Crucial Influence in Catalytic Performance by Atom-Level Manipulation on Surface of Bimetallic AuPd Nanoicosahedra

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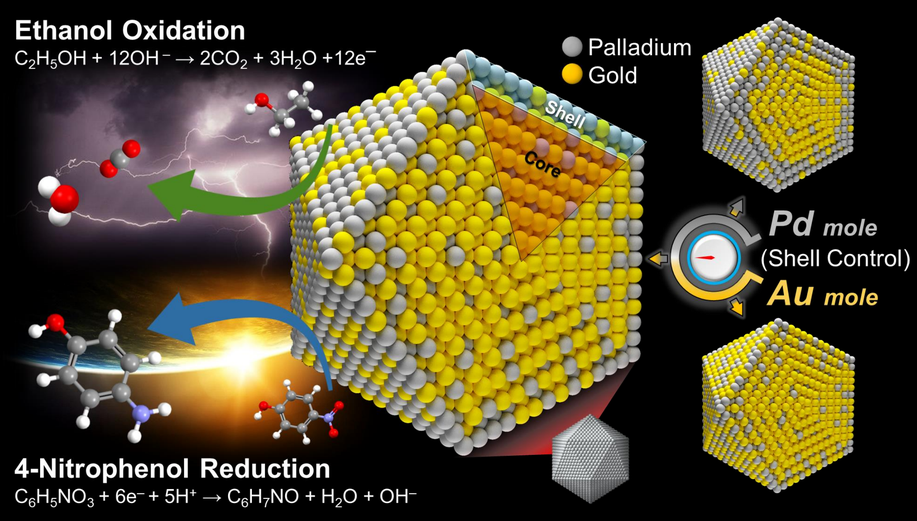
Introduction

In this work, we demonstrate the one-step aqueous strategy for synthesis of bimetallic Au-Pd nanoicosahedra as the efficient photocatalysts for 4-nitrophenol (4-NP) reduction and fuel cell anodic ethanol oxidation reaction (EOR), by which we tried to examine the optimized nanostructure and composition through tuning $[AuCl_4^-]/[PdCl_4^-]$ in the co-reduction process. By turning the molar ratio of Au and Pd precursors, the nanoicosahedra could be made with their cores in close Au-Pd compositions (Pd ~20%) yet their surfaces are largely flexible (Pd: 20-70%). In the model reactions, electrochemical ethanol oxidation and 4-NP reduction, the AuPd (1:1) sample with the surface of $Au_{55}Pd_{45}$ displayed the most superior activities. By XAS analysis, it brings to light the electronic structures of AuPd nanoicosahedra with Pd-poor surfaces ($Au_{79}Pd_{21}$ and $Au_{60}Pd_{40}$) keep Au characteristics while those with Pd-rich surfaces are more Pd-like. The AuPd (1:1) sample ($Au_{83}Pd_{17}$-$Au_{55}Pd_{45}$) hence plays a turnover line in-between them, suggesting the best Au-Pd interplay towards catalytic performances. Our findings in catalyst designs at atomic scale will bring deep insights into the fields of nanosynthesis and heterogeneous catalysis, which will be beneficial for further scientific breakthroughs.



