

Supplementary Information

Electrochemical sensors cleaned by light: a proof of concept for on site applications towards integrated monitoring systems.

V. Pifferi^{†,a,b}, G. Soliveri^{†,a,b}, G. Panzarasa^c, S. Ardizzone^{a,b}, G. Cappelletti^{a,b}, D. Meroni^{a,b} and L. Falciola^{a,b*}

^a Dipartimento di Chimica, Università degli Studi di Milano, Via Golgi 19, 20133 Milano, Italy.

^b Consorzio Interuniversitario Nazionale per la Scienza e Tecnologia dei Materiali (INSTM), Via Giusti 9, 50121 Firenze, Italy.

^c Dipartimento di Scienze e Innovazione Tecnologica, Università del Piemonte Orientale “Amedeo Avogadro”, Viale T. Michel 11, 15100 Alessandria, Italy.

[†] These authors contributed equally.

Supporting Information

Experimental

Materials

All chemicals were of reagent grade purity and used as received. Distilled water (18 M Ω cm⁻¹) purified with a Millipore Milli-Q apparatus was used to prepare solutions and sols.

Preparation of the device

Device assembly was accomplished according to a previously reported protocol [1]. The fluorine-doped tin oxide coated glass slides (FTO, Sigma-Aldrich[®], ~ 7 (Ω sq), 2x3 cm) adopted as conductive supports were cleaned by sonication in a H₂O : acetone : propanol = 1:1:1 mixture and then irradiated for 1 hour under UV light from a halogenide lamp (see below).

The silica sol was prepared by the procedure previously reported by Wang *et al.* [2]. Briefly, 10 g of TEOS were added dropwise into a solution containing 225 g of ethanol and 4.5 g of hydrochloric acid (0.1 M). The mixture was stirred at room temperature for 2 hours and then refluxed at 60 °C for 60 min. Eventually, 225 g of a CTAB (cationic surfactant) solution in ethanol (2 g in 25 mL) was mixed with the as-obtained solution under gentle stirring at room temperature for 1 hour. The FTO was dip-coated with the obtained sol and calcined at 500 °C for 1 hour under N₂ flow.

Before functionalization by (3-aminopropyl)triethoxysilane (APTES), the silica layer was irradiated under UV for 1 hour and dipped into anhydrous toluene under N₂ at 70 °C for 1 hour. The functionalization was performed by immersing the substrate into a solution of 50 μ L APTES in 20 mL anhydrous toluene, for 3 hours at 70 °C. The sample was post-treated by sonication for few minutes in toluene, ethanol and

water to desorb the un-grafted siloxane molecules and eventually dried under a nitrogen stream.

The sample was then immersed in a solution of Ag NPs for 15 minutes to allow their attachment and dried under nitrogen. The top titania layer was obtained by dipping the sample in a titania sol and calcining it under N₂ flow for 1 hour at 400 °C. The titania sol was developed in our group and was previously reported [3]. Briefly, 0.9 mL of HCl 37 % was added to a solution of Ti(OC₃H₇)₄ in ethanol (0.1 mol in 100 mL) under stirring. Then, 0.47 g of Lutensol ON70 (BASF) was added to the sol after being dissolved in 100 mL of ethanol.

Silver nanoparticles (Ag NPs) were synthesized by adapting the procedure reported by Panzarasa [4]. Briefly, 0.15 g of silver nitrate were dissolved in 25 mL of water and this solution was added under stirring to a solution of 0.5 g of trisodium citrate and 0.25 g of poly(vinylpyrrolidone) (PVP10, M_w ~ 10000 (g mol⁻¹)) in 125 mL of water. The resulting solution was poured in a three-necked, round-bottomed 250 mL flask equipped with a mechanical stirrer and a dropping funnel. The solution was cooled in an ice bath and an ice-cooled solution of sodium borohydride, obtained by dissolving 12 mg of solid in 30 mL of water, was added dropwise under stirring. The resulting dark brown suspension was left under stirring for 5 minutes after the addition, aged at + 4 °C for 24 hours before use and stored at this temperature.

Electrochemical measurements

Electrochemical measurements were performed in a standard three electrode cell, equipped with a saturated calomel as reference electrode, a platinum wire as counter electrode and the nanocomposite device as working electrode.

Differential pulse voltammograms were recorded in 0.1 M phosphate buffer (PBS, pH=7.4), using an Autolab PGStat30 (Ecochemie, The Netherlands) potentiostat/galvanostat controlled by GPES software. The parameters are the following: potential range from -0.1 V to $+0.4$ V, modulation time 0.05 s, interval time 0.5 s, step potential 0.005 V, modulation amplitude 0.05 V.

Detailed fouling/cleaning procedure

- 1) The background signal of the device dipped in the supporting electrolyte was recorded as previously described.
- 2) Dopamine was added to a final concentration of 1 mM and a voltammogram was recorded to observe the oxidation of dopamine at the electrode.
- 3) The electrode was immersed in a new solution of supporting electrolyte and a voltammogram was recorded to attest the effective fouling degree of the electrode.
- 4) The electrode was dried and placed under UV light or stored in the dark for a chosen interval of time.
- 5) A new voltammogram in supporting electrolyte was performed to demonstrate the effect of the cleaning procedure.

