

# Effect of Crystalline Orientations of Gold on Surface-enhanced Raman Scattering Spectroscopy of Polypyrrole

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Surface-enhanced Raman scattering (SERS) occurring on roughened metal substrates in principle provides a powerful means of obtaining vibrational information on adsorbate-surface interactions in view of its unique sensitivity and excellent frequency resolution. The mechanism of SERS as it is now generally accepted consists of two major components. One of the electromagnetic enhancement,<sup>1,2</sup> resulting from an apparent increase in the Raman cross section, is quite well understood. However, the other of the chemical enhancement,<sup>3,4</sup> concerning about the charge transfer on the adsorbate-metal surface, is poorly understood compared to the electromagnetic enhancement. Parsons<sup>5</sup> reported that the behavior of polycrystalline metals is a complex average which is difficult to understand without measurement on simpler systems and the redox behavior of metal in cyclic voltammetry (CV) is markedly dependent on the face of crystal exposed. Also, Bukowska et al.<sup>6</sup> reported that the change of the surface structure via ORC treatment significantly influences the corresponding SERS effect. Furtak and Roy<sup>7</sup> reported that SERS is sensitive to molecular orientation and to direct proximity with the substrate. These studies revealed that the crystalline orientation of metal is an important factor influencing the SERS enhancement. Therefore, Sanda et al.<sup>8</sup> studied the vibrations and structure of pyridine chemisorbed on single-crystal Ag (111). Caldwell et al.<sup>9</sup> studied the highly ordered self-assembled monolayer film of an azobenzalkane thiol on single-crystal Au (111).

Since SERS effect takes place at the interface of roughened metal, a complex film formed on the activated metal during an ORC treatment thus plays an important role. However, few efforts concerning about the effects of metal orientations on the complex formed in ORC treatment and on the SERS effects had been made. In this study, PPy films were originally electropolymerized on Au substrates with different predominant orientations of (111) and (220), respectively, roughened by a triangular-wave ORC in an aqueous solution to investigate the relationship between crystalline orientations of gold and SERS spectroscopy of PPy. Also a mechanism of the roughening procedure on gold was also proposed to illustrate the resulting complex and its effect on the SERS enhancement. The results indicate that the (220) crystalline orientation of gold was partially changed into (111) one after gold was roughened with ORC treatment. The SERS spectroscopy of PPy deposited on gold with a predominant (111) orientation exhibits higher intensity, more than four fold, and more excellent resolution. Meanwhile, the redox behavior and complex formed on gold in ORC was strongly sensitive to the crystalline orientation. The complexes are  $\text{Au}(\text{ClO}_4)_4^-$  and  $\text{AuCl}_4^-$  for Au substrates with predominant orientations of (111) and (220), respectively.

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