Electronic Supplementary Material (ESI) for Faraday Discussions.

Photocatalytic ammonia production enhanced by plasmonic near-field and hot electrons originating from aluminium nanostructures

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Supplementary data

Nanosphere lithography

The mask for AlNTs fabrication was developed using nanosphere lithography on fused silica and ITO coated fused silica substrates. Prior to ITO deposition the fused silica wafers were treated with standard RCA 1 without HF (mixture of H_2O:25%NH_4OH:30%H_2O_2 with volume ratio 5:1:1 and at 75º C for 15 min) and RCA 2 (mixture of H_2O:37%HCl:30%H_2O_2 with volume ratio 6:1:1 at 75º C for 15 min) solutions to remove residual organics from the surface and rendering the surface hydrophilic. This process improves the adhesion of ITO on fused silica substrate. A 150 nm thick indium tin oxide (ITO) layer was deposited on fused silica substrates (samples used for electrochemical measurements) using Pfeiffer Spider 600, radio frequency magnetron sputtering (RF-MS) system with RF power of 500 W and an argon flow of 15 sccm at a pressure of around 5×10^{-3} mbar. The bare fused silica and ITO deposited substrates were diced into 2.5×2.5 cm^2 pieces. A 5% aqueous polystyrene (PS) bead suspension (Microparticles GmbH, Germany), bead diameter 340 nm, was spin-coated onto the prepared chips as followed: The suspension to spin-coat was prepared by mixing the 5% polystyrene bead solution with ethanol and TritonX-100 (400:1 volume ratio) at volume ratio1:1. Subsequently, 100 µL of the suspension was dropped onto the substrates fixed on the spin coater at atmospheric pressure. TritonX-100 was added to improve surface wetting. A three step spin coating process was used to get uniform hexagonal arrangements of polystyrene beads. After dropping the spin coating suspension onto the substrate, a waiting time of 120 s was introduced to allow a better dispersal of the solution. Afterwards the substrate was rotated at rotational speed of 200 rpm for 30 s (first step) followed by 1000 rpm for 60 s (second step) and 6000 rpm for 15 s (third step). Close packing and uniform surface covering of the PS beads was achieved by the first step. The second step plays an important role in the orientation and compactness of the monolayered PS beads (growth process). The periodic arrangement and solvent evaporation take place in the third step. After preparing the PS bead mask, a thin Al film was evaporated onto the substrate prior to a lift-off step in toluene for 10 min ultrasonication. This approach is very convenient for preparing two-dimensional masks over large areas. Fig. S1 shows a schematic drawing of the aluminium nanotriangles fabrication process using nanosphere lithography and SEM images of the PS bead arrangement and individual aluminium nanotriangles after the lift-off step.

