

# Lateral Etching of Core-Shell Au@Metal Nanorods to Metal-Tipped Au Nanorods with Improved Catalytic Activity

Xia Guo<sup>†</sup>, Qiao Zhang<sup>†</sup>, Yanghui Sun<sup>‡</sup>, Qing Zhao<sup>‡</sup>, and Jian Yang<sup>†§</sup>

<sup>†</sup> School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou 510640, People's Republic of China

<sup>‡</sup> State Key Laboratory for Mesoscopic Physics, and Electron Microscopy Laboratory, Department of Physics, Peking University, Beijing 100871, People's Republic of China

<sup>§</sup> School of Chemistry and Chemical Engineering, Shandong University, Jinan 250100, People's Republic of China

ACS NANO, Article ASAP

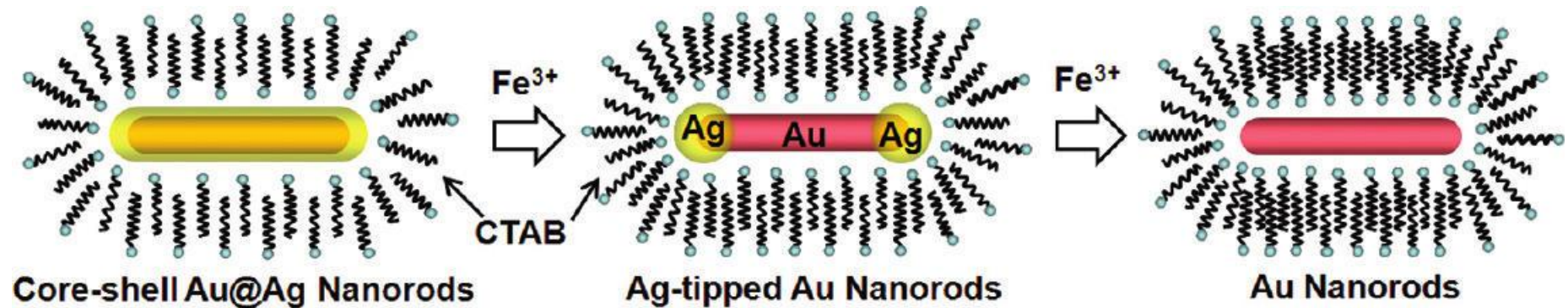
Anirban Som  
24-02-2012

# Introduction

- Efficient organization of different building blocks into well-defined nanostructures has attracted extensive attention, due to diverse organization modes, tunable physical properties, and great application potential.
- Small size of the building blocks on the order of nanometers brings about obvious challenges for this assembly.
- Great efforts have been devoted to this field for years, particularly in the formation of dumb-bell like nanocrystals where different building blocks are located in a linear alignment.
- Till date, the dumb-bell like nanohybrids are usually achieved by the selective growth of a second component material at the ends of nanorods.
- Selective growth in this cases originate from the high reactivity of the crystal facets at the ends of the nanorods, which might be caused by less surface passivation, highindex crystal facets, and/or large surface curvature.
- Selective growth always necessitates special seeds, complex surfactants, and strict experiment conditions. Otherwise, the growth control will be lost in the product.

