Electronic Supplementary Information

Synthesis of TaON nanotube arrays by sonoelectrochemical anodization followed by nitridation: a novel catalyst for photoelectrochemical hydrogen generation from water

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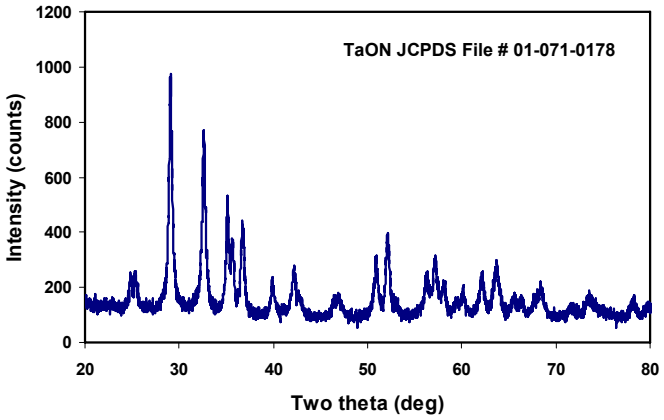

Fig. S1 GXRD pattern of TaON NTs. No peak for Ta_3N_5 is observed

Synthesis of Tantalum pentoxide nanotube arrays. Synthesis of tantalum pentoxide (Ta_2O_5) nanotubes are carried out on a tantalum foil in an organic medium comprising of 3% water in ethylene glycol + 0.5 wt% NH_4F using sonoelectrochemical anodization method (100 W, 42 KHZ, Branson 2510R-MT) under various conditions. The said processes are carried out using a two electrode system (flag shaped 1.0 cm^2 metal foil as anode and Pt foil, 3.75 cm^2 as cathode; the distance between cathode and anode is kept at 4.5 cm). The anodized samples are properly washed with distilled water to remove the occluded ions, dried in an air oven and processed for nitridation.

Synthesis of TaON NTs. The Ta_2O_5 NTs thus made are heating them in an atmosphere of flowing NH_3 (flow rate: 10 ml min^{-1}) at 700 ^oC for 6 h. Annealing is also done along with nitridation which reduces the defects in the material and also crystallizes it. The Ta_2O_5 which are of grey colour turned into yellow-orange color (inset of Fig. 2(A)).

Characterization. A field emission scanning electron microscope (FESEM; Hitachi, S-4700) is used to analyze the nanotube formation and morphology of the Ta_2O_5 and TaON nanotubes. Diffuse reflectance ultraviolet and visible (DRUV–Vis) spectra of the samples are measured from the optical absorption spectra using a UV-Vis spectrophotometer (UV-2401 PC, Shimadzu). Fine $BaSO_4$ powder is used as a standard for baseline and the

spectra are recorded in a range 200-800 nm. A scanning transmission electron microscope (STEM; Phillips CM 300) equipped with ESVision software is used for mapping and crystal distribution of the samples. A small amount of sample is placed in a carbon coated Cu-grid and subjected for High Resolution Transmission Electron Microscopy (HRTEM) measurement. Glancing angle X-ray diffraction (GXRD) is done using a Philips 12045 B/3 diffractometer. The target used in the diffractometer is copper (λ = 1.54 Å), and the scan rate is 1.2°/min.

Photoelectrochemical tests. The experiments on H_2 generation from water are carried out in a glass cell with photoanode (metal oxide NTs/metal or metal oxynitride NTs/metal) and cathode (Pt foil) compartments. The compartments are connected by a fine porous glass frit. Silver/silver chloride (Ag/AgCl) is used as the reference electrode. The cell is provided with a 60 mm diameter quartz window for light incidence. The electrolyte used is an aqueous solution of 1 (M) potassium hydroxide (KOH). A computer-controlled potentiostat (SI 1286, England) is used to control the potential and record the photocurrent generated. A 300-W solar simulator (69911, Newport-Oriel Instruments, USA) is used as the light source. An AM 1.5 filter is used to obtain one sun intensity, which is illuminated on the photoanode (87 mW/cm^2, thermopile detector from Newport-Oriel is used for the measurements). The effect of visible light (> 400 nm) irradiation was carried out by using a longpass filter (Edmund optics, VIS Longpass Filter #47-614) in combination with an AM1.5 filter. The samples are anodically polarized at a scan rate of 5 mV/s under illumination and the photocurrent is recorded. All the experiments are carried out under ambient conditions.