Electronic Supplementary Information

Hollow copper sulfide nanosphere-doxorubicin/graphene oxide core-shell nanocomposite for photothermo-chemotherapy

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Preparation and characterization of hollow CuS nanoparticles

Hollow CuS nanospheres are prepared using the template-assisted approach. Briefly, $CuCl_2 \cdot 2H_2O$ (0.017 g, 0.1 mmol) is dissolved in 60 ml of 2-propanol containing PVP K30 (0.2 g), followed by the addition of a NaOH solution (1 mmol). Then 0.4 ml of $N_2H_4 \cdot H_2O$ (35 wt%) is added in the mixture and stirred for 10 min. Thereafter, the obtained Cu_2O nanospheres are collected by centrifugation at 15000 rpm for 10 min and washed by deionized water, then re-dispersed in water. 35 μl of $(NH_4)_2S$ aqueous solution (20 wt%) is added to the Cu_2O nanospheres suspension to obtain hollow CuS nanospheres. After stirring for 2 h at room temperature, the products are centrifuged and re-suspended in water for further use.

XRD pattern of these CuS crystals as illustrated in Figure S1 reveals that all the primary diffraction peaks are consistent with the standard data of covellite-phase CuS (PDF card No.: 00-001-1281). The specific surface area and pore volume of the hollow CuS nanoparticles are 25.3 $m^2 g^{-1}$ and 0.18 $cm^3 g^{-1}$, respectively.

Preparation and characterization of the GO-PEG nanosheets

GO nanosheets are prepared according to the modified Hummers' method. Briefly, 10 g of graphite powder is firstly mixed with 10 g of $K_2S_2O_8$ and 10 g of P_2O_5 in H_2SO_4 (30 ml), and stirred rigorously at 80°C for 6 h. After washed with water until to neutral, the product is collected and dried at 60°C. Then 5 g of the obtained pre-oxidized graphite is added into 184 ml of H_2SO_4 under mechanical stirring in an ice bath, followed by addition of 4 g of $NaNO_3$. Subsequently, 24 g of $KMnO_4$ is slowly added into the mixture. After kept at 35°C for 30 min, the mixture is mechanically stirred at room temperature for two weeks. The reaction is finally terminated by the introduction of excess H_2O_2 aqueous solution (3%, v/v). Thereafter, the GO nanosheets are obtained by centrifugation at 10000 rpm for 5 min, followed by washing with HCl (1.2 mol l^{-1}) and water alternatively. Then 100 ml of GO solution (1 mg ml^{-1}) is mixed with 5 g of NaOH and $ClCH_2COOH$ under sonication for 6 h to prepare carboxylic GO (GO-COOH). After centrifugation at 12000 rpm for 20 min, the product is washed with water and then re-dispersed in water. 1 g of

NH_2-PEG-NH_2 and 0.4 g of EDC are added into 100 ml of GO-COOH (1 mg ml^{-1}), and stirred for 24 h at room temperature. The product (GO-PEG) is then purified by dialysis with a cellulose membrane (MWCO 14000) for 3 days, and stored at 4℃ for further use.

UV-vis-NIR absorption spectra (Figure S2) of GO-COOH and GO-PEG indicate their light-absorbing capability in NIR region. With the conjugation of PEG, zeta potential of the GO nanosheets changes from -23.2 mV (GO-COOH) to -12.6 mV (GO-PEG). The stability of GO-PEG under physiological condition is extremely improved with respect to that of GO-COOH (inset in Figure S2). Moreover, morphological analyses (Figure S3) demonstrate the average thickness of GO-COOH and GO-PEG are ca.1.3 and ca.1.8 nm, respectively.

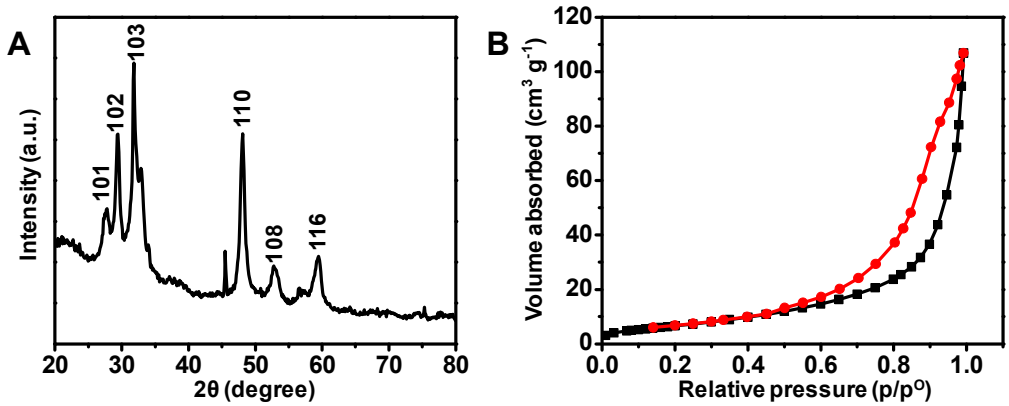

Figure S1. XRD pattern (A) and nitrogen adsorption-desorption isotherms (B) of the hollow CuS nanospheres.

