Electronic Supplementary Material (ESI) for Journal of Materials Chemistry

Electronic Supporting Information

Superhydrophobic supported Ag-NPs@ZnO-Nanorods with photoactivity in the visible.

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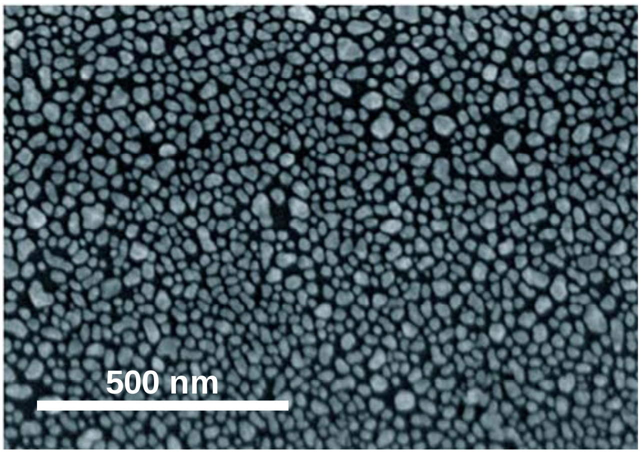

Figure S1. Heterostructured Ag/Si(100) substrate after the heating pretreatment at 135 ºC in O_2 atmosphere at 4 x 10^{-3} Torr during 60 minutes.

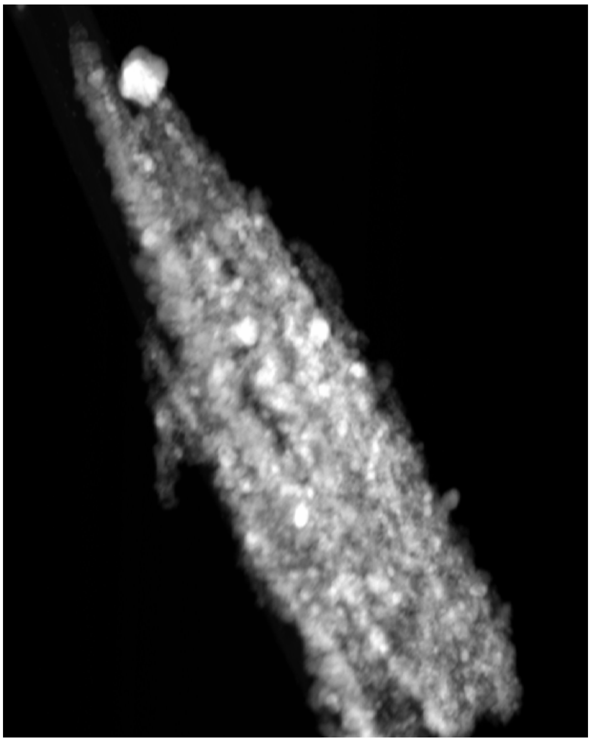

Figure S2. STEM micrograph of several Ag-NPs@ZnO NWs showing a silver nanoparticle on the top of one of the nanowires.

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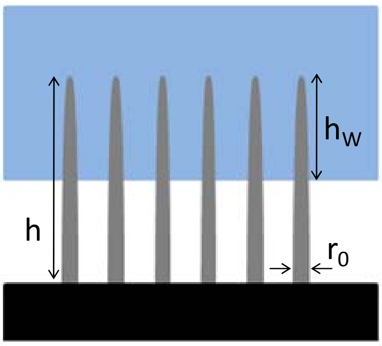
Water contact modelling.

In the present case, the water contact angle (WCA) of a surface formed by a high density of Ag-NPs@ZnO-NWs (Fig. 1 e) is higher than > 150º (i.e., a superhydrophobic behaviour, see insets in Figure 4). Since the WCA of a rather flat ZnO reference thin film (deposited in the same conditions on a Si(100) substrate) is ~ 110º, we can relate the superhydrophobicity found for the NW surfaces with the number of NWs per unit area, their length and diameter.[1, 2] With such purpose we have evaluated the application to our system of two classic models: the Wenzel Model, which main parameter is the roughness of the surface (Eq. 1) and the Cassie-Baxter Model taking into account the effect of air trapped in the porous structure of the NWs film (Eq. 2).[2-3]

$$\cos\theta' = r\cos\theta \qquad (1)$$

$$\cos\theta' = -1 + \phi_S(1+\cos\theta) \qquad (2)$$

Where θ´ is the actual contact angle, θ the contact angle of the equivalent flat and compact surface, r the roughness factor and ϕ_S the fraction of solid in contact with the liquid. In order to calculate the roughness of our system we have modelled the individual nanowire as a circular paraboloid of height h = 860 nm and radius of the basis r_0 = 34.5 nm (see Scheme 1).



Scheme 1. Schematic of the Ag-NPs@ZnO-NWs, where r_0 is the radius of the NW basis, h the total length of the NW and h_W the length of the in contact with the micrometric droplet.

Thus, the area of a single Ag-NPs@ZnO NW is ca. A_{NW} = 1.245 x 10^5 nm^2. The roughness factor r is given by the ratio between the total and geometrical areas: applied to a 1 μm x 1 μm surface, the total area (A_{total}) corresponds to the relation established in Eq. 3.

$$A_{total} = 1\times10^{6}\,nm^{2} + N\cdot A_{NW} - N\cdot\pi r_{0}^{2} \qquad (3)$$

Where N addresses the number of wires per μm^2. For the surface shown at Fig. 1 N is ~70 NW μm^{-2}, therefore $r = A_{total}/A_{geometric} = 9.45$. Such a high value of roughness factor yields an unreal value of equivalent contact angle (θ) in Eq. 1 when θ´~150º. On other hand, it is well known that for a high roughness surface the air trapped in the system plays a key role in the contact angle.[3] Since the contact angle of the water in air is 180º, the contact angle of a rough surface with open porous structure is expected to be higher than the corresponding to the equivalent compact and flat material. Thus, the Cassie-Baxter model might be the more appropriated to describe the NWs-film surface. The factor ϕ_S in Eq. 2 indicates the solid fraction in contact with the drop. In a simple approximation the drop in contact with the surface follows the profile depicted in Scheme 1, i.e. the water contact line with the NW does not reach the substrate. ϕ_S is related through Eq. 4 to the NWs parameters (h, r_0), density (N) and the length of the NW in contact with the water drop (h_W).

$$\phi_S = \frac{\pi a/6((a^2+4h_W)^{3/2}-a^3)}{1\mu m^2 - N\pi r_0^{2} + \pi a/6((a^2+4h)^{3/2}-a^3)} \text{ with } a=\sqrt{\frac{r_0^{2}}{h^2}} \qquad (4)$$

$\phi_S = 0.2036$ when θ´= 150º and θ = 100º in Eq. 2. Consequently, h_W can be calculated from Eq. 4 with a result ~ 300 nm. In summary, for the surface formed by a high density of Ag-NPs@ZnO-NWs the micrometric water drops wet the NWs approximately a third part of their length.

1 A. Borras, A. Barranco and A. R. Gonzalez-Elipe, *Langmuir*, 2008, **24**, 8021.
2 A. Borras and A. R. Gonzalez-Elipe, *Langmuir*, 2010, **20**, 15875.
3 A. Lafuma and D. Quere, *Nature Mater.*, 2003, **2**, 457.