Supporting Information

Microfluidic electrochemical growth of vertically aligned TiO_2 nanotubes for SERS optofluidic devices

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Experimental Details

Materials: Titanium foils (thickness 200 µm, 99.6 purity, Goodfellow) were used as starting material for the grown of TiO_2 NT arrays. The metal foils and the Fluorine-doped tin oxide (FTO) covered glasses (7 Ω/sq, Solaronix) were cut in 2×2 cm^2 substrates before microfluidic cell assembly. The anodic oxidation was performed at 25 °C into ethylene glycol solution containing ammonium fluoride (NH_4F, 98% Sigma-Aldrich) 0.5 wt% and deionized water (DI-H_2O) 2.5 wt%.

0.1 M $AgNO_3$ (Sigma-Aldrich) in water and ethanol was used as silver nanoparticle precursor under 60 mW/cm^2 illumination (fiber UV-lamp, LC8 Lightningcure, Hamamatsu).

Characterizations: The morphological characterizations of the TiO_2 NTs sample before and after Ag decoration were performed by Field Emission Scanning Electron Microscopy (FESEM, Zeiss Supra 40) equipped with an Energy Dispersive X-ray spectrometer (EDX, Oxford INCA Energy 450) for compositional analyses.

X-ray diffraction technique was used to determine the crystalline structure of the films (Panalytical PW1140–PW3020, Cu K_α X-ray source). The scans were performed in a parallel beam geometry with a fixed angle of incidence ω=1.5°, in order to minimize the contribution of the substrate.

Raman spectroscopy was performed by means of a Renishaw inVia Reflex micro-Raman spectrophotometer, equipped with a cooled CCD camera. Samples were excited with an Ar-Kr laser source with a wavelength of 514.5 nm.

Additional results

As comparison TiO_2 NTs were grown into a standard electrochemical cell (two parallel electrode immersed into electrolytic solution) and the obtain lengths as a function of time are reported in Figure S1.

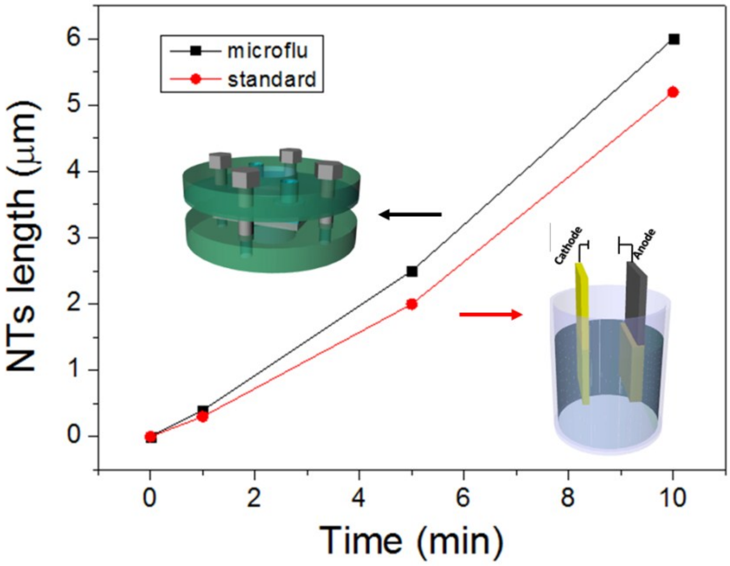

Figure S1. Comparison between NTs length grown by standard and microfluidic procedure.

Growing rate seems to be weekly dependent by the setup with NTs length slightly higher for the microfluidic configuration. The walls of the tubes are smooth (Figure S2a) thanks to the polar organic nature of the electrolytic solution. The tubes have an average external diameter of around 110 nm with wall thickness of around 20 nm and exhibit a perfect vertical alignment and hexagonal assembly (see Figure S2b).