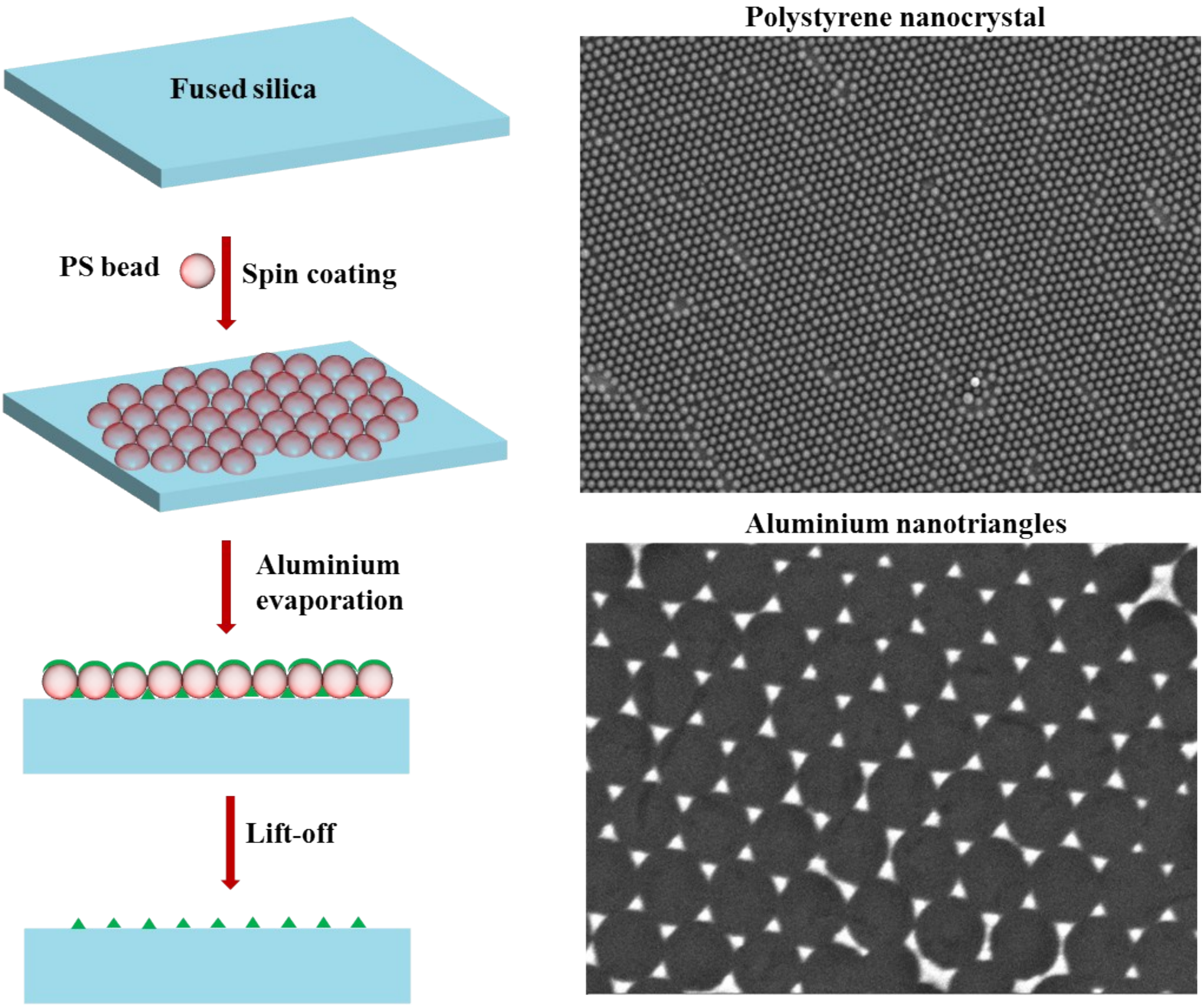

Figure S1: Schematic drawing of aluminium nanotriangles fabrication using nanosphere lithography (Left side). The SEM images (right side) of the PS beads nanocrystal after spin coating process (top) and aluminium nanotriangles after lift-off process (bottom).

Calculation of TiO_2 bandgap

Measurement of TiO_2 band gap is important to determine the threshold energy for electron/hole pair generation. Tauc plot is a common method to calculate the band gap of the semiconductors using absorbance spectrum (transparent substrate) or diffuse reflectance spectrum (non-transparent substrate). In this study, transparent fused silica substrates were used and hence the band gap (E_g) was calculated using the following relation,[1]

$$(\alpha h\upsilon)^n = A(h\upsilon - E_g)$$

Where, A is a proportionality constant, h is the plank's constant, hυ is energy of the incident light and α is an absorption coefficient. The absorption coefficient has been calculated using the relation

$$\alpha = 2.303(A/d)$$

Where, d is the thickness of the film and A is an optical absorbance of the film. The absorbance spectrum of the 100 nm TiO_2 film was measured using an UV-Vis-NIR Spectrometer (UV-2600). For allowed transition, n = 1/2 and 2 for direct and indirect bandgap semiconductors, respectively. For indirect band gap anatase TiO_2 we plotted hυ vs. $(\alpha h\upsilon)^{1/2}$ as shown in Fig. 2C (main paper). The value of photon energy (hυ) extrapolated to $\alpha = 0$ gives an absorption edge at 3.18 eV which corresponds to a band gap E_g.

Reference

1 R. López and R. Gómez, *J Sol-Gel Sci Technol*, 2012, 61, 1–7.