

Electronic Supplementary Information (ESI)

## **Photocatalytic growth of hierarchical silver nanostructures as SERS substrate**

Katrien G.M. Laurier,<sup>a</sup> Michel Poets,<sup>b</sup> Frederik Vermoortele,<sup>b</sup> Gert De Cremer,<sup>b</sup> Johan Martens,<sup>b</sup> Hiroshi Uji-i,<sup>a</sup> Dirk E. De Vos,<sup>b</sup> Johan Hofkens<sup>a</sup> and Maarten B.J. Roeffaers<sup>a,b</sup>

<sup>a</sup>*Laboratory of Photochemistry and Spectroscopy, Department of Chemistry, K.U.Leuven, Celestijnenlaan 200 F, 3001 Leuven, Belgium,*

<sup>b</sup>*Centre for Surface Chemistry and Catalysis, Department of Microbial and Molecular Systems, K.U.Leuven, Kasteelpark Arenberg 23, 3001 Leuven, Belgium.*

## 1. Synthesis of zinc oxide crystals

The ZnO crystals are synthesized according to a method described by Wen *et al.*<sup>1</sup> First 4.4 g of  $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$  was dissolved in 20 ml distilled water under vigorous stirring. Next, the pH of the clear zinc acetate solution was adjusted to pH 8 with a 4M aqueous NaOH solution. The resulting reaction mixture was then transferred to a Teflon-lined stainless steel autoclave and heated to 428 K where the mixture was kept for 48 h. After cooling down to room temperature, the solid product was filtered from the reaction liquid. The resulting crystals were thoroughly washed with distilled water. The obtained ZnO crystals were dried overnight in an oven at 353 K prior to use.

## 2. Photocatalytic experiments

Metallic silver nanostructures were directly formed from an aqueous  $\text{AgNO}_3$  solution (Janssen chemical) via a photocatalytic reduction at the surface of the ZnO crystals. For these experiments 100-150  $\mu\text{g}$  ZnO crystals were deposited on glass cover slides and submerged in an aqueous silver nitrate solution with a concentration of 1 mM. Illumination of the sample was performed in a photoreactor (Rayonet, RPR-100) or on a fluorescence microscope setup (Olympus FluoView 500 and 1000) equipped with a UV light source.

### 2.1. Bulk synthesis of dendritic silver nanostructures

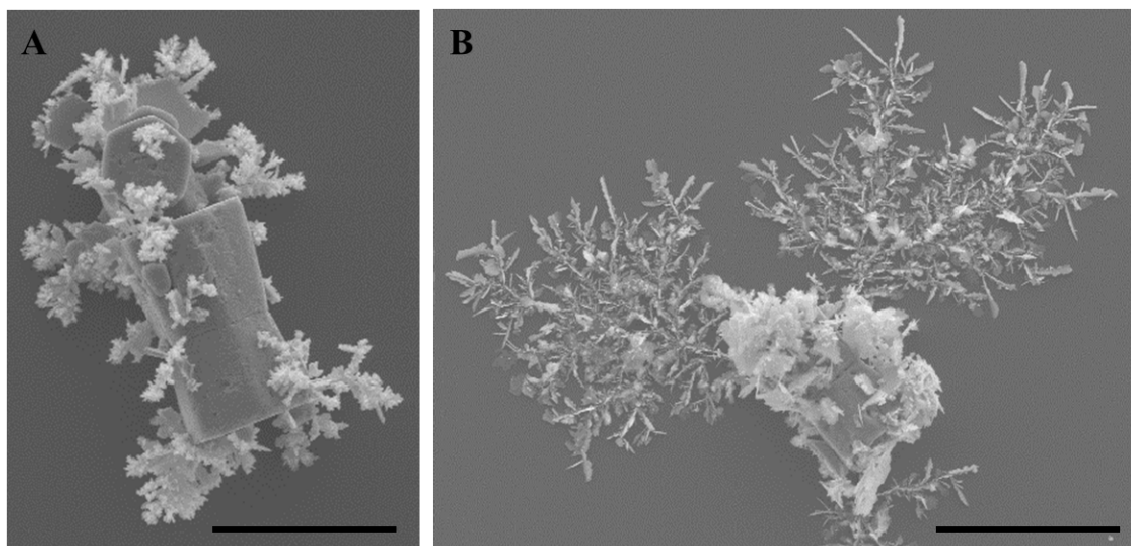
For the bulk photocatalytic formation of dendritic silver nanostructures on ZnO photocatalysts, fluorescent UV lamps in a photoreactor (Rayonet, RPR-100) were used. The samples, covered with 300  $\mu\text{l}$  silver nitrate solution, were illuminated by 16 UV lamps (Rayonet RPR-3500; 315-400 nm).