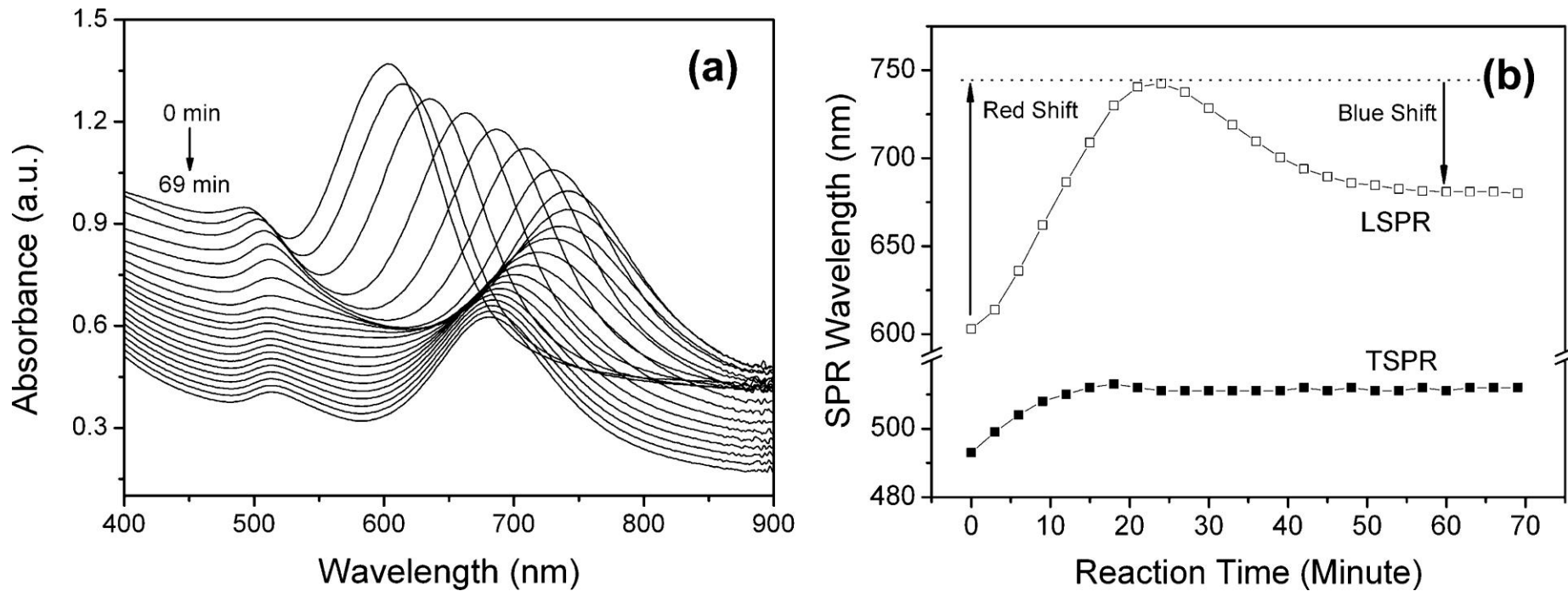
- Preferential etching of one-dimensional nanostructures is concentrated on the single-component systems so far.
- Preferential etching of the gold nanorods was achieved either by oxygen in the presence of  $\text{Cu}^{2+}$  and ascorbic acid or by  $\text{Fe}^{3+}$  in the presence of CTAB.

