

USING GOLD CORE PALLADIUM SHELL NANOPARTICLES AS SURFACE-ENHANCED RAMAN SCATTERING SUBSTRATES

J. W. Hu, Y. Zhang, S. G. Sun and Z. Q. Tian *

State Key Laboratory for Physical Chemistry of Solid Surfaces, Xiamen University, Xiamen 361005, P. R. China; E-Mail: zqtian@xmu.edu.cn

Keywords: *nanoparticle, SERS, core-shell structure, gold, palladium, adsorption*

Abstract: This contribution explores the possibility of using highly monodispersed Au core Pd shell nanoparticles to obtain SERS from adsorbate at transition metal surfaces. Using CO as a probe molecule, we observe that Au@Pd core-shell nanoparticles exhibit strong SERS activity.

Since the discovery of surface-enhanced Raman scattering (SERS), most works were restricted to three SERS-active metals, Au, Ag and Cu, which show the highest SERS activity [1]. Considering practical importance of transition metals in catalysis, people have dedicated to extend SERS to transition metals for a long time in order to provide insight to the interface processes between a solid-phase catalyst and its adsorbate at a molecule-level. With the advent of confocal Raman instrument and special procedures to rough metal electrode, our group has obtained SERS spectra from many transition metals [2]. However, the SERS activity from transition metals is considerably weaker than that from the typical SERS substrates such as Au and Ag. To overcome this problem, a “borrowing method” in virtue of the long-range effect of electromagnetic mechanism of SERS was employed, i.e., coating an ultrathin transition metal film on a SERS-active metal [3–5]. We therefore explored the possibility of using highly monodispersed Au core Pd shell nanoparticles to obtain SERS from adsorbate at palladium metal surface. This approach is partly assisted by the ever-developing techniques of nano-science. It may provides nanostructures with tailored elements (size, shape and arrangement etc.) that are important for gaining the knowledge about SERS and the nanostructures.

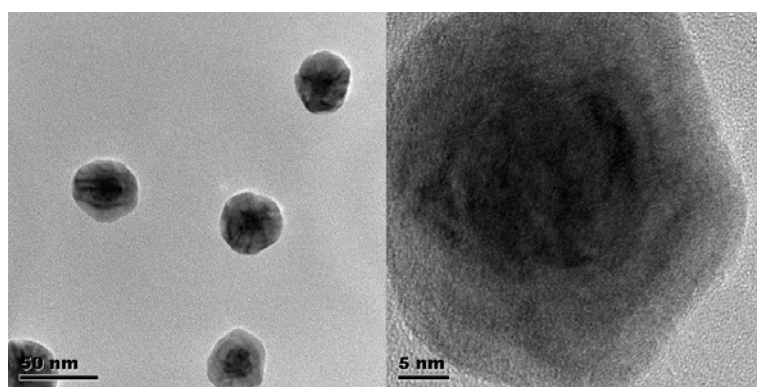


Fig.1. High resolution TEM images of the *Au@Pd* nanoparticles.

A series of high monodisperse, uniform Au@Pd nanoparticles with controllable size were first synthesized by the Au seed mediated chemical reaction procedure [6]. The as-prepared nanoparticle solution was then dried on a SERS-inactive glass carbon electrode, which serves as the SERS substrates [7]. Fig. 1 shows the high resolution TEM images of the core-shell nanoparticles; a core encapsulated with a shell can be clearly distinguished. Cyclic voltammograms of these nanoparticle assembled substrates (denoted as Au@Pd/GC) confirm undoubtedly that the electrochemical property of these nanoparticles are identical to the pure Pd metal, without any interference from the

encapsulated Au cores. It indicates that continuous Pd shells, being free of “pinholes”, are formed around the Au cores. Carbon monoxide (CO) was then chosen as a probe molecule for the present study, because it shows characteristic SERS features on different metals. Fig. 2 shows the potential-dependent SERS spectral sequences for a saturated CO adlayer on the Au@Pd/GC electrode in 0.1 M H₂SO₄. Two C-O stretching bands around 1915-1975 and 2025-2095 cm⁻¹ appear at the high frequency regions, which are attributed to the bridge and atop bonded CO respectively [2]. In the low frequency regions, only a single broad band at about 365 cm⁻¹ is present and attributed to the Pd-C bond of the bridge-bonded CO [2]. No band is observed at ca. 2110–2135 cm⁻¹, characteristic of the C-O stretching of CO bound to Au. This also demonstrates that the “pinhole-free” Au@Pd nanoparticles exhibiting high SERS activity can avoid spectral interference of the Au cores. The core-shell nanoparticle systems may have great potential for investigating not only electrocatalysis but also the SERS mechanism.

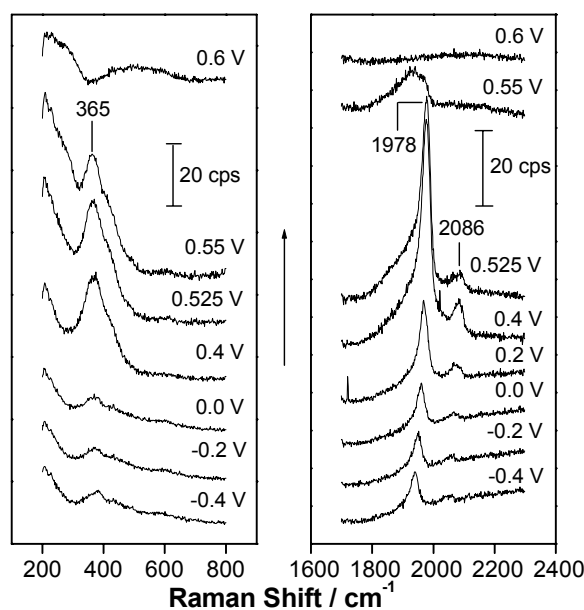


Fig. 2. Potential-dependent SERS spectra for a saturated CO adlayer on the Au@Pd/GC electrode. Potentials were changed stepwise from -0.4 to 0.6 V. Each spectrum was acquired for a single 100 s accumulation at 632.5 nm excitation.

Acknowledgements:

We thank NSFC for Financial support (20021002 and 90206039).

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