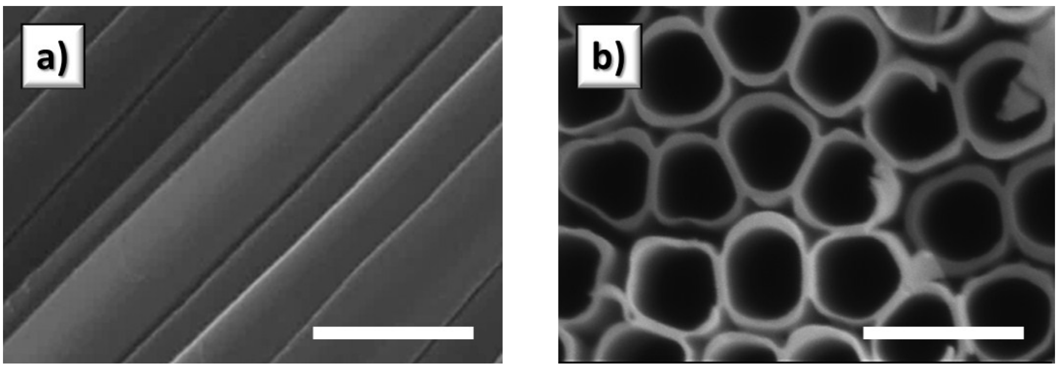

Figure S2. FESEM micrographs showing high magnification cross-section (a) and top view (b) of the TiO_2 nanotubes array grown in microfluidic electrochemical reactor (scale bars are 200 nm).

X-ray diffraction (XRD) patterns of as-grown and Ag-decorated TiO_2 nanotubes are shown in Figure S3. The spectrum of the bare NTs present only peaks associated to titanium substrate since the as-anodized TiO_2 nanotubes are fully amorphous. After the Ag synthesis peaks assigned to the diffraction of (111), (200), and (220) planes of face-centered cubic (fcc) silver (JCPDS card n. 4-783, a = 4.08 Å) appear.

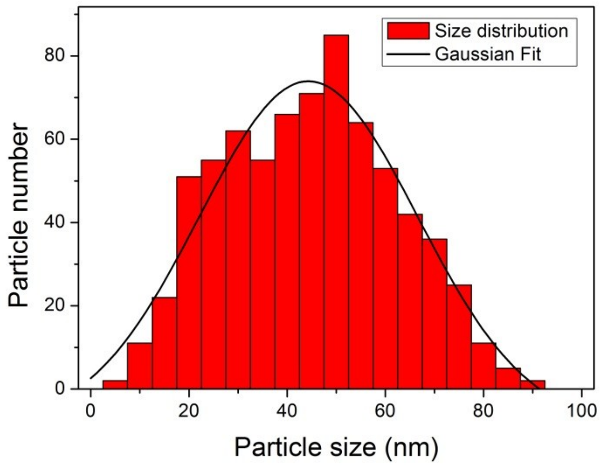

Figure S3. Size distribution of Ag nanoparticle on TiO_2 NTs.

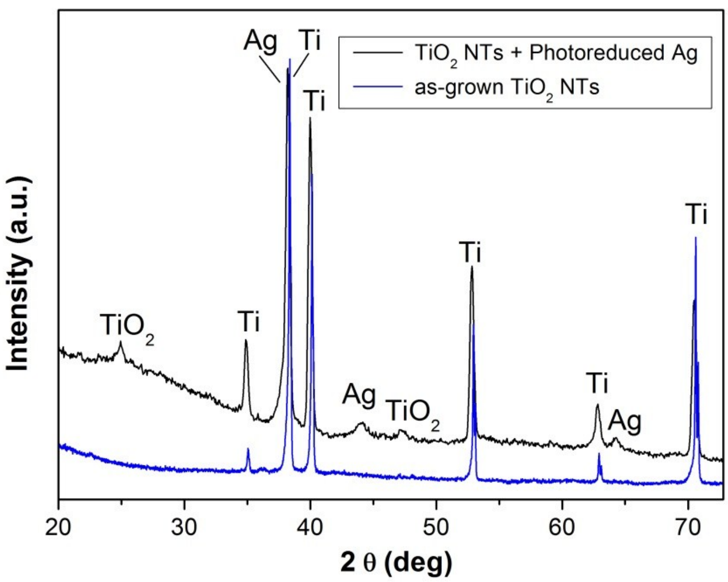

Figure S4. XRD spectra of TiO_2 nanotubes before and after the $AgNO_3$ photo-reduction.

