Electronic Supplementary Material (ESI) for Nanoscale Advances.

Supplementary Information for

Solvent-Induced Local Environment Effect in Plasmonic Catalysis

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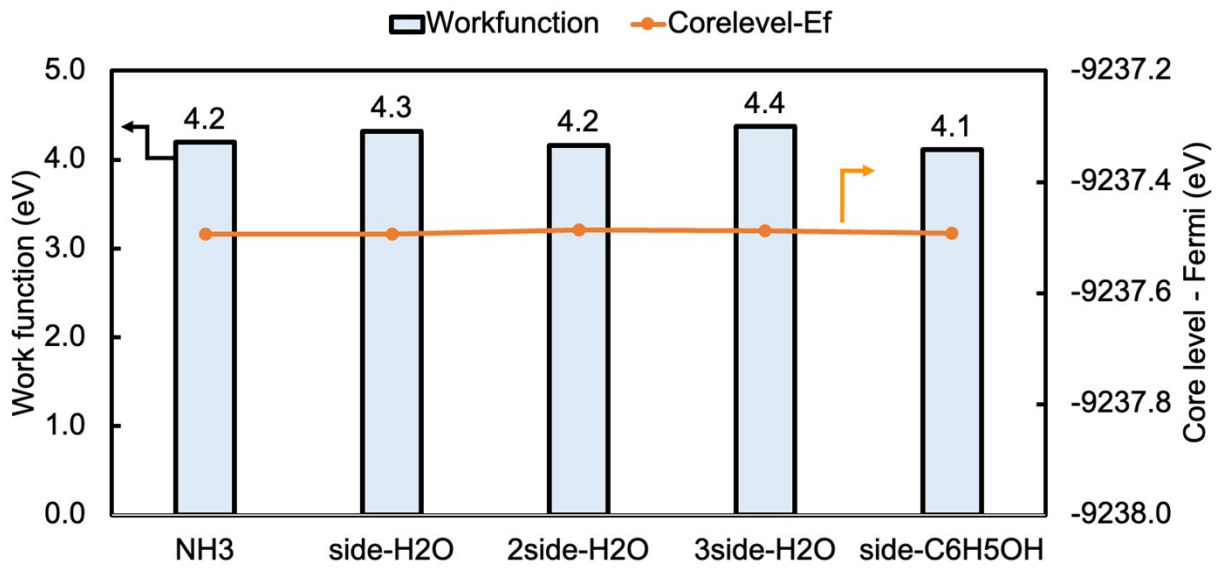

Figure S1: The changing of work function and the energy difference between core level of Cu 1s with respect to the Fermi level as the number of H_2O/C_6H_5OH molecules increases.

