Electronic Supplementary Material (ESI) for Nanoscale

Experimental Details

Materials and chemicals

Bovine β-casein, bovine serum albumin, ovalbumin, trypsin (from bovine pancreas, TPCK treated), ammonium bicarbonate (NH_4HCO_3), Dithiothreitol (DTT), iodoacetamide (IAA) and 2, 5-dihydroxybenzoic acid (DHB) were purchased from Sigma Chemical (St. Louis, MO). Acetonitrile (ACN) and trifluoroacetic acid (TFA) were purchased from Merck (Darmstadt, Germany). All aqueous solutions were prepared using Milli-Q water by Milli-Q system (Millipore, Bedford, MA). Graphene was purchased from Shanghai Boson Technology Co. Ltd. All other chemicals and reagents were of analytical grade and were purchased from Shanghai Chemical Reagent.

Characterization of TiO_2/graphene composites

The morphologies of the as-synthesized TiO_2/graphene composites were studied under transmission electron microscopy (JEM-2100F) and scanning electron microscopy (XL30) respectively. Powder X-ray diffraction (XRD) patterns were recorded on a Bruker D4 X-ray diffractometer with Ni-filtered Cu K_R radiation (40 kV, 40 mA). Nitrogen adsorption and desorption isotherms were measured using Micromeritics ASAP 2020. The samples were degassed in a vacuum at 200^{o}C for 8 h prior to measurement. The Brunauer-Emmett-Teller (BET) method was utilized to calculate the specific surface areas (S_{BET}) using adsorption data in a relative pressure range from 0.18 to 0.35. By using the Barrett-Joyner-Halenda (BJH) model, the pore

volumes and pore size distributions were derived from the desorption branches of the isotherms, and the total pore volumes (V_t) were estimated from the adsorbed amount at a relative pressure P/P0 of 0.992.

Preparation of standard protein digests

Bovine β-casein, ovalbumin and Bovine serum albumin (BSA) were dissolved in 25mM NH_4HCO_3 buffer at pH 8.3 and treated with trypsin (2%, w/w) for 16 h at 37 °C respectively. Before the digestion, ovalbumin and BSA were reduced with DTT and carboxamidomethylated with iodoacetamide respectively. Bovine β-casein was digested directly.

Selectively enrichment of phosphopeptides from tryptic digestion of standard proteins

First, the peptide mixtures originating from tryptic digestions were diluted by 50% acetonitrile and 0.1% TFA aqueous solution (v/v), and suspension of TiO_2/graphene composites (400μg) was added into 200 μL of diluted peptide mixture. Then the mixed solutions were vibrated at 25°C for 30 min. After that, through centrifugation, the pellucid solutions were taken out. After that, the TiO_2/graphene composites were washed with 50% acetonitrile and 0.1% TFA aqueous solution (v/v) for three times. Finally the peptides captured by TiO_2/graphene composites were eluted with 5 μL of 0.4M ammonia aqueous solution for 10min and the eluate was analyzed by MALDI-TOF MS.

MALDI-TOF MS analysis

MALDI-TOF MS experiments were performed in the reflector TOF detection modes on a 5800 Proteomics Analyzer (Applied Biosystems, USA) with the Nd-YAG laser at 383 nm, a repetition rate of 200Hz and an acceleration voltage of 20 kV. All spectra were taken from signal-averaging of 800 laser shots with the laser intensity kept at a proper constant.

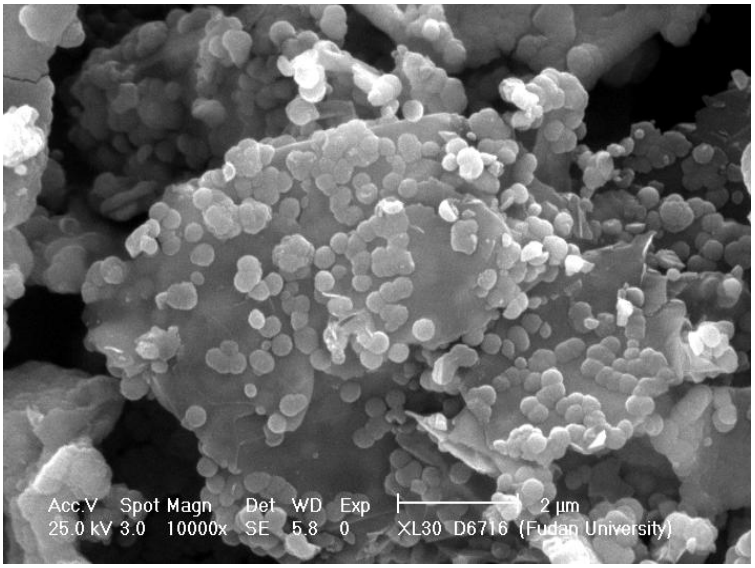

Figure S1. SEM image of TiO_2 nanospheres on graphene sheets.

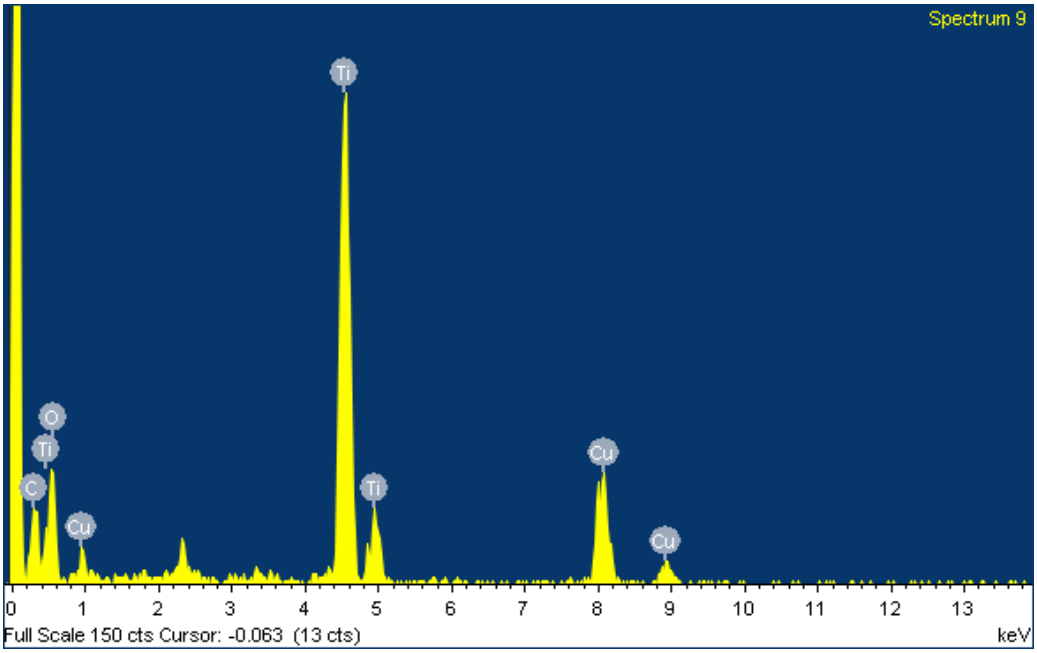

Figure S2. The energy-dispersive X-ray analysis (EDXA) of the illuminating electron beams on TiO_2/graphene composites.