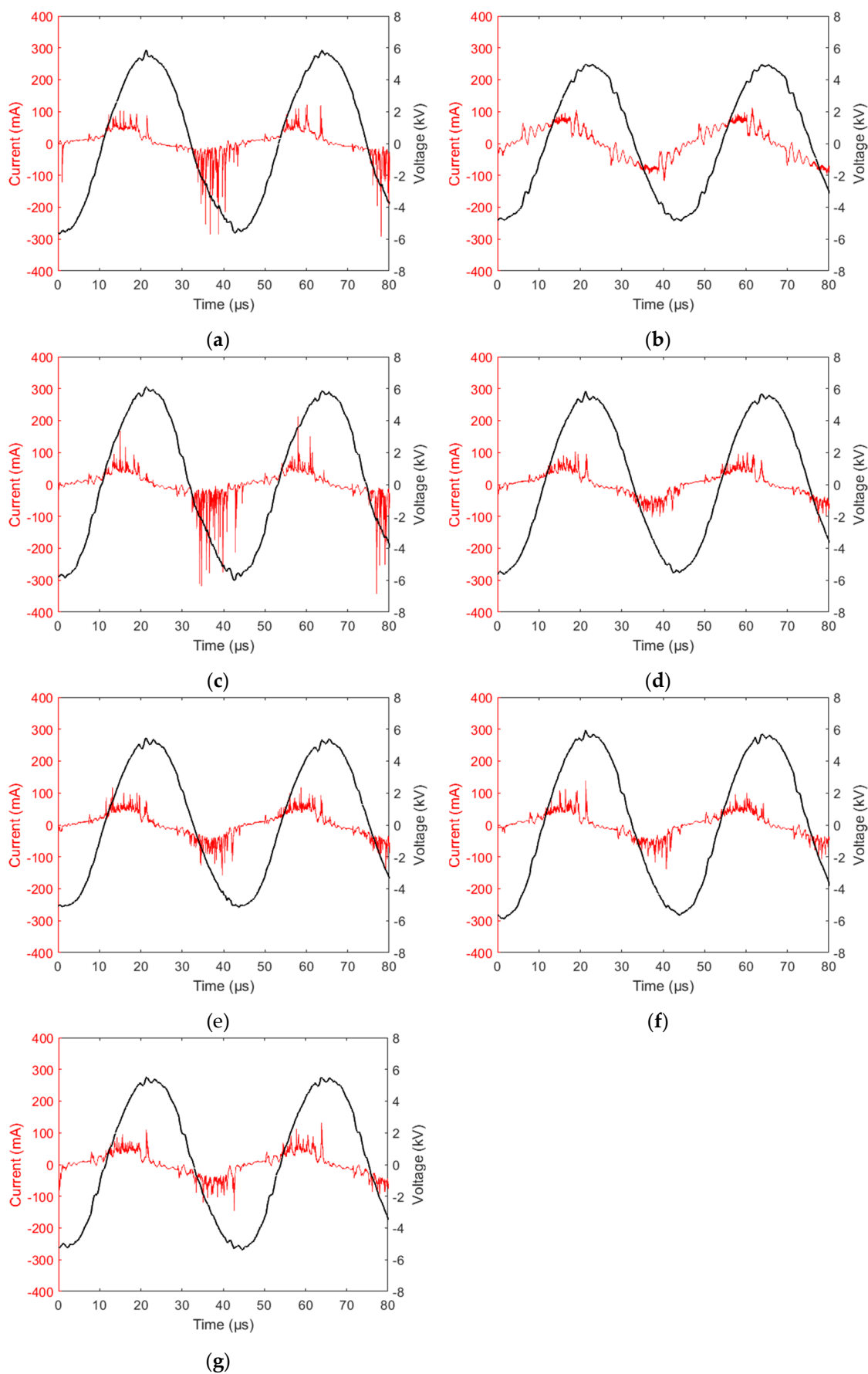


Figure S3. Current and voltage waveforms for the plasma-catalytic NH_3 synthesis experiments with different Al_2O_3 -supported catalysts and pristine Al_2O_3 , at different H_2/N_2 ratios in the feed gas. (a) Al_2O_3 at the 1:1 H_2/N_2 gas ratio; (b) 10 wt% $\text{Fe}/\text{Al}_2\text{O}_3$ at the 1:1 H_2/N_2 gas ratio; (c) 10 wt% $\text{Ru}/\text{Al}_2\text{O}_3$ at the 1:1 H_2/N_2 gas ratio; (d) 10 wt% $\text{Co}/\text{Al}_2\text{O}_3$ at the 1:1 H_2/N_2 gas ratio; (e) 10 wt% $\text{Cu}/\text{Al}_2\text{O}_3$ at the 1:1 H_2/N_2 gas ratio; (f) 10 wt% $\text{Co}/\text{Al}_2\text{O}_3$ at the 1:3 H_2/N_2 gas ratio; (g) 10 wt% $\text{Co}/\text{Al}_2\text{O}_3$ at the 3:1 H_2/N_2 gas ratio.