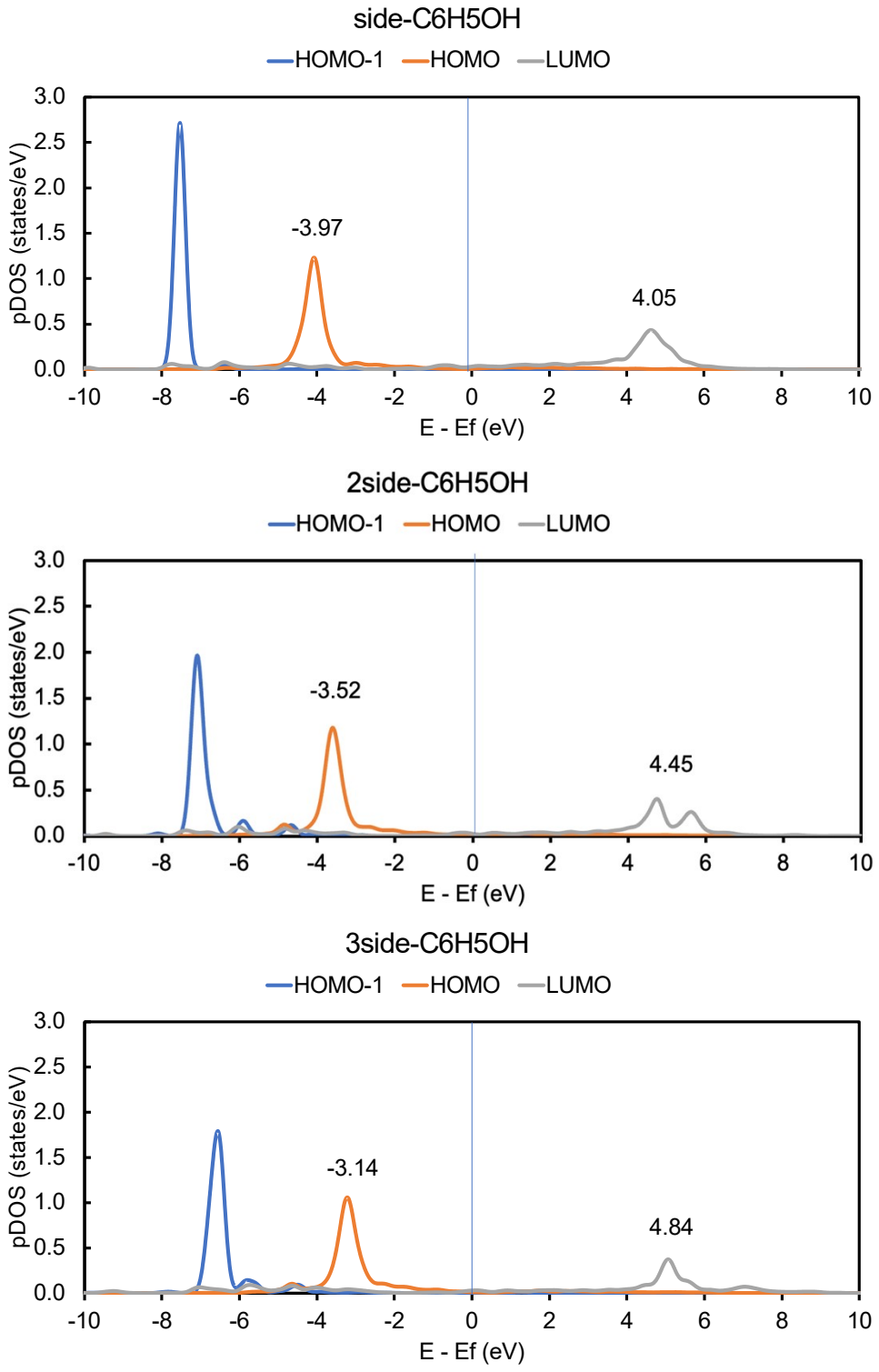

Figure S2: Density of states projected onto frontier orbitals of adsorbed NH_3 surrounded by C_6H_5OH. The center of the HOMO and LUMO of NH_3 are shown above the main peak.

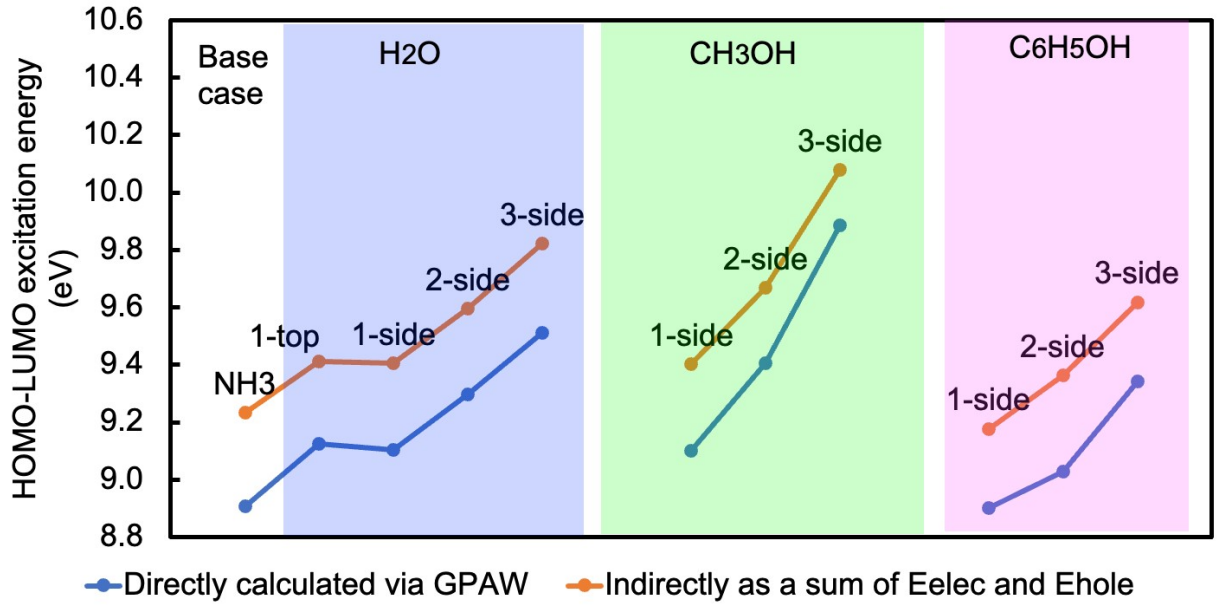

Figure S3: Comparison of the HOMO-LUMO gap when it is directly calculated via GPAW versus when it is indirectly calculated as a sum of E_{elec} and E_{hole}.

