Plasmonic-enhanced Photo-catalysis using Collapsible Nano-fingers

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Photocatalytic decomposition plays an important role in the treatment of pollutants. It utilizes light radiation to decompose contaminants into non-toxic substances. While TiO_2 is one of the most widely used photocatalysts, visible light can hardly be used to drive TiO_2 due to the short wavelength cutoff of TiO_2 . Plasmon-enhanced photo-catalysis can extend the wavelength range due to higher order effects. However, previously reported work has limited efficiency, because the hot spots were not optimized and the TiO_2 located outside the hottest part of the hotspots. Here, we invented a technology to fabricate collapsible nano-fingers to achieve large-area high density optimized hotspots with TiO_2 film located at the hottest part of the hotspots. We demonstrated highest photo-catalysis efficiency that we are aware of.

First, UV nanoimprint resist and lift-off underlayer were spin-coated onto silicon substrates (Figure 1a). Then, pillar arrays were patterned on the top two layers using UV-curable nanoimprint lithography and reactive ion etch (Figure 1b). Au film was deposited on the sample followed by lift-off process to form gold nanoparticle arrays with diameter of 50 nm and pitch of 200 nm on the bottom layer (Figure 1c). After nano-fingers were fabricated using RIE (Figure 1d), 2 nm TiO_2 film was deposited on the sample using atomic layer deposition (Figure 1e). After the arrays were exposed to ethanol solutions and air-dried, the fingers closed together in groups of four (Figure 1f). The scanning electron microscopic (SEM) image of nano-fingers is shown in Figure 2.

The photocatalytic activities were tested using methyl orange (MO) photodegradation as the model reaction. MO solution and sample were added into a standard quartz cuvette sealed with a sealing film. The decay in absorbance of the solution after 10 h exposure to laser (532 nm, 3 W) irradiation are used to quantify the photocatalytic decomposition rate. As a control experiment, we firstly performed experiment under same illumination condition with a silicon wafer coated with 2nm TiO₂ film, no MO photodecomposition was observed after 10 h irradiation. When using the sample before collapsing, the absorption of the MO solution is observed to drop 4.9% after 10 h illumination. However, with collapsed sample, a 30% reduction of the MO absorbance was observed. This over 6-fold enhancement demonstrates a stronger plasmonic enhancement after nano-fingers being collapsed, which means this novel structure is a great platform to study plasmonic enhancement.



Figure 1: Fabrication procedure of nano-fingers: (a) Spin coating three resist layers. (b) Nanoimprinting using daughter mold. (c) After etching residual layer, metal evaporation, and lift-off, gold particles array was left on the bottom layer. (d) Etching the UV nanoimprint resist. (e) ALD deposition of dielectric films. (f) Soaking and air-drying of the ethanol to induce the collapse of nanofingers.



Figure 2: Scanning electron micrograph of nano-fingers (a) before and (b) after collapsing



Figure 3: UV–Vis spectra of methyl orange aqueous solution before (black) and after (red) 10 h illumination using sample (a) before and (b) after collapsing.