Result & Discussion

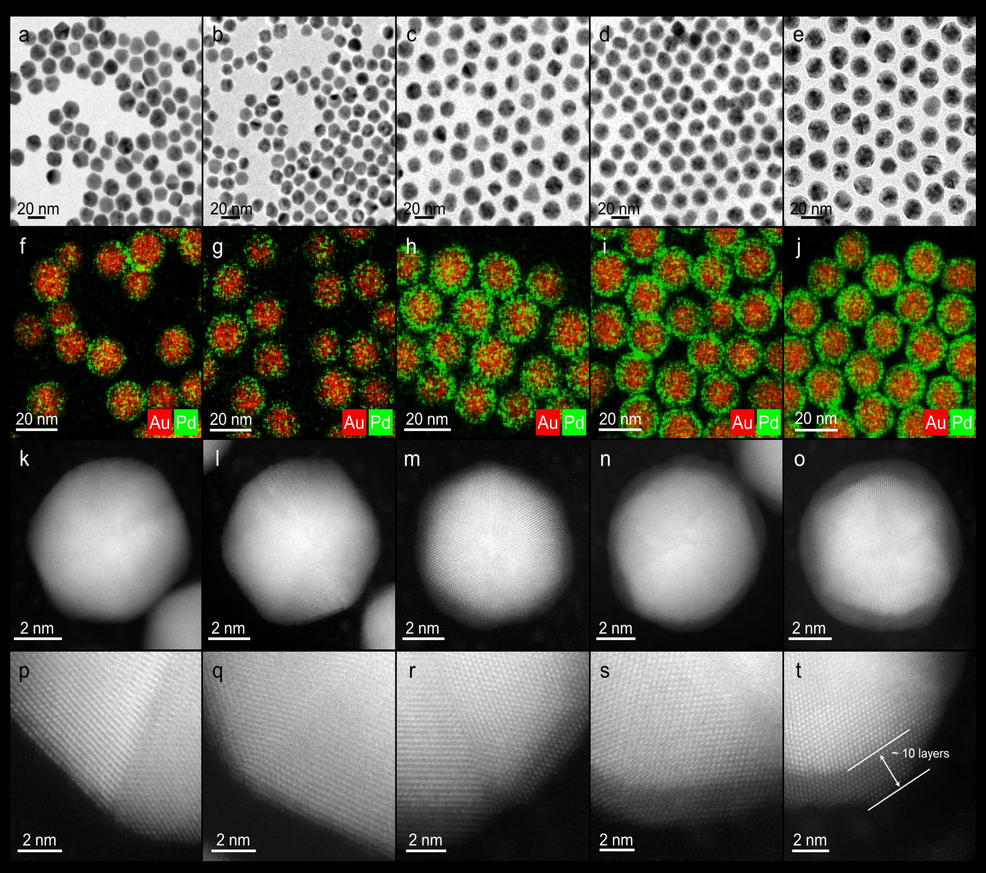


Figure 1. (a-e) Bright-field TEM images of core-shell AuPd nanoicosahedra made in different $HAuCl_4/H_2PdCl_4$ ratios of (a) 3/1, (b) 2/1, (c) 1/1, (d) 1/2, (e) 1/3, and (f-j) their corresponding distributions of Au and Pd in the structures obtained by STEM-EDS mapping. (k-o) HAADF-STEM images of single AuPd nanoicosahedra taken from the samples in (a-e), and (p-t) atom-resolved HAADF-STEM imaging on one of their corner sites.

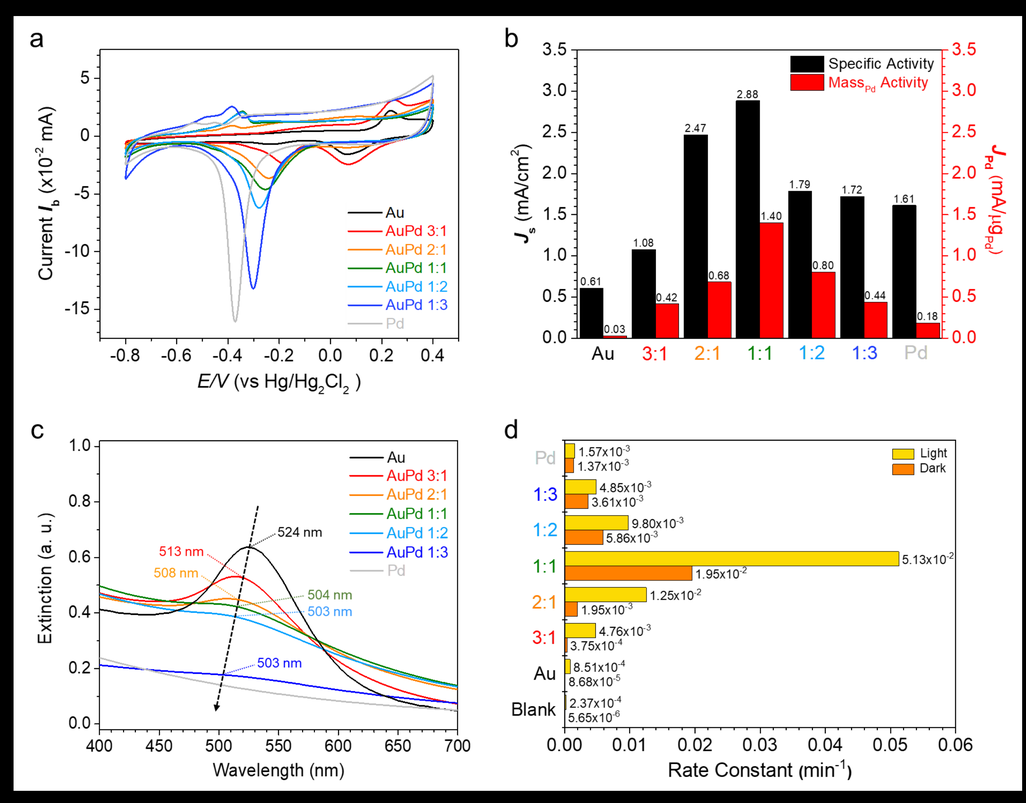


Figure 2. (a) CVs of AuPd, Au and Pd nanoicosahedra scanned in a 0.5 M KOH electrolyte at the rate of 50 mV s^{-1}. (b) Column chart of specific (black) and Pd mass activities (red) in electrocatalytic ethanol oxidation catalyzed by AuPd, Au and Pd nanoicosahedra in the 1 M EtOH/0.5 M KOH electrolyte. (c) UV-visible spectra of AuPd, Au and Pd nanoicosahedra made in different $HAuCl_4/H_2PdCl_4$ ratios. (d) Reaction rate constants (min^{-1}) of 4-nitrophenol reduction catalyzed by AuPd, Au and Pd nanoicosahedra in dark and under illumination of visible light. The condition of blank indicates no catalyst used in the reaction.