## In this paper

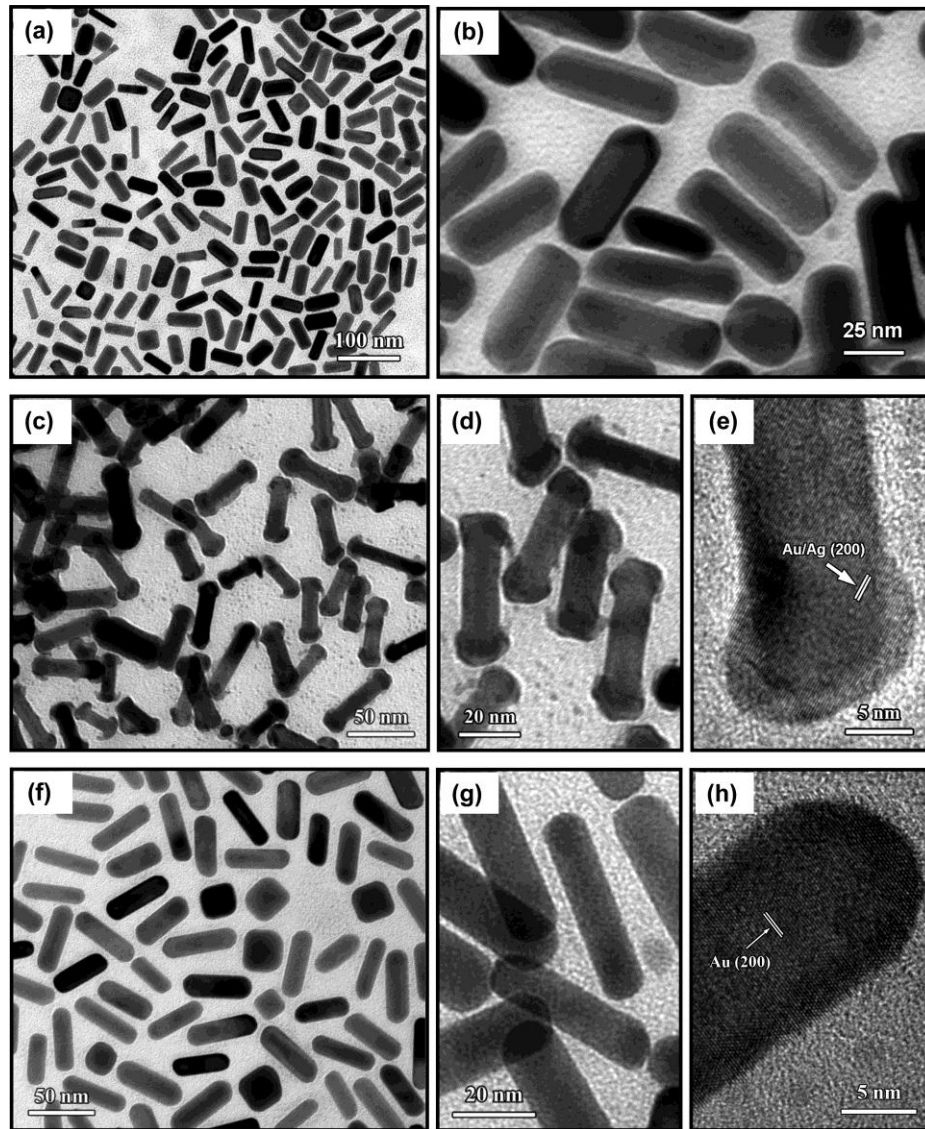


- The preferential etching has been successfully extended for other metal-tipped gold nanorods that have not been synthesized by the selective growth.
- The dumbbell-like Ag-tipped Au nanorods are demonstrated to be an excellent catalyst for