STEM and EDS Studies of AuAg@Au Core-shell Nanotips for Electrocatalytic Reduction of CO_2 to CO

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Converting greenhouse gas carbon dioxide (CO_2) to value-added chemicals is an appealing approach to tackle CO_2 emission challenges. The chemical transformation of CO_2 requires suitable catalysts that can lower the activation energy barrier, thus minimizing the energy penalty associated with the CO_2 reduction reaction. Au and its alloys are regarded as the most promising CO_2 electric-catalytic reduction catalysts due to their efficient catalytic performance, excellent selectivity and stability. However, the high price of Au limits its application in the CO_2 electric catalytic reduction. There are wo possible alternatives, either replace Au with other cheap elements or improve the performance of Au and its alloy catalysts.

In this work, AuAg@Au Core-Shell Nanotips were synthesized by ascorbic acid assisted galvanic reaction approach. SEM analysis shows that urchin-like Au nanoparticles (NPs) with average size of 130nm were synthesized and the nanotips radiated from the solid spherical core were also observed. TEM images indicate that the NPs contain a unchin-like morphology covered with high-density of nanotips, which is 55±5 nm in length and 4~10 nm in width. In order to examine the microstructure as well as the chemical distribution of the NPs, high-angle annular dark-eld (HAADF) imaging and energy dispersive X-ray spectroscopy (EDS) mapping were performed. The STEM and EDS elemental mapping in Fig. 1 shows that the nanotips are composed of Au with an ultra-thin layer (about 1.3 nm). The EDS elemental line scans, which examine the elemental distribution across several individual nanotips, verify that both Ag and Au elements are found in the thin layer out of the tip and form AuAg binary alloys. Therefore, the nanotips from the urchin-like NPs are proved to be a typical core-shell structure, i.e. the Au core covered with an ultrathin AuAg alloy shell.

Combining with microstructure analysis, we found that by changing the ratio of Au/Ag, the thickness of the thin layer can be systematically varied thus the performance in CO_2 reduction can be accordingly tailored. The experimental results demonstrate that the as-synthesized catalysts exhibits an efficient and selective manner for the CO_2 reduction to CO. The large improvement of the catalytic properties can be attributed to both the urchin-like shape induced tip-enhanced field effect and the ultra-thin AuAg alloy skin with a high density of corn and edges. The catalysts exhibit a high faradaic efficiency of 95% and current density of 34 milliamperes per square centimeter at −0.35 volts, equivalent to a 6-fold improvement in activity compared with that of urchin-like gold NPs with pure Au nanotips.

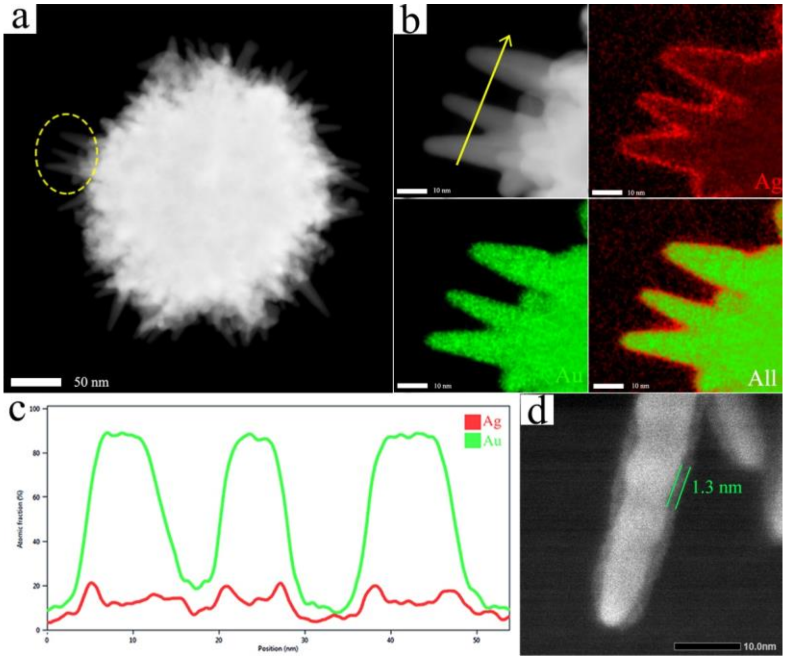

Fig. 1(a) HAADF-STEM image of urchin-like gold NPs (b) EDS mapping of the selected region showing elemental distribution of Ag , Au and their overlay; (c) EDS elemental linescan taken along the yellow line in (b) to demonstrate the elemental composition of nanotips; (d) HAADF-STEM image of nanotips to demonstrate the thickness of the alloy layer.