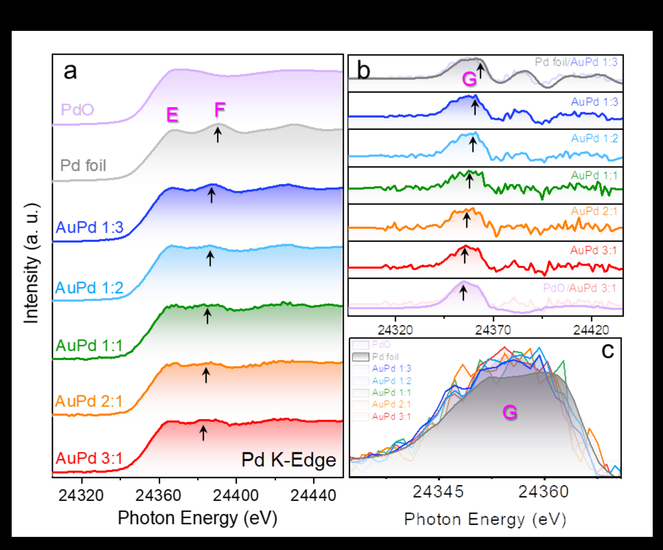


Figure 3. (a) Pd K-edges of AuPd nanoicosahedra along with Pd foil (bulk) and PdO for references. (b) Stacked and (c) overlaid first-differential spectra converted from (a).

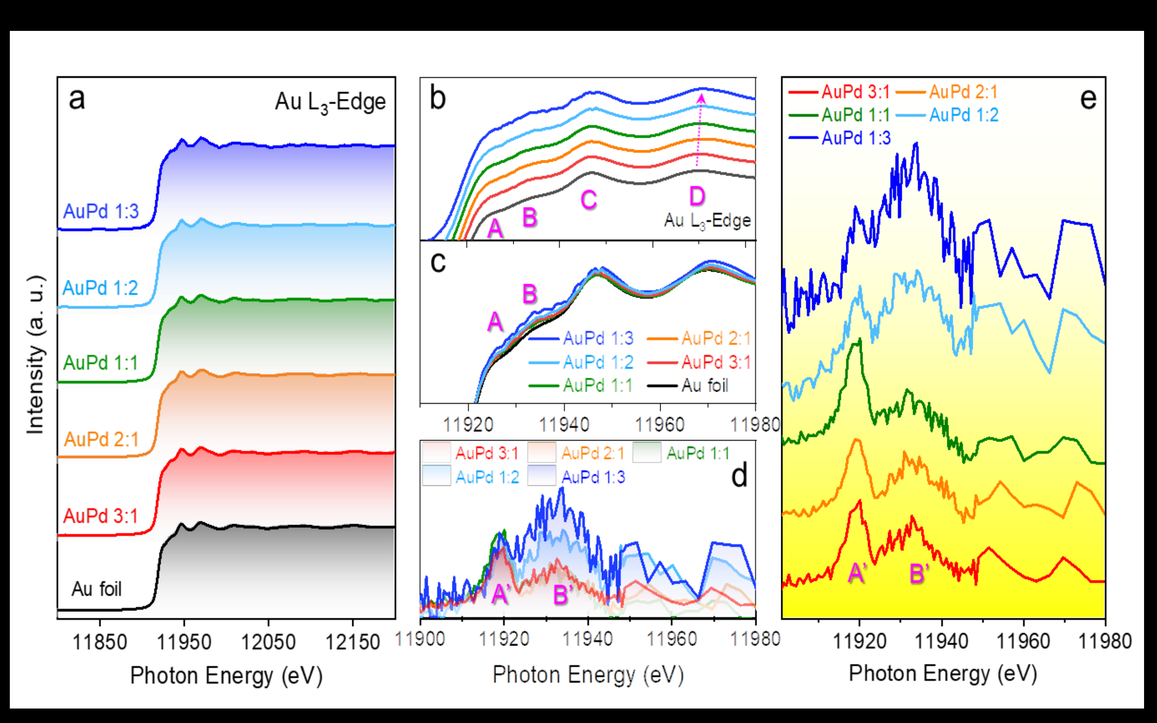


Figure 4. (a) Au L_3-edge of AuPd nanoicosahedra along with Au foil (bulk) for reference. (b) Stacked and (c) overlaid edge spectra in the interested energy range. (d) Derivative spectra obtained by subtracting the spectrum of Au foil from those of AuPd nanoicosahedra. (e) Evolutions in the features A' and B' revealed in the stacked spectra from (d).

References

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