the reduction of p-nitrophenol at room temperature, much better than the gold nanorods and the coreshell nanorods.

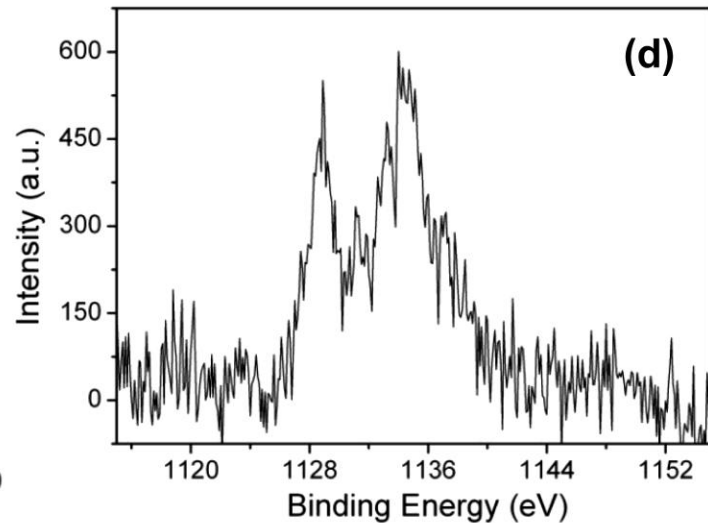
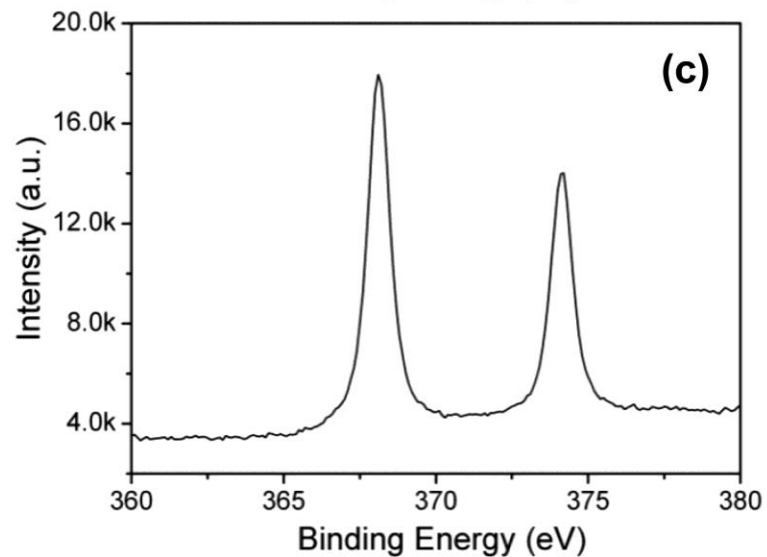
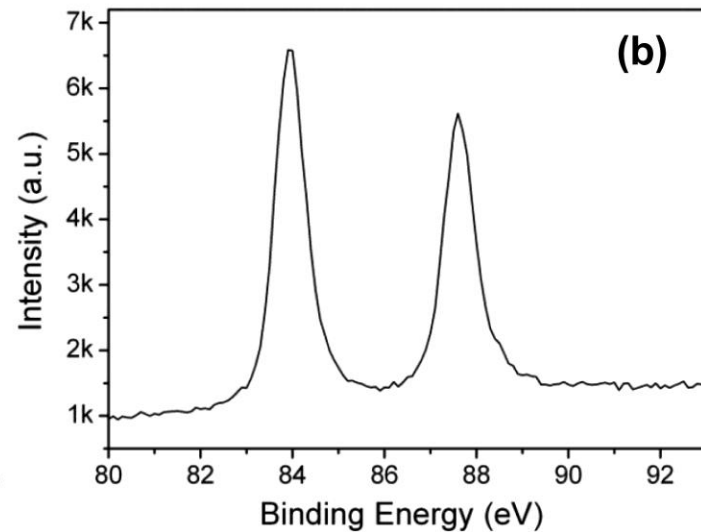
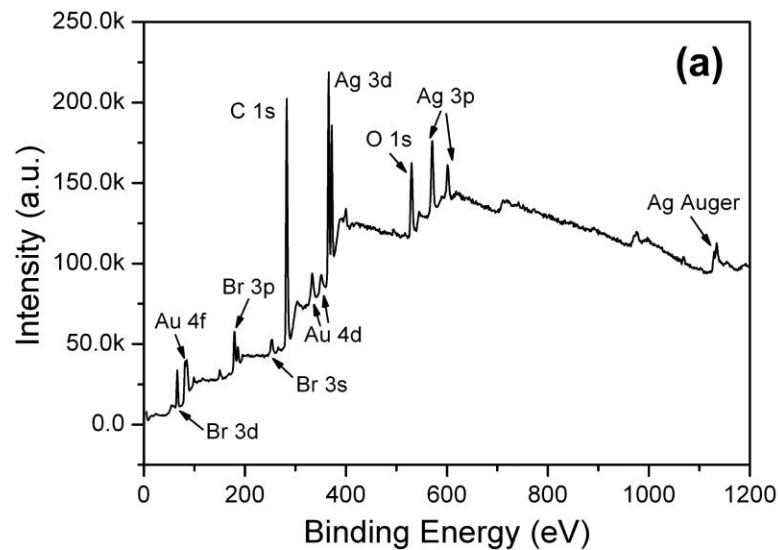
# Result and Discussion