### 2.2. Microscopic *in situ* synthesis of silver nanostructures

In the photocatalytic experiments on the microscope (see also section 3 of ESI) the cover slides were put in a liquid cell and submerged in a 500  $\mu\text{l}$  silver nitrate solution. UV stimulation of the photocatalytic process comes from a mercury-arc lamp equipped with a 400 nm short pass filter ( $\lambda < 400$  nm, 7600  $\mu\text{W}/\text{cm}^2$ ).

### 3. Scanning Electron Microscopy

Scanning electron micrographs of dendritic silver structures grown in bulk, after 5 and 10 minutes UV stimulation of the ZnO core, the photocatalysts are visible as hexagonal prisms. The SEM micrographs were recorded using a Philips XL30 FEG after coating with Au.



**Figure S1.** SEM images of silver dendritic structures: (A) After 5 minutes of UV illumination; (B) After 10 minutes of UV illumination. Scale bar = 10  $\mu\text{m}$ .

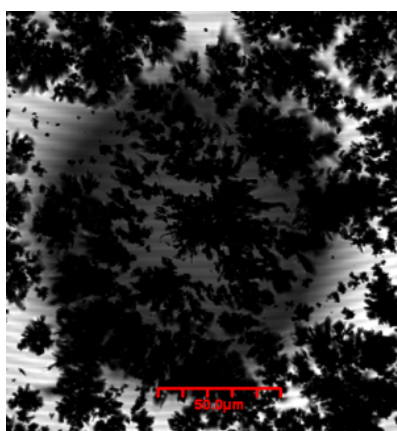
### 4. Confocal fluorescence microscopy studies

Confocal fluorescence microscopy (Olympus, FluoView 500/1000) was used to study the formation of metallic silver nanostructures. The FluoView 500 uses a 543 nm green HeNe laser while the FluoView 1000 is equipped with a 532 nm laser diode. For both microscopes the laser power was adjusted to approximately 50  $\mu\text{W}/\text{cm}^2$ .

Morphological changes are observed in the transmitted light channel. Simultaneous scanning with a green laser allows visualizing the luminescence of the sample in a confocal channel (550-650 nm). To follow the growth mechanism of the silver nanostructures *in situ*, the confocal fluorescence microscope (Olympus, FluoView 500) was used since it allows simultaneous wide-field UV stimulation.

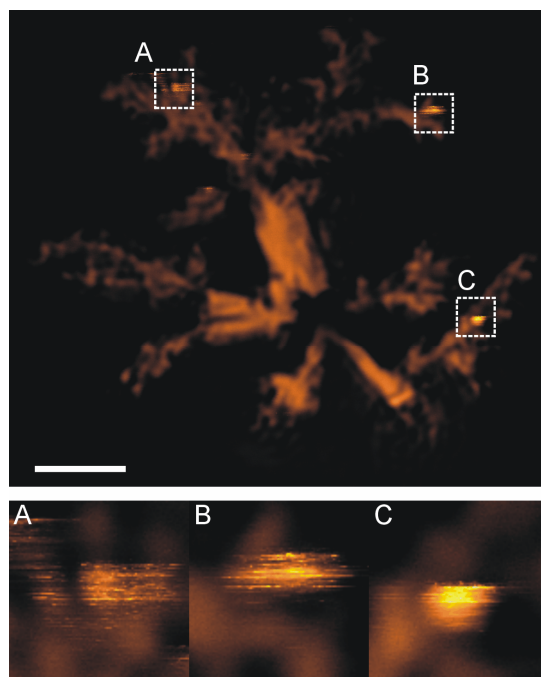
## 5. Photocatalytic water oxidation: formation of oxygen gas bubbles at elevated $\text{Ag}^+$ concentrations

At elevated silver ion concentrations, e.g. 100 mM, the second photocatalytic half reaction was observed upon UV illumination: the generation of oxygen gas bubbles. (Figure S2) This oxygen evolution is a direct result of the completion of the photocatalytic cycle: next to the reduction of silver ions to silver nanostructures with the photoelectrons, the light-generated holes are simultaneously oxidizing the solvent (water) to yield molecular oxygen. This oxygen production can under some circumstances be observed with our optical microscope via the formation of gas bubbles. This of course only occurs when the rate of oxygen formation is sufficiently large to generate observable gas bubbles.