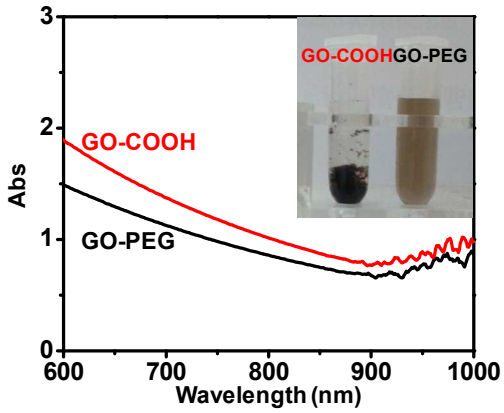

Figure S2. UV-vis-NIR absorption spectra of GO-COOH (1 mg ml^{-1}) and GO-PEG (1 mg ml^{-1}). Inset: digital images of GO-COOH and GO-PEG dispersed in PBS (10 mmol l^{-1}, pH 7.4).

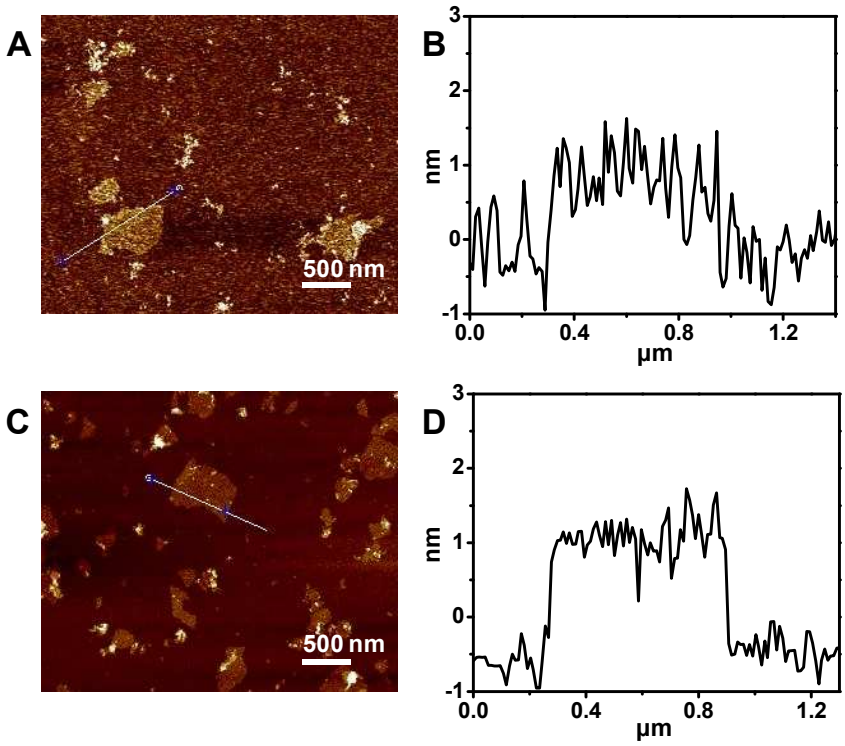

Figure S3. AFM images and height profiles of GO-COOH (A, B) and GO-PEG (C and D).

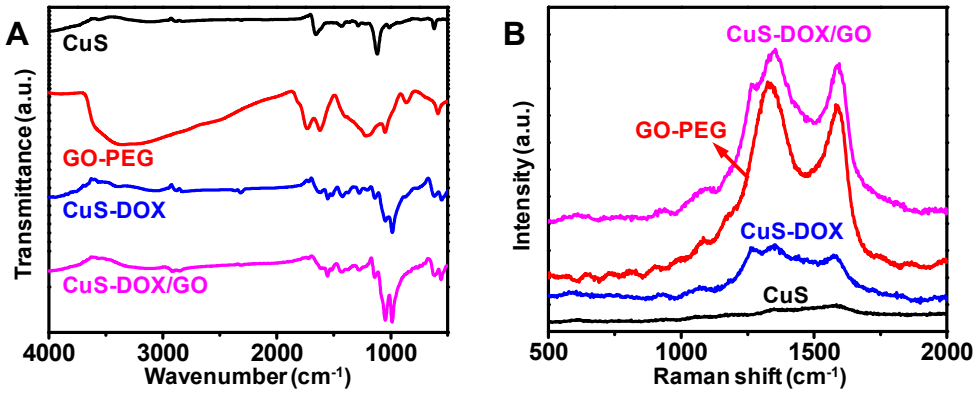

Figure S4. FT-IR spectra (A) and Raman spectra (B) of CuS, GO-PEG, CuS-DOX and CuS-DOX/GO.