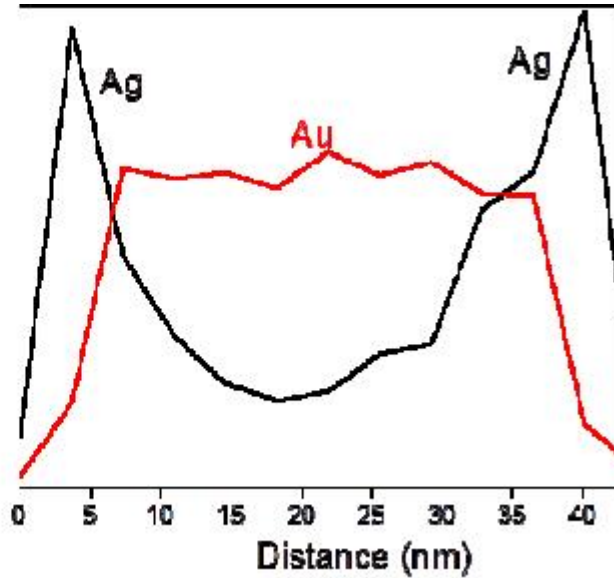
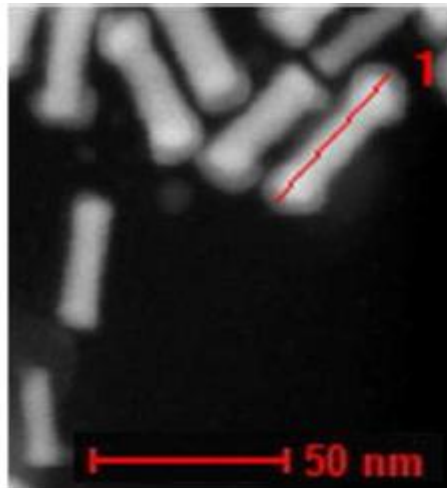
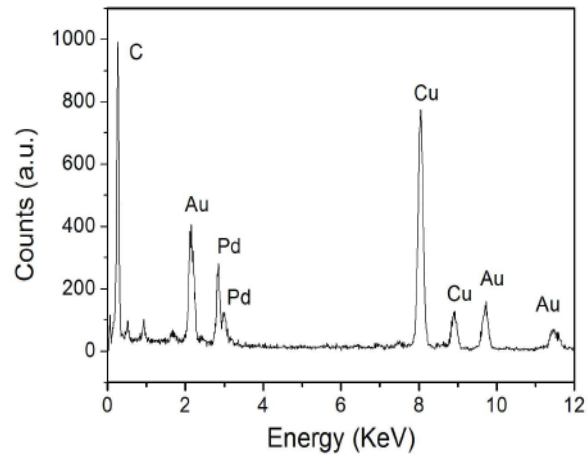
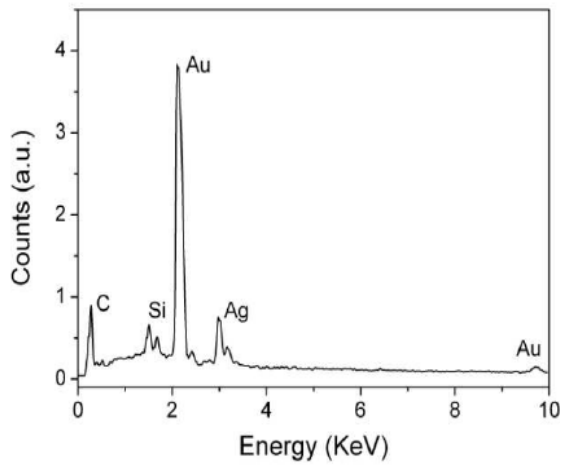
(a) UV-vis absorption spectra of the solution in which Au@Ag core-shell nanorods reacted with 25  $\mu\text{L}$  of 10 mM  $\text{FeCl}_3$ . The absorption spectra were measured at a regular interval. (b) Temporal evolution of the SPR peak positions (longitudinal surface plasmon resonance, LSPR, and transverse surface plasmon resonance, TSPR) during the reaction.



