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Synthesis of hybrid Ta_2O_5@PDA/Au nanocomposites

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Experimental

S1. Synthesis of Ta_2O_5 nanoparticles (NPs)

Specifically, 0.468 mL of tantalum (V) ethoxide (99.98%, Sigma- Aldrich, USA) was added in a drop-by-drop manner to 45 mL of anhydrous isopropyl alcohol (IPA; Chimmed, Russia) under an inert atmosphere. Then, polytetrafluoroethylene cup filled with the obtained mixture was transferred to autoclave and heated in a furnace at 200°C for 12 h, resulting in a transparent sol of primary particles in IPA. To prepare the hydrosol of Ta_2O_5 NPs, the sol of primary particles was mixed with deionized water in a volumetric ratio of 1.25:1. The mixture was slowly heated to evaporate IPA while maintaining a temperature below its boiling point (82.5°C). The final concentration of Ta_2O_5 NPs in the hydrosol was 10 mg/mL, as determined by gravimetric measurement.

S2. Surface modification of Ta_2O_5 NPs with polydopamine (PDA)

To coat the obtained Ta_2O_5 NPs with a PDA shell, 0.5 mg/mL dopamine hydrochloride solution (ACS Reagent, Sigma-Aldrich, USA) and 3 mg/mL hydrosol were mixed at 1:1 volume ratio. To start dopamine polymerization, 0.1 M NaOH (ACS Reagent, Sigma-Aldrich, USA) was dropwise added until the pH of the dispersion reached ≈8.5. Then the mixture was placed on Rotamix shaker (ELMI, Latvia), where it was slowly rotated for 1.5 h at room temperature. The as-prepared PDA-coated NPs were centrifuged at 14000 rpm for 20 min using Universal 320R machine (Hettich, Germany). The collected particles were resuspended in deionized water under 30 s ultrasonication using Elmasonic S10H bath (Elma, Germany). The centrifugation/resuspension cycle was repeated 3 times. Final concentration of the Ta_2O_5@PDA NPs was 1.5 mg/mL.

The formation of PDA layer on the Ta_2O_5 particles was qualitatively evaluated using Nicolet 380 FTIR spectrometer (Thermo Electron Corporation, USA). The spectra were measured in a diffuse reflectance mode in the wavenumber range of 400–4000 cm^{-1}.

S3. Synthesis of Au NPs

The Au NPs were synthesized by irradiation of 0.6 mM aqueous solution of $HAuCl_4$ (Aurat, Russia) containing 10 vol.% of IPA as a hydroxyl radical scavenger. Prior to irradiation, the solution was bubbled with argon to eliminate dissolved oxygen. Two-milliliter samples were irradiated with electrons with maximum energy in the spectrum of 10 MeV using ILU-14 (transliterated from Russian ИЛУ-14) accelerator[S1] in Eppendorf-type microcentrifuge tubes (GenFollower, China) at room temperature. The absorbed dose was set at 5 kGy. The dose rate was set at 2.5 kGy/min. Its control was carried out using SO PD(F) E-5/50 (transliterated from Russian СО ПД(Ф) Э-5/50) and SO PD(E) R-1/10 (transliterated from Russian СО ПД(Э) Р-1/10) dosimetric films (VNIIFTRI, Russia).

S4. Synthesis of hybrid Ta_2O_5@PDA/Au NPs

To form the Ta_2O_5@PDA/Au NPs by mixing, the appropriate volumes were chosen to give a nominal loading of the Au NPs of 20% by mass. The pH of resulting mixture was ≈4. After 1 h, the product was centrifuged at 14000 rpm for 20 min and then redispersed in deionized water. This process was repeated 3 times to ensure thorough purification.

To form the Ta_2O_5@PDA/Au NPs by radiolitic reduction of Au^{3+}, an appropriate volume of Ta_2O_5@PDA hydrosol was mixed with $HAuCl_4$ water solution to give a 20% nominal loading of Au NPs (by mass). The pH of dispersion was adjusted to ≈10 by 0.1 M NaOH solution. Prior to irradiation, the solution was also bubbled with argon. Irradiation conditions were fully consistent with those described above. The absorbed dose was set at 5, 10 and 20 kGy. The dose rate was set at 2.5 kGy/min.

S5. Characterization of NPs

The size and morphology of the obtained hybrid NPs were determined using Libra 120 HRTEM microscope (C. Zeiss, Germany) operating at an accelerating voltage of 120 kV. The samples were prepared by holding a drop of their aqueous dispersion on a formvar-coated copper grid for 1 min and then removing it with a filter paper. Histograms of the particle size distribution were obtained by counting at least 150 particles. Particle size was analyzed using an ImageJ software.

The extinction spectra of the NP solutions were measured in quartz cells with optical path length of 10 mm (Hellma, Germany) using SF-104 spectrophotometer (Aquilon, Russia).

References

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