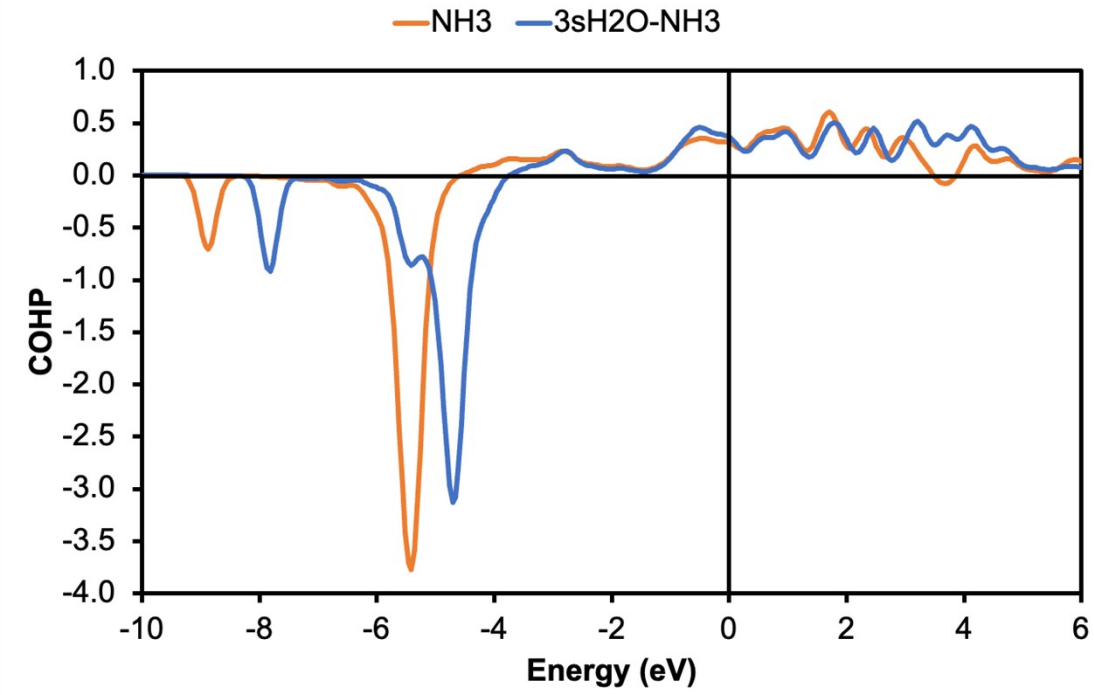

Figure S4: The COHP of Ru-N bond of NH_3 (orange), and NH_3 surrounded by 3 H_2O molecules (blue).

Table S1: The adsorption energy of NH_3 on the Ru-doped Cu surface ($RuCu_{83}$) vs the Cu surface (Cu_{84}). Unit: eV.

	NH_3	**topH_2O**	**side-H_2O**	**2side-H_2O**	**3side-H_2O**
$RuCu_{83}$	-1.40	-1.61	-2.02	-2.59	-3.12
Cu_{84}	-0.88	-1.07	-1.51	-2.11	-2.68

Table S2. The adsorption energy of individual solvent molecules on the Ru-doped Cu surface ($RuCu_{83}$) as compared to NH_3 on the same surface. Unit: eV.

	NH_3	**H_2O**	**CH_3OH**	**C_6H_5OH-(ring ads)**	**C_6H_5OH (OH ads)**
E_ads	-1.40	-0.71	-0.90	-1.47	-1.19

Table S3: The excitation energy of an electron from the Fermi level to the LUMO of NH_3 of the Cu surface (Cu_{84}). Unit: eV.

Cu_{84}	**NH_3**	**topH_2O**	**side-H_2O**	**2side-H_2O**	**3side-H_2O**
Fermi level to LUMO	3.21	3.29	3.57	3.93	4.33

Table S4: The Kamlet-Taft solvent parameters (http://www.stenutz.eu/chem/solv26.php)

Solvent	**α (hydrogen bond donor)**	**β (hydrogen bond acceptor)**
Phenol	1.65	0.30
Water	1.17	0.47
Methanol	0.98	0.66