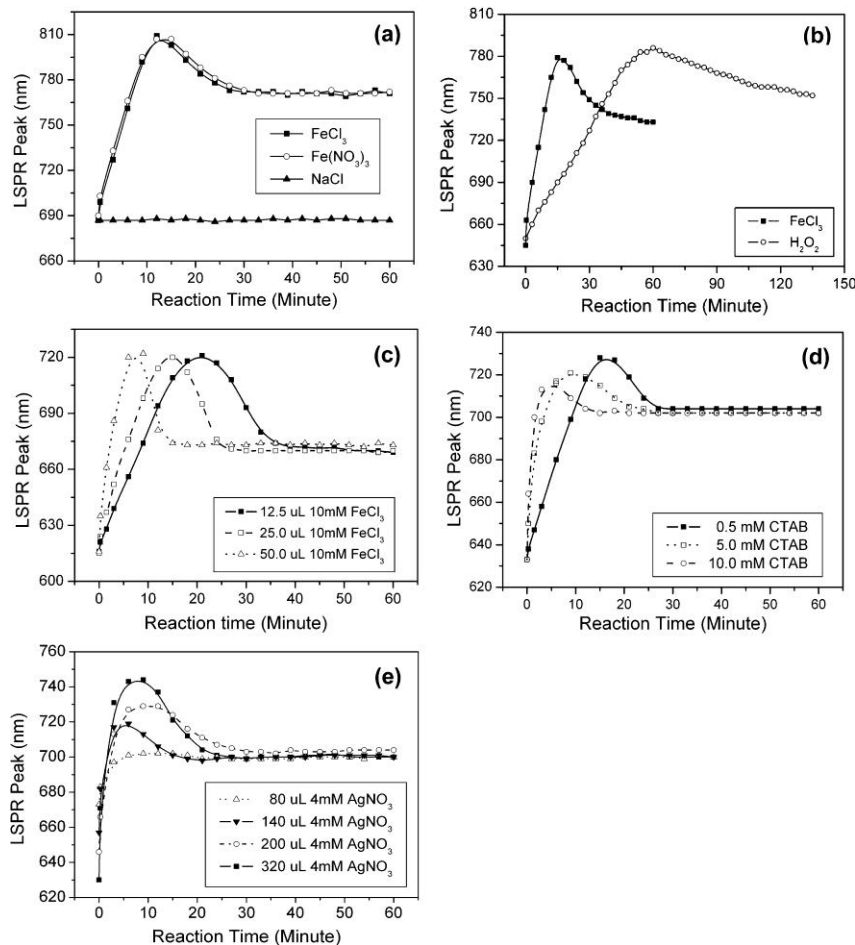
TEM and HRTEM images of Au@Ag core-shell nanorods (a,b), the etched product (c-e), and the final product when LSPR stops moving (f-h).



