Photoelectrochemical Aptasensor for Tetracycline based on the Self-assembly of 2D MoS_2 on 3D ZnO/Au/ITO Electrode

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Reagents and Instrumentations

Zinc acetate dihydrate, zinc nitrate hexahydrate, hexamethylenetetramine (HMTA), 1,3-diaminopropane, doxycycline (DOX), chloramphenicol (CAP), kanamycin (KAN), chlortetracycline (CTC) and neomycin (NEO) were obtained from Aladdin Reagents Ltd (Shanghai, China). Chloroauric acid tetrahydrate ($HAuCl_4 \cdot 4H_2O$), was purchased from Sinopharm Chemical Reagent Co.

Transmission electron microscope (TEM) images were obtained using an HT7700 TEM instrument (HITACHI, Japan). X-ray diffraction (XRD) spectra were recorded by a D8 Advance X-ray diffractometer (Bruker, Germany) using Cu Kα radiation (λ = 1.5418Å). Scanning electron microscope (SEM) image characterized with a Helios G4 CX field emission scanning electron microscope (Thermo Scientific).

Electrode preparation

3D ZnO/Au was prepared by hydrothermal growth method and ultrasonic treatment and drop coated on ITO electrode (3D ZnO/Au/ITO) in Figure S1. The ITO electrode was ultrasonically cleaned in the order of acetone, ethanol, and deionized water, and then blown dry with N_2. The ZnO/Au powder was prepared as a 2.0 mg/mL solution, and 40 μL of the solution was coated on the ITO electrode by drop-casting method. Then it was dried in an oven at 37 °C and used as the photoelectrode for the PEC test.

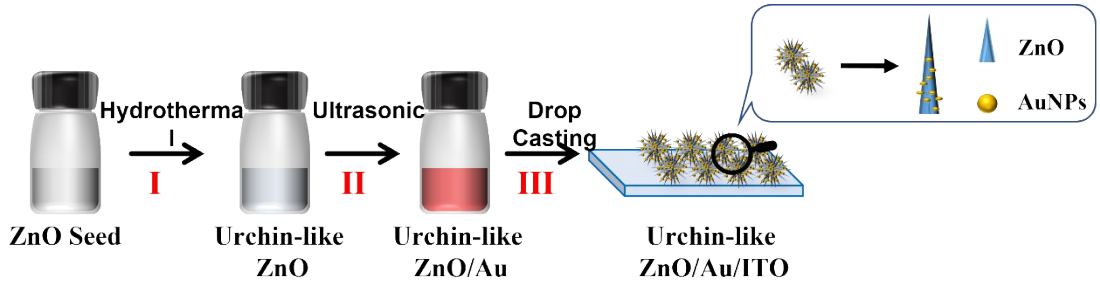

Figure. S1. Schematic diagram of the main preparation process of 3D ZnO/Au.

Materials characterization

Figure S2(A) shows that the synthesized 3D ZnO has a smooth surfaces with a size of about 3 μm. It consists of a large number of nanorods with diameters of 200 - 300 nm, which all point to the same center and are shape like sea urchins. Figure S2(D) clearly shows that the prepared ZnO is with a 3D geometry. Figure S2(B) shows the TEM images of Au NPs with the particle size of 30 - 60 nm uniformly reduced on the surface of 3D ZnO. From the SEM images of ZnO/Au (Figure S2(E)), it can be found that the spatial stereometric structure of ZnO was not damaged after sonication in $HAuCl_4$ precursor solution. The TEM images of MoS_2 in Figure S2(C) adequately demonstrate the planar lamellar structure of MoS_2. The SEM images of MoS_2 is shown in Figure S2(F), which exhibits a nanosheet shape.

