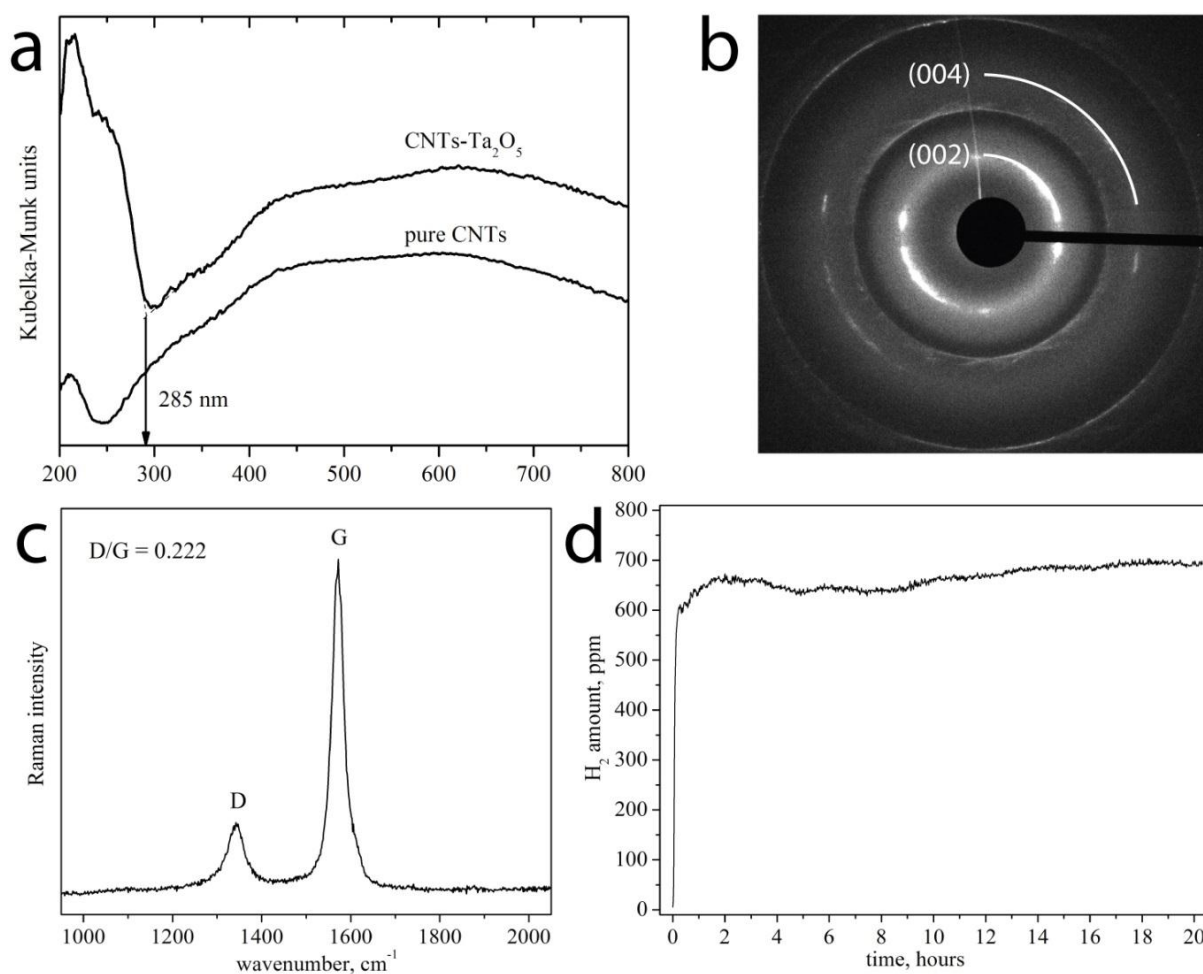


**Fig. S1** Typical SEM images of the CNTs-Ta<sub>2</sub>O<sub>5</sub> hybrids of H1 (A) and H2 (B) types demonstrating thick and thin homogeneous coatings of CNTs with the oxide, respectively, of the GO-Ta<sub>2</sub>O<sub>5</sub> hybrid (C) demonstrating distributed Ta<sub>2</sub>O<sub>5</sub> nanoparticles over the GO surface, and Ta<sub>2</sub>O<sub>5</sub> nanotubes reference sample (D) demonstrating hollow oxide tubes preserving tubular morphology.



**Fig. S2** UV-VIS-NIR reflectance spectra of pure CNTs and a typical CNTs-Ta<sub>2</sub>O<sub>5</sub> hybrid demonstrating the broad absorption of the hybrid as the result of successful hybridization with CNTs (A). Electron diffraction of pure MWCNTs annealed in argon at 1000 °C, highlighted halos is due to (00n) reflections associated with the two dimensional periodicity of the graphene layers (B).<sup>1</sup> Raman spectrum of pure MWCNTs annealed in argon at 1000 °C showing small D/G bands ratio indicating a few structural defects (C).<sup>2</sup> Hydrogen evolution rate of CNTs-Ta<sub>2</sub>O<sub>5</sub> hybrid in a 20 hours experiment demonstrating stable photocatalytic performance (D).

