カルボニル化合物の吸着・化学反応における ZnO/(Cu$_{1-x}$Zn$_x$)O コアシェルヘテロナノワイヤ表面上 Cu^{2+}サイトの役割

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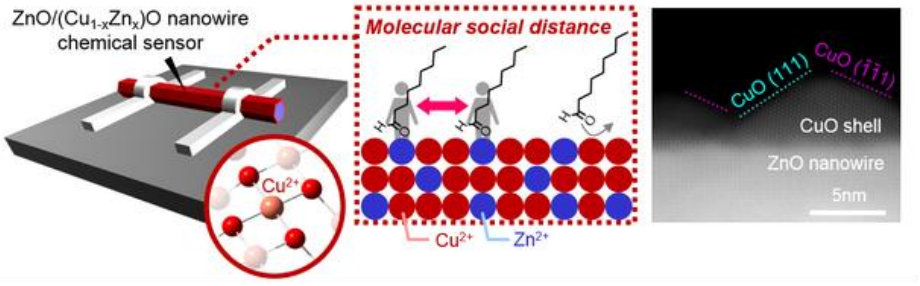
Surface cation composition of nanoscale metal oxides is well known to significantly affect the surface molecular behaviors in various applications including inhomogeneous catalysts, molecular sensing, and others. Since various molecular reaction pathways are induced via interacting sequentially or simultaneously with different cation species on the surface, investigating the effect of surface cation composition on the surface molecular behaviors is of crucial importance for designing the properties of above applications.

In this study, we performed a cation diffusion-based gradual modulation of cation composition on ZnO/(Cu$_{1-x}$Zn$_x$)O heterostructured nanowire surface to study the effect of surface cation composition (Cu/Zn) on the adsorption and chemical transformation behaviors of volatile carbonyl compounds (nonanal: biomarker). We found that a surface exposed copper significantly suppresses the adsorption of nonanal, which is not consistent with our initial expectation since the Lewis acidity of Cu^{2+} is strong enough and comparable to Zn^{2+}. In addition, an increase of Cu/Zn ratio on the nanowire surface suppresses the aldol condensation reaction of nonanal. Surface spectroscopic analysis and theoretical simulations reveal that the nonanal molecules adsorbed at surface Cu^{2+} site are not activated, and a coordination-saturated in-plane square geometry of surface Cu^{2+} is responsible for the observed weak molecular adsorption behaviors. This inactive surface Cu^{2+} well explains the mechanism of suppressed surface aldol condensation reactions by preventing a neighboring of activated nonanal molecules. We apply this tailored cation composition surface for electrical molecular sensing of nonanal and successfully demonstrate the improvements of durability and recovery time as a consequence of controlled surface molecular behaviors.



References

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