An electrochemical method to deposit a monolayer of thiols with very few defects on a gold substrate was developed. The methodology consists in using cyclic voltammetry to oxidatively deposit a monolayer and reductively removing it from a gold substrate for up to 10 times. This first step is followed by a deposition of a monolayer at a fixed potential for less than 15 minutes. The characterization of the resulting monolayers by electrochemical AC impedance spectroscopy reveals a resistance to the charge transfer of a redox couple (ferri/ferrocyanide) that is much larger than the one of monolayers deposited in absence of an electric field. This resistance is found to increase with the thickness of the monolayer. IRAS spectra are compatible with the electroformation of relatively ordered monolayers. A method to generate holes of nanometric dimension in these low defect monolayers by reductively removing a controlled amount of adsorbed thiols is being developed. Preliminary atomic force microscopy results show that circular holes of a few tens of nanometers of diameter can be created by reductive desorption. These holes will used to grow metal nanoparticles and to form mixed monolayers.