XPS spectra of the dumbbell-like Ag-tipped gold nanorods. (a) Survey spectrum, (b–d) high-resolution spectra of Au 4f, Ag 3d, Ag M<sub>2</sub>V.

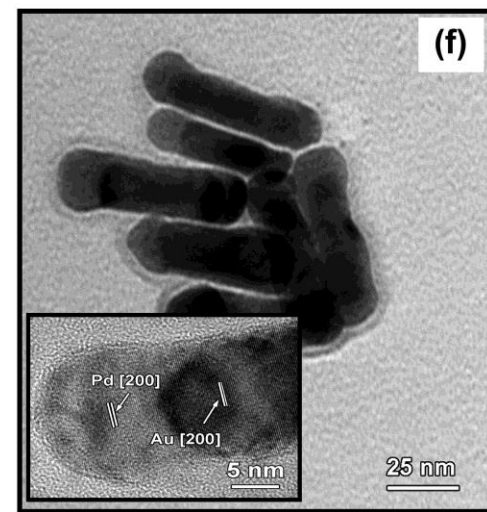
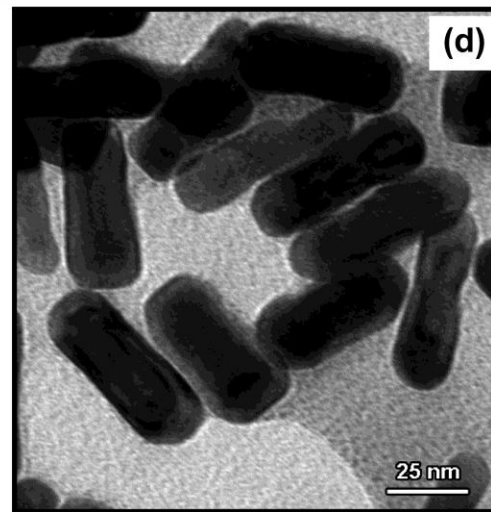
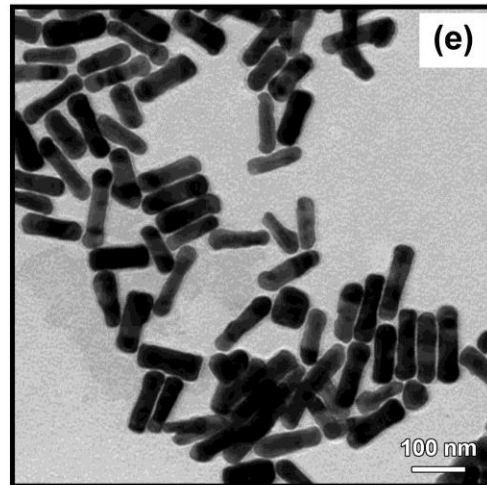
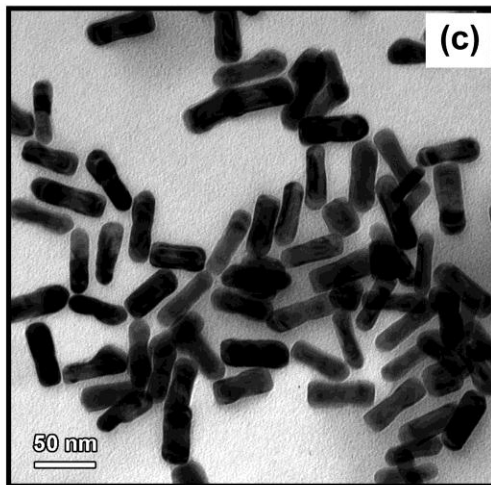
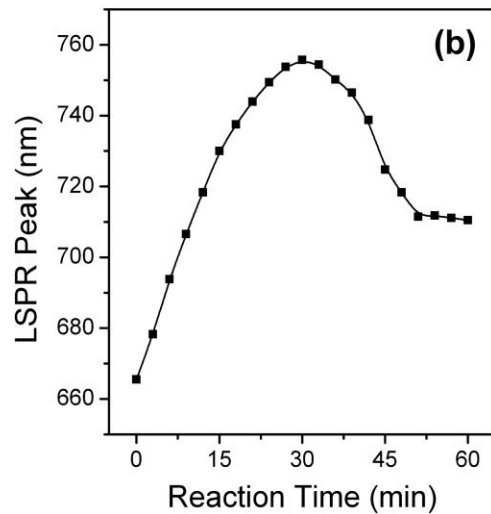
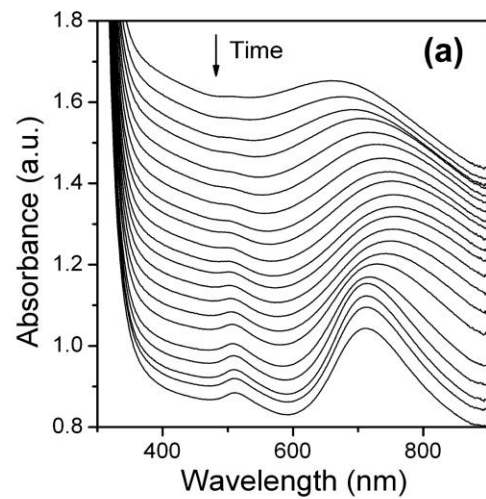


