Chinese Researchers Continue to Make Progress in Anti-Galvanic Reaction Research

A new study entitled "Hard-Sphere Random Close-Packed $Au_{47}Cd_2(TBBT)_{31}$ Nanoclusters with a Faradaic Efficiency of up to 96% for Electrocatalytic CO_2 Reduction to CO" recently appeared in the journal of *Angewandte Chemie International Edition*.

This work was done by Professor WU Zhikun's group at the CAS Institute of Solid State Physics (ISSP) under Hefei Institutes of Physical Science in collaboration with YANG Jun's group at the CAS Institute of Process Engineering (IPE).

They accomplished this by exploring a new concept dubbed "Anti-galvanic reaction (AGR)", which is reaction formally opposite to the classic "galvanic reaction (GR)" with a history of about 240 years. The GR, named after Italian scientist Luigi Galvani, involves the spontaneous reduction of a noble-metal cation by a less noble metal in solution driven by the difference in electrochemical potentials – *e.g.*, bulk metal silver can readily reduce Au(I)/Au(III), but bulk metal Au can hardly reduce Ag(I) under normal conditions. The idea of GR prevails in the industries of electroplating and

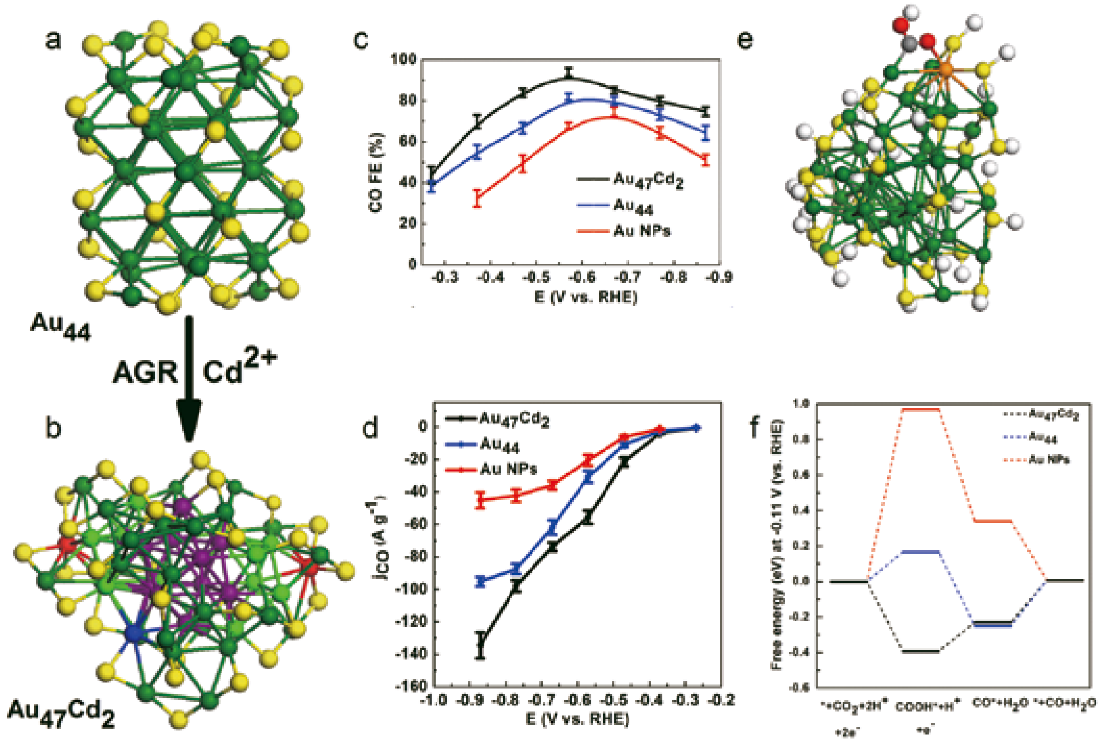

Fig.1. a) $Au_{44}(TBBT)_{28}$; b) $Au_{47}Cd_2(TBBT)_{31}$; c) CO Faradaic efficiency of the investigated catalystsath differently applied potentials; d) The partial current density of CO normalized by Au mass in the catalyst; e) the adsorption configuration of COOH* on $Au_{47}Cd_2$; f) Free energy diagram for electrocatalytic CO_2 reduction to CO on $Au_{47}Cd_2(TBBT)_{31}$, $Au_{44}(TBBT)_{28}$ and Au NPs. (Image by ZHUANG Shengli)

corrosion, as well as in the research areas of nanoscience and nanotechnology. However, the opposite of GR, that is, reduction of metal ions by less reactive (or more noble) metals, has long been regarded as a virtual impossibility