Table S1. Atomic concentration (%) of elements by EDX investigation on TiO_2 NTs before and after Ag deposition.

Element	as-grown	Ag photoreduction
	Atomic %	Atomic %
C	7,6	2,9
F	25,3	16,9
Ti	17,3	25
O	49,8	53,9
Ag	0	1,3

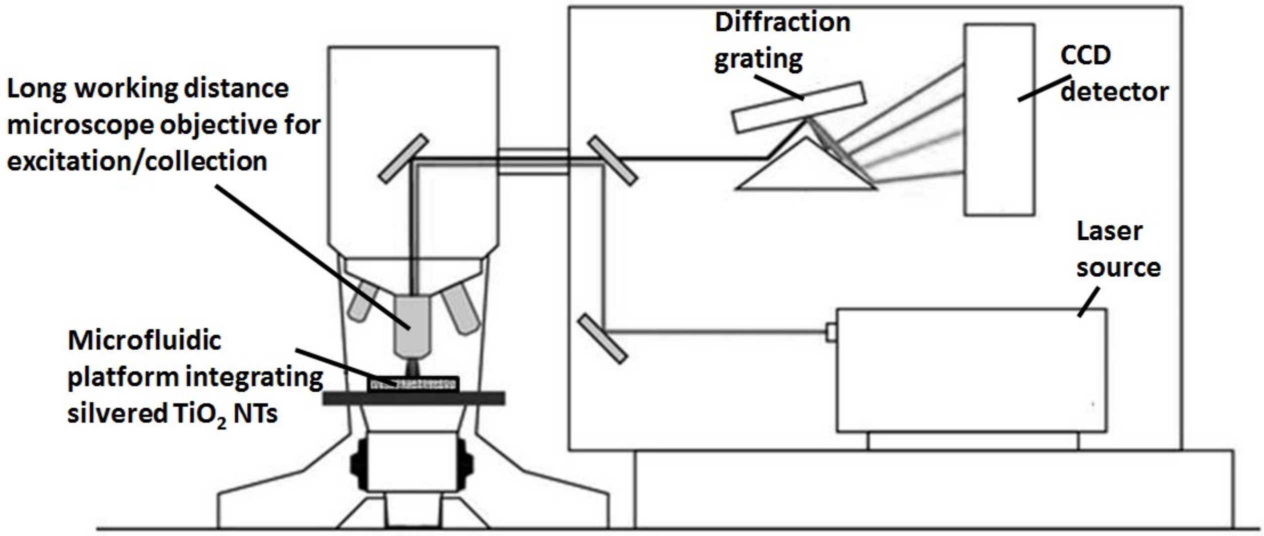

Figure S5. Raman spectroscopy set-up (backscattering configuration).

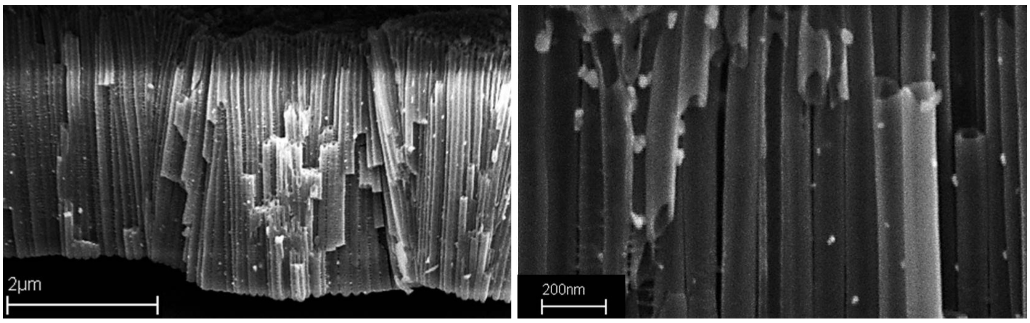

Figure S6. FESEM micrographs at different magnifications showing the samples after UV-cleaning (30 min).