EDS spectrum and line-scanning element analysis of a single dumbbell-like nanorod.

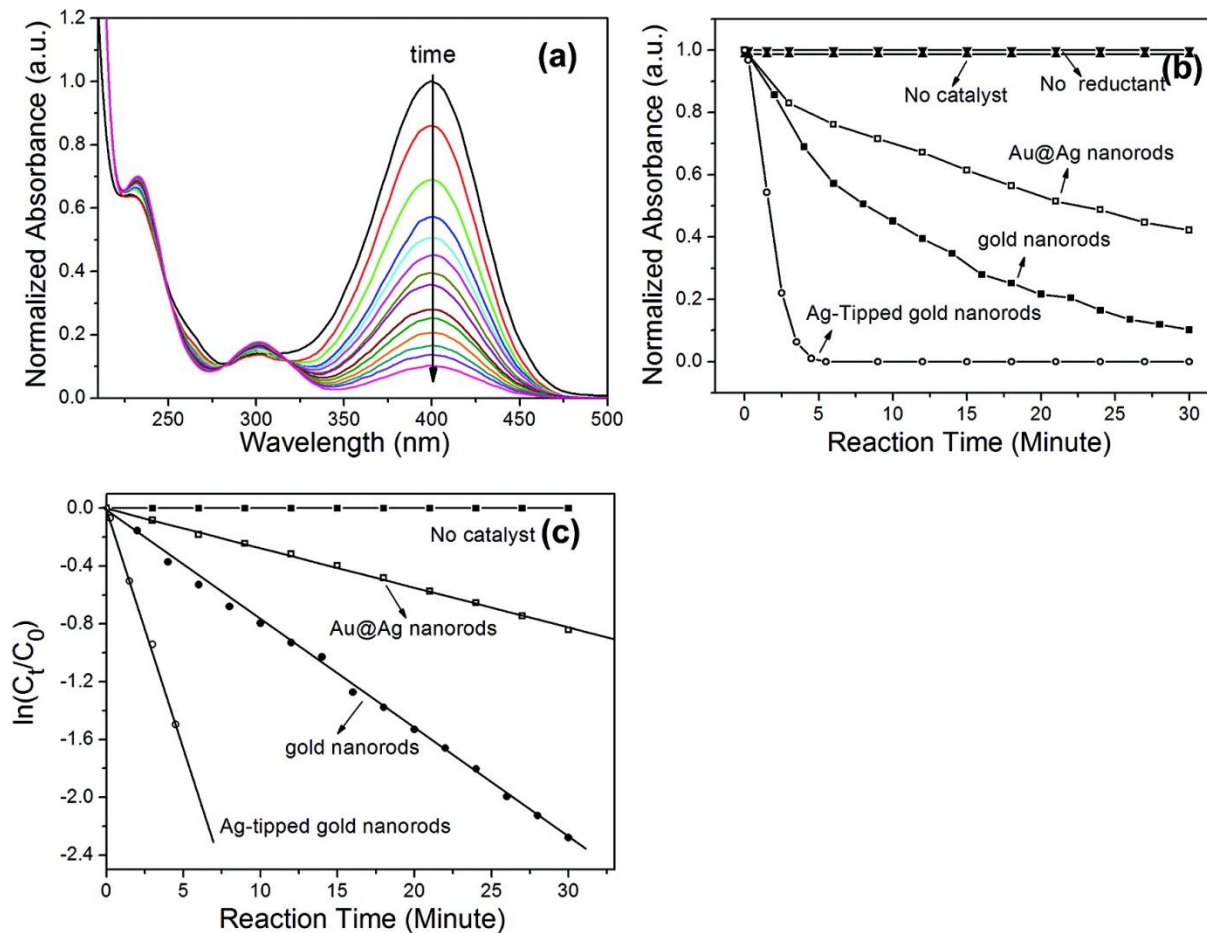


(a,b) Time dependence of the LSPR peak of the product obtained by the etching of core-shell Au@Ag nanorods with different reagents in the presence of 0.5 mM CTAB. (c,d) Time dependence of the LSPR peak of the product obtained by the etching of core-shell Au@Ag nanorods with different amounts of  $\text{FeCl}_3$  or CTAB. (e) Time dependence of the LSPR peak of the product obtained by the etching of core-shell Au@Ag nanorods in different shell thicknesses. The core-shell nanorods with different shell thicknesses were prepared by using different amounts of  $\text{AgNO}_3$  from the same batch of the gold nanorods.





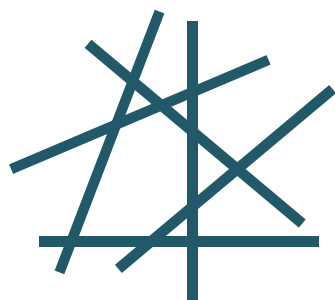
(a) UV-vis absorption spectra of the Au@Pd core-shell nanorods reacted with  $\text{H}_2\text{O}_2$  at different reaction times. (b) Dependence of the LSPR peak on the reaction time. (c,d) TEM images of the Au@Pd core-shell nanorods. (e,f) TEM images of the Pd-tipped Au nanorods. The inset in (f) is the HRTEM image of a Pd-tipped Au nanorod.



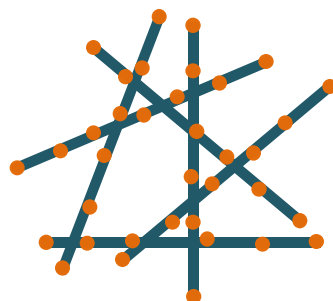
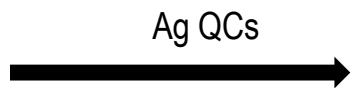
(a) Evolution of the UV-vis absorption spectra of *p*-nitrophenol reduced by  $\text{NaBH}_4$  in the presence of gold nanorods. (b) Normalized absorbance of *p*-nitrophenol at 400 nm as a function of reaction time based on different nanorods as the catalyst. (c) Plots of  $\ln(C_t/C_0)$  versus reaction time for different nanorods as the catalyst.

# Summery

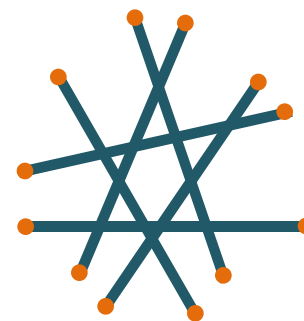
- Monodisperse Ag-tipped gold nanorods were prepared by the preferential etching of the core-shell Au@Ag nanorods with  $\text{FeCl}_3$  in the presence of CTAB.
- Different from the gold nanorods, the side of the core-shell Au@Ag nanorods exhibits a higher reactivity than the tips in the mild oxidation of silver.
- The preferential etching could be extended to other core-shell nanorods, such as Au@Pd nanorods, indicating the promising potential of this preferential etching.
- Catalytic activity of dumb-bell like nanorods is much higher than those of the gold nanorods and the core-shell nanorods, which could be attributed to the electronic effect between gold and silver and the unique structure of dumb-bell nanorods.
- This result shows the great potential of the dumbbell-like nanorods in practical applications, such as catalytic reactions, ultrasensitive detection, and optoelectronic devices.



Te NWs



Ag NPs decorated Te NWs



Dumbbell shaped NWs

Thank You