The concept of AGR was firstly proposed by WU in 2012, marking the beginning of a new era, in which AGR received widespread attention and was extensively studied. Subsequently, WU's group conducted researches on its mechanism and application (including application in ion recognition, synthesis, and so on) of anti-galvanic reaction, and made a series of progresses.

In the early stage, TIAN Shubo, *et al*. revealed that "AGR" depends on the ion precursor and ion dose (*Chem. Commun.*, 2015, 51, 11773), inspired by which, ZHUANG Shengli, *et al*. established the "two-phase AGR" method taking advantage of the high reaction activity of the surface and interface, and synthesized the $Au_{47}Cd_2$ clusters that cannot be obtained by the single-phase method (Fig. 1a, b), which provides a new routine for the accurate synthesis of alloy nanoclusters.

It is interesting that this novel alloy cluster not only exhibits a special hard-sphere random close-packed structure (Fig. 1b), but also shows a higher Faraday efficiency (96%, Fig. 1c) for electrocatalytic reduction of CO_2 to CO. Its performance is better than not only the precursor clusters, but also most of the reported catalysts, and is among the list of highest electrocatalytic efficiency reported so far.

As we all know, cadmium is a heavy metal that endangers the environment. The introduction of cadmium into gold clusters through "two-phase AGR" can significantly improve the catalytic efficiency of the precursor clusters, and therefore turn bane into boon, having important implication for environmental improvement. The accurate compositions and structures of metal nanoclusters provide prerequisites for deep understandings of catalytical mechanisms.

Further theoretical calculation shows that the introduction of active metal Cd changes the adsorption configuration of intermediate product COOH* on the cluster surface (see Fig. 1e), and changes the reaction kinetics (see Fig. 1f), thus significantly improving the catalytic efficiency.

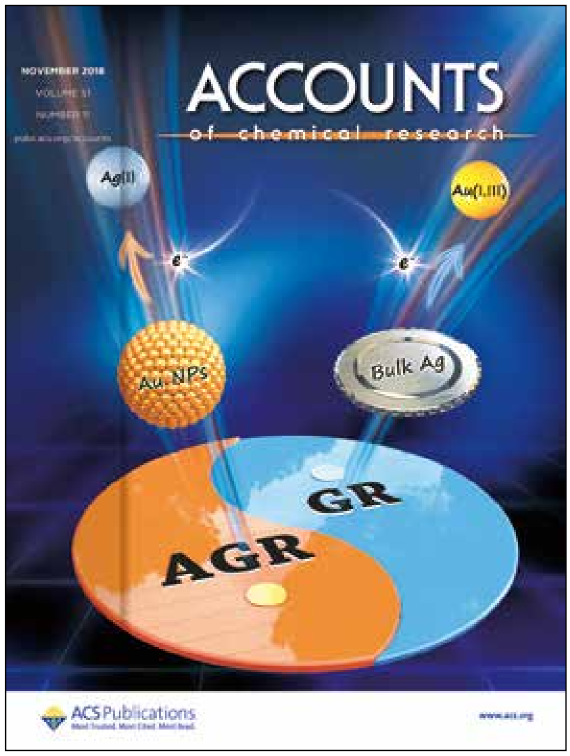

Fig. 2. This artwork, appeared as the cover for one issue of the *Accounts of Chemical Research*, illustrates the unexpected antigalvanic reaction (AGR) and its application in engineering metal nanoparticles, sensing, and anti-oxidation. (Credit: WU's lab, ISSP)

Given WU's pioneering contribution to the AGR, he was invited to write a review entitled "Discovery, Mechanism, and Application of Antigalvanic Reaction" in the famous review journal (*Acc. Chem. Res*. 2018, 51, 11, 2774-2783) to summarize many great advances that have been made on the AGR, as well as to expect to draw more brilliant minds into this exciting area.

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References

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