**Figure S2.** Photocatalytic generation of molecular oxygen, simultaneously with the photocatalytic reduction of silver ( $[\text{Ag}^+] = 100 \text{ mM}$ ).

## 6. Bright luminescent nanoparticles present on the dendritic silver structure



**Figure S3.** Fluorescence image of a dendritic silver structure under green excitation showing bright luminescent silver nanoclusters. Scale bar = 2  $\mu\text{m}$ , zoomed areas 0.8x0.8  $\mu\text{m}^2$ .

## 7. Ramanmicrospectroscopy

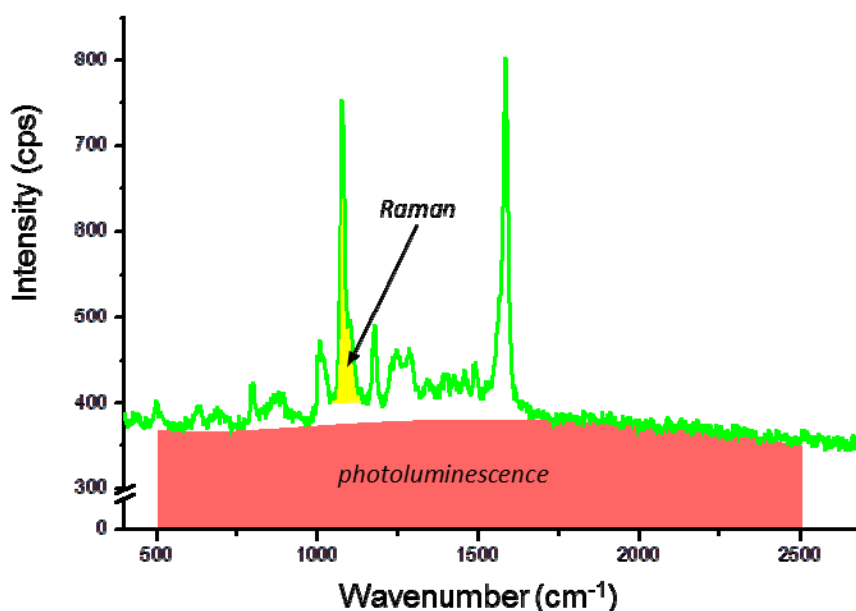
All Raman experiments were performed on a home-built Raman microscope that was assembled around a Nikon EclipseTi-U microscope. The 632.8 nm excitation light from a red HeNe laser (Model 1145P, JDS Uniphase Co.) is focused on the sample using a 100x oil immersion objective lens (Nikon, 1.3 N.A.). The Raman scattering signal is collected in a backscattered configuration using an Andor Technology system, consisting of a Shamrock SR-303i spectrograph and a Newton EM-CCD (CU970P-BV). Separation of Raman scattered light from the excitation light was done with a 632 nm dichroic mirror (Chroma). Further removal of the strong excitation light was done with a 645nm long pass filter (LP HQ 645, Chroma). The transmission image was recorded with a Hamamatsu CCD camera (C9100-13) and a white light source was aligned to Koehler illumination. Calibration of the Raman setup consists of recording the spectrum of pure toluene as reference. The spectral resolution was about 1  $\text{cm}^{-1}$  (pinhole 100  $\mu\text{m}$ ). As Raman probe for the SERS measurements 4-methoxythiophenol (4-MOTP) was used.

### 7.1. Individual Raman spectra

During these Raman measurements the samples were submerged in an ethanolic solution of 4-MOTP with concentrations ranging from 1 nM till 100  $\mu\text{M}$ . Low excitation powers were used (32  $\mu\text{W}$  at the sample) with an integration time of 120 seconds.

### 7.2. Raman Mapping

For the Raman mapping, the samples were submerged in an ethanolic solution of 4-MOTP with a concentration of 100  $\mu\text{M}$ . The samples were placed on the scanning stage of the microscope. These experiments were conducted using 370  $\mu\text{W}$  at the laser focus, with an integration time of 1 second. Figure S4 shows an example of the intensities that were used to calculate the Raman map, integration of Raman peak in the region 1060-1120  $\text{cm}^{-1}$ , and the photoluminescence image i.e. integration of the 'background' in the region 500-2500  $\text{cm}^{-1}$  which corresponds to 650-750 nm.



**Figure S4.** Calculation of the photoluminescence and Raman image based on emission spectra recorded in every point.

### References

1. F. S. Wen, W. L. Li, J. H. Moon, et al., *Solid State Communications*, 2005, **135**, 34-37.