Supplementary Material (ESI) for Chemical Communications

Supporting information

In-source photocatalytic reduction of disulfide bonds during laser desorption ionization

Liang Qiao, Hongyan Bi, Jean-Marc Busnel, Baohong Liu and Hubert H. Girault

Department of Chemistry, Fudan University, Shanghai 200433, China, and Laboratoire d'Electrochimie Physique et Analytique, Ecole Polytechnique Fédérale de Lausanne, Station 6, CH-1015 Lausanne, Switzerland.

Reagents:

Titanium dioxide nanoparticle was obtained from Degussa (P25, Germany). Acetonitrile (ACN, 99.9%) and ethanol (99.8%) were purchased from Fluka, Germany. Trifluoroacetic acid (TFA, 99%) was purchased from Acros organics, Belgium. L-glucose (98%), citric acid (99%), 2,5-Dihydroxybenzoic acid (DHB, 98%) and human insulin were obtained from Sigma-Aldrich, Germany. All these reagents were used as received without further purification. Deionized water (18.2 MΩ.cm) used for all experiments was obtained from a Milli-Q system (Millipore, Bedford, MA, USA).

Preparation of TiO_2 modified target plate:

The P25 TiO_2 nanoparticles were heated at 300°C for 2h and then separated in a mortar for another 2h to remove impurity and decrease aggregation. After separating, the nanoparticles were suspended in 89% ethanol (100mg/ml), followed by sonication for 1 h. Before use, this suspension was diluted in deionized water by 25 times. The diluted suspension of TiO_2 nanoparticles was dropped on a stainless steel plate as an array of spots (~2μL) and dried at room atmosphere and temperature overnight. The Resulting modified plate is subsequently heated in an oven at 400°C for one hour (The oven temperature rises from room temperature to 400°C in 30 minutes) and naturally cooled-down to room temperature and stored at 60°C in an oven.

In-source reduction of disulfide bond:

The human insulin was diluted in water and kept as a stock solution with a concentration of

17μM. 1μL of the solution was deposited on the sintered TiO_2 nanoparticle spots. The solution was left to dry for ~10 min in ambient condition, and then covered by an overlayer of 1μL glucose or citric acid solution (10mg/ml, dissolved in water) and left to dry for another ~10 min. For conventional MALDI-MS analysis, 1μL of 17μM human insulin was dropped on a commercial steel target plate and dried for ~10 min in ambient condition. The DHB matrix (10mg/ml in 50% acetonitrile, 0.1% trifluoroacetic acid) was deposited as an overlayer and dried for ~5 min. All the mass spectra were obtained in positive linear mode using a Bruker Microflex equipped a nitrogen laser with a wavelength of 337nm.