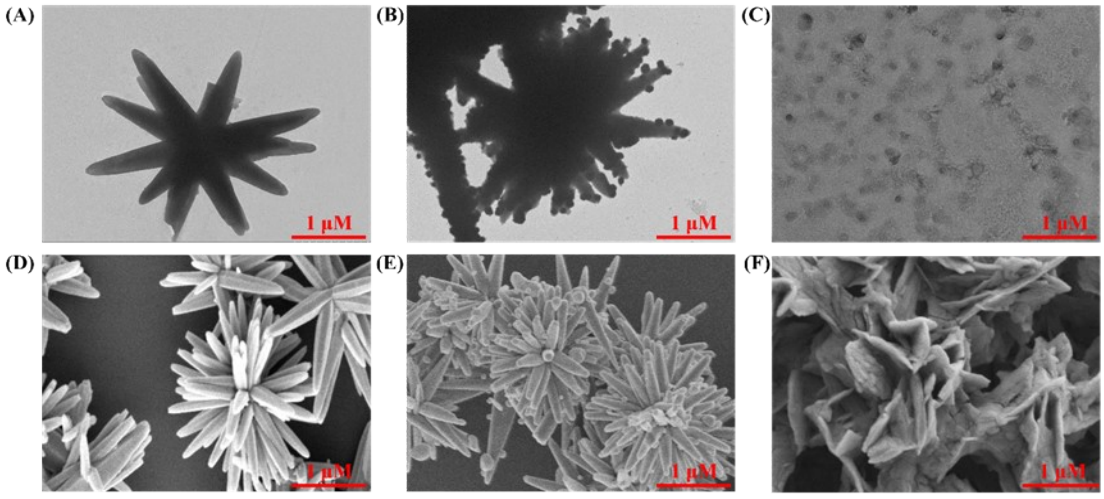

Figure. S2. (A, B) TEM and (D, E) SEM diagrams of 3D ZnO and ZnO/Au.

The crystal structures of the prepared materials were studied by energy dispersive X-ray spectroscopy (XRD). Figure S3 shows the XRD spectra of the ZnO and ZnO/Au samples. Compared with the ZnO standard card, ZnO exhibits mainly six diffraction peaks distributed at 2θ = 31.9°, 34.6°, 36.4°, 47.7°, 56.8° and 63.0°. They correspond to the crystallographic planes (100), (002), (102), (110) and (103) of ZnO crystals, respectively. After in situ growth of Au NPs, the ZnO /Au diffraction pattern shows characteristic peaks similar to those of pure ZnO, but with a non-negligible diffraction peak at 38.3°, which is typical of the (111) crystallographic plane of Au. The weaker diffraction peak of Au compared to ZnO is due to the relatively low content of Au in ZnO/Au.

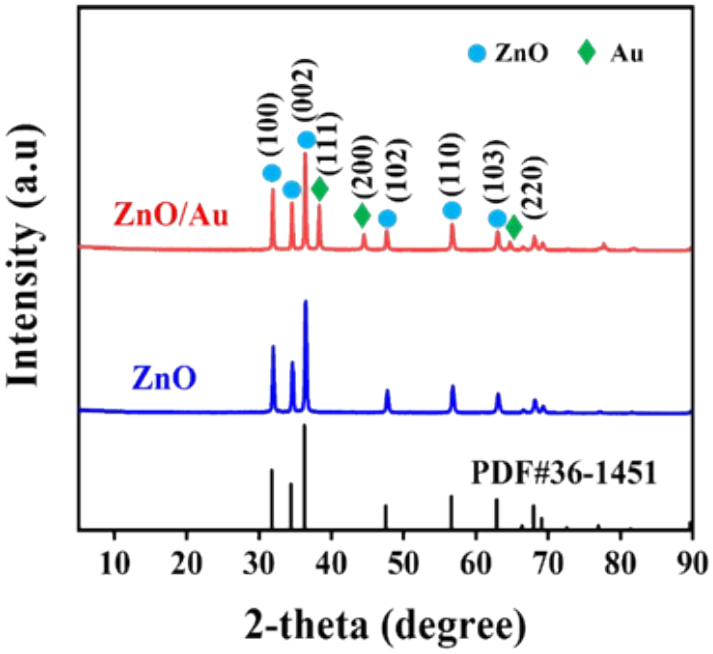

Figure. S3. XRD patterns of ZnO and ZnO/Au.