

ELECTROCHEMICAL SURFACE-ENHANCED RAMAN SPECTRA AND PLASMON-DRIVEN PHOTOELECTRO-CHEMICAL REACTION OF P-AMINOTHIOPHENOL ON SILVER ELECTRODE OF NANOSTRUCTURES

MENG ZHANG, DE-YIN WU^a, ZHONG-QUN TIAN, *College of Chemistry and Chemical Engineering, Xiamen University, Xiamen, China.*

Surface plasmon resonance (SPR) of noble metal nanoparticles (NPs) provides a pathway to efficiently absorb and confine light to nanoscale surface electrons, thereby bridging photonics and photoelectrochemistry. This not only produces the giant Raman intensity enhancement in surface-enhanced Raman spectroscopy (SERS), but also results in plasmon-driven chemical reaction on metal nanostructures. We have studied the surface-enhanced Raman spectra of p-aminothiophenol adsorbed on silver electrodes of nanostructures. In this work, we studied SPR-enhanced photoelectrochemical synergistic reactions by SERS to improve chemical reaction activity and examine changes in reaction selectivity. We first demonstrate that hot carriers arising from SPR decay contribute to the surface catalytic coupling reaction of PATP on a silver NP electrode. Then, by using potential step electrochemical SERS, we further inspect the kinetics of the surface catalytic coupling reaction by monitoring the time-dependent SERS intensity of the characteristic band at 1436 cm^{-1} , which can be attributed to the stretching vibration of the N=N double bond of p,p'-dimercaptoazobenzene (DMAB). When synergistically combined with the modulation of pH at electrochemical interfaces, SPR-enhanced photoelectrochemical reactions can be further gain reaction efficiency and selectivity for the formation of DMAB and other surface species at higher potentials. The electrochemical SPR effect provides a viable approach for studying the photoelectrochemistry through combining SERS at the interface of nanoparticle-modified metal electrodes and electrolytes.

^aEmail: dywu@xmu.edu.cn