UV Lamps

Three different lamps were adopted for the cleaning step (Figure S2):

- UV-LAMP: UV iron halogenide lamp Jelosil HG500: effective power density 45 (mW cm^{-2}) at 40 cm (sample location), emitting mostly between 350 and 450 nm;
- TLC-LAMP: Spectroline Model ENF-240C/FE: effective power density 1.7 (mW cm^{-2}), emitting between 280 and 400 nm;

- UV LED TORCH: HQRP[®] effective power density 14 (mW cm⁻²), maximum emission at 380 nm.

The emission spectra and the effective power densities were measured by a SM442 Spectrometer (Spectral Products) and a PM100A Optical Power Meter (Thorlabs), respectively.

The absorption spectrum of the device was measured by a UV-2600 UV-vis spectrophotometer (Shimadzu).

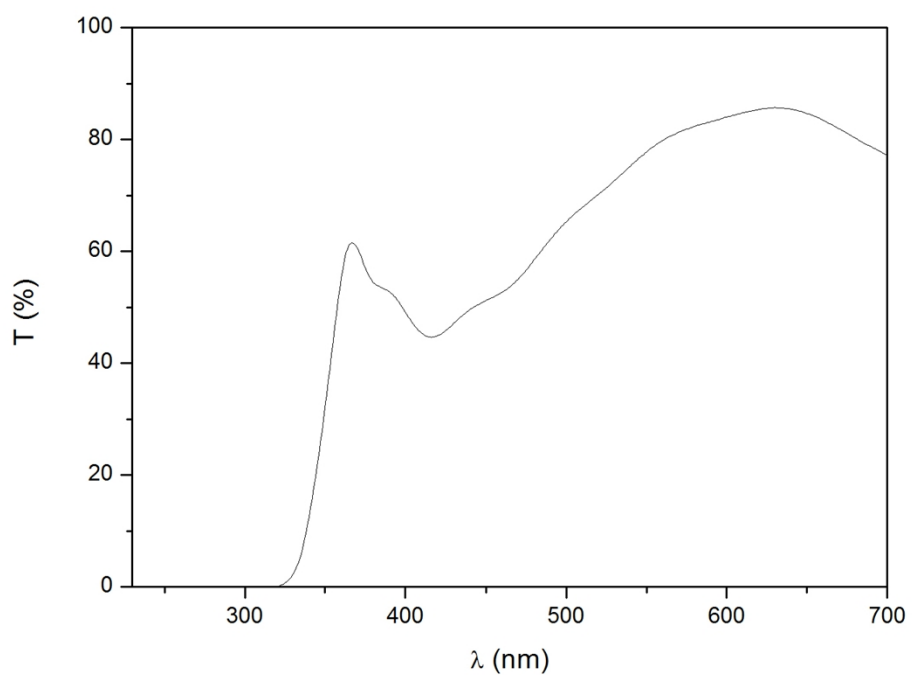


Figure S1: UV-Vis transmittance spectrum of the device.

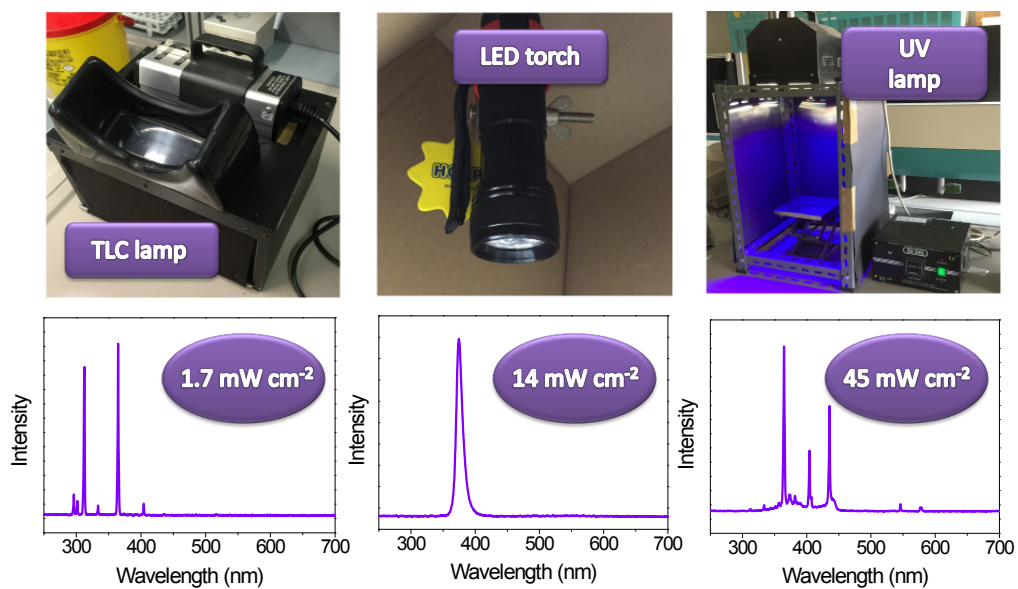


Figure S2. Photographs, emission spectra and effective power density of the three lamps employed for self-cleaning experiments.