## Methods

**Synthesis of CNTs.** Multi-walled carbon nanotubes were grown *via* a continuous-flow CVD process in a tube furnace reactor using ferrocene as the catalyst precursor and toluene as the feedstock.<sup>3</sup> The reaction temperature was kept at 760 °C and Ar was used as the carrier gas (flow 400 ml/min). In a typical experiment, 22 ml of 4 wt% ferrocene in toluene solution was injected into the reactor at a rate of 5.4 ml/h. After cooling the reactor, the CNTs were mechanically removed from the tube and purified by annealing in argon at 1000 °C, in order to remove amorphous carbon. The average outer diameter of the nanotubes was about 70 nm and the length was between 200 and 250 µm, however, both dimensions can be controlled by the reaction conditions.

**Synthesis of graphene oxide.** Graphene oxide was produced *via* chemical exfoliation of graphite following the modified Hummer's route by dispersing natural graphite flake powder (3 g) and sodium nitrate (3 g) in concentrated H<sub>2</sub>SO<sub>4</sub> (150 ml).<sup>4</sup> Afterwards, KMnO<sub>4</sub> (9 g) was gradually added and the mixture was stirred at 40 °C for 2 h. Subsequently, 150 ml de-ionized water was added gradually, causing an increase in temperature to 98 °C. After 20 min, H<sub>2</sub>O<sub>2</sub> (30 ml 80% solution) was added to the mixture. After stirring for 10 min, DI water (80 ml) was added and the GO material was sedimented for 2 days. After decantation, the material was washed with diluted HCl and DI water until a neutral pH was obtained. The obtained GO was dried at room temperature under light vacuum and grinded afterwards.

**Synthesis of hybrids.** The CNTs were hybridized with Ta<sub>2</sub>O<sub>5</sub> *via* an aqueous sol-gel route using Ta(OEt)<sub>5</sub> (VWR, 99.9 %) as precursor, ethanol as solvent and benzyl alcohol (BA, ABCR, 99.9%) as linking agent to have a composition of the reaction solution of BA:H<sub>2</sub>O:EtOH = 1:2.13:1. In a typical experiment, 100 mg of CNTs were suspended into 60 ml ethanol, which included 50 µl deionised water and 140 µl benzyl alcohol (BA), and ultrasonicated for 15 minutes. 400 and 800 mg of Ta(OEt)<sub>5</sub> (for H2 and H1, respectively) was

dissolved in 20 ml of absolute ethanol under argon atmosphere and added drop-wise to the CNT suspension. After 24 hours of aging at room temperature, the solid material was filtered, washed in ethanol in order to removed unreacted precursor, and subjected to hydrothermal treatment at 150 °C for 48 hours. After drying, the samples annealed at 500 °C or 700 °C. To hybridize GO with Ta<sub>2</sub>O<sub>5</sub> the procedure was kept similar with the exception that no benzyl alcohol was used due to the hydrophilic nature of the GO.

**Characterization of materials.** The morphology of the samples was investigated by scanning electron microscopy (Zeiss XB 1540 EsB) using an acceleration voltage of 2 kV and a secondary electron detector for imaging, and by transmission electron microscopy (Zeiss Libra 200) using 200 kV electron beam acceleration voltage. The samples for TEM were prepared by sonication of a small sample amount in EtOH and dropping it on a carbon coated copper grid (mesh 200).

Physisorption measurements were carried out on a Micromeritics ASAP 2010. To remove moisture and absorbed gases, the samples were weighed in glass tubes and heated to 110 °C under vacuum for 24 h. The measurement itself was carried out at T = 77 K with Nitrogen (N<sub>2</sub>) as adsorbate. The total surface area was calculated according to Brunauer-Emmett-Teller (BET) theory.

Structural characterization was performed by means of X-ray spectroscopy (XRD) using a RINT-Ultima III from Rigaku with Cu K<sub>α</sub> irradiation. Absorption spectra were recorded by UV-VIS-NIR spectroscopy (Jasco V-670 UV-Vis photo spectrometer) using a diffuse reflectance unit containing an Ulbricht-sphere. Samples were fixed in micro sample holder with diameter of 3 mm. The data was processed implementing the Kubelka-Munk theory. Raman spectra were measured using a Jobin Yuon Horiba LABRAM HR with a Ne:YAG-Laser (lambda = 532 nm). The dispersive Raman spectrometer is equipped with a CCD for detection and an optical microscope (Olympus BX41).

Chronoamperometry measurements (I-t curves) were taken *via* Autolab electrochemical workstation. A bucky paper of CNTs-Ta<sub>2</sub>O<sub>5</sub> was prepared by filtering and drying the sample. An external bias of 0.01 V was applied to direct the photoexcited electrons flow. Current was measured with time, while the bucky paper was periodically illuminated with UV light (light off, light on cycles).

**Photocatalytic experiments.** A closed circulation system with 450 W inner type irradiation mercury UV light source was used. Typically 50 mg of the photocatalyst was immersed into 450 mL of a H<sub>2</sub>O:CH<sub>3</sub>OH 50:50 solution and added to the quartz reactor, which was evacuated several times prior to the reaction to ensure that no air remained in the reaction vessel. The photocatalyst was loaded *in situ* with 0.5 wt% Pt *via* photodeposition of H<sub>2</sub>PtCl<sub>6</sub> (Fluka, 8% water solution). A typical reaction proceeded for 5 hours, while the evolved gases were analysed by gas chromatography (GC-8A, TCD, Ar carrier, MS 5A columns).

Long term stability test of the CNTs-Ta<sub>2</sub>O<sub>5</sub> hybrids were performed using a different photocatalytic set up (inner irradiation, flow system), while similar reaction conditions (50:50 reaction mixture, amount of sample, Pt loading, lamp type and power output) were used. During the measurement amount of evolved H<sub>2</sub> gas was monitored on-line *via* X-Stream gas analyser.

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