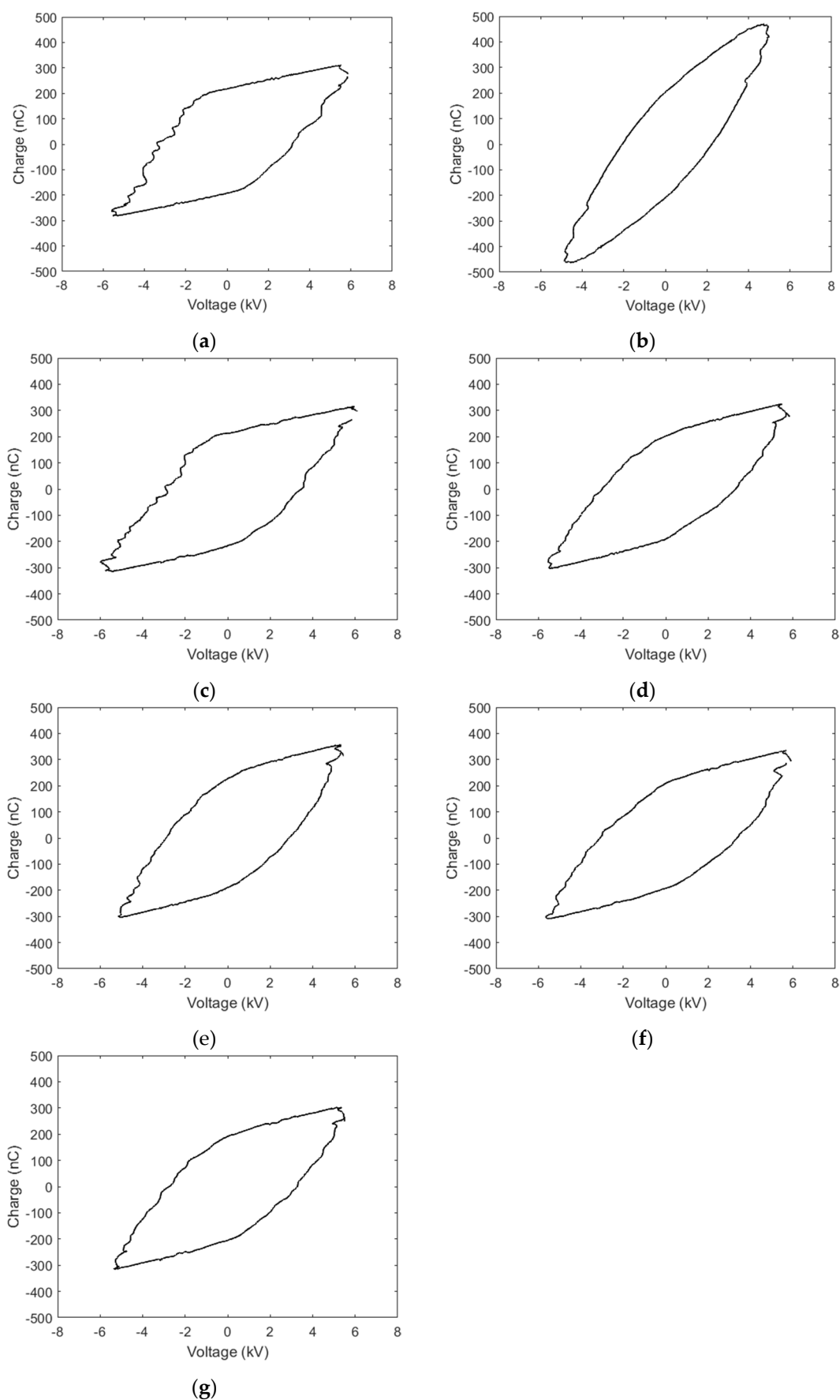


Figure S4. Lissajous figures for the plasma-catalytic NH_3 synthesis experiments with different Al_2O_3 -supported catalyst and pristine Al_2O_3 , at the different H_2/N_2 ratios in the feed gas. (a) Al_2O_3 at the 1:1 H_2/N_2 gas ratio; (b) 10 wt% $\text{Fe}/\text{Al}_2\text{O}_3$ at the 1:1 H_2/N_2 gas ratio; (c) 10 wt% $\text{Ru}/\text{Al}_2\text{O}_3$ at the 1:1 H_2/N_2 gas ratio; (d) 10 wt% $\text{Co}/\text{Al}_2\text{O}_3$ at the 1:1 H_2/N_2 gas ratio; (e) 10 wt% $\text{Cu}/\text{Al}_2\text{O}_3$ at the 1:1 H_2/N_2 gas ratio; (f) 10 wt% $\text{Co}/\text{Al}_2\text{O}_3$ at the 1:3 H_2/N_2 gas ratio; (g) 10 wt% $\text{Co}/\text{Al}_2\text{O}_3$ at the 3:1 H_2/N_2 gas ratio.

Table S2. The amount of the used catalyst, and the production rate of NH_3 (in $\text{mg}/(\text{h} \times \text{g}_{\text{cat}})$) in our work compared to literature reports.

Reference in the main text	Catalyst amount (g)	NH ₃ production rate	
		mg/h	mg/(h \times g _{cat})
[35]	17	119	6.9
[36]	173	32	0.2
[39]	3.6	76	21
[42]	100	17	0.2
[46]	0.5	25	50
this work	12	42	3.5