SERS and Photocatalysis of Oxygen Reduction at Bis-(4-Pyridyl)Acetylene-Covered Silver

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We have observed that, when 1,2-bis-(4-pyridyl)acetylene (BPA) is adsorbed at an electrochemically roughened silver electrode, reduction of dissolved oxygen commences upon irradiation at voltages (e.g., -0.1V vs. Ag/AgCl) better than 200 mV positive of where reduction occurs in the dark (-0.3V). Catalysis of the oxygen reduction reaction is an important target of research efforts directed toward improving the efficiency of fuel cell energy production[1].

Unlike adsorbed stilbazole, which is photooxidized to hydroxy-stilbazole when irradiated in the presence of oxygen [2], BPA is not appreciably oxidizable, serving instead as a stable electron source for oxygen reduction during irradiation. The light appears to excite a silver-to-BPA electron transfer leaving a radical anion (BPA⁻) that readily delivers reducing equivalents to oxygen, catalyzing its reduction. That same excitation may resonantly enhance the surface Raman intensity.

While not easily oxidized, BPA undergoes electroreduction itself, albeit at potentials slightly more cathodic than oxygen reduction. As shown in Fig. 1, the SERS of BPA at -0.1V compares readily with the normal Raman in chloroform. At -0.5 V, cathodic of the first reduction wave in the cyclic voltammogram, the SERS indicates reduction of the triple bond with loss of intensity at 2231 cm⁻¹ (C≡C str) and at 1154 cm⁻¹ (φ-C str). Additional spectral changes accompany continuation of the cathodic sweep to -1.0 V, over a second reduction wave in the cyclic voltammogram that commences near -0.9 V, where a double bond stretch at 1636 cm⁻¹ is observed, among other lines that are characteristic of an ethylenic bridge between the pyridyl groups (indicated in red). These results indicate sequential one-electron reductions, separated by about a half volt, from acetylenic to ethylenic bridging between the pyridyl groups.

We have observed further that, upon irradiation, adsorbed BPA photocatalyzes the electroreduction of other solution-bound reducible molecules besides oxygen and including the electroreduction of solution-bound BPA itself.

References