

Supporting Information

Dewetting of PtCu Nanoalloys on TiO₂ Nanocavities Provides a Synergistic Photocatalytic Enhancement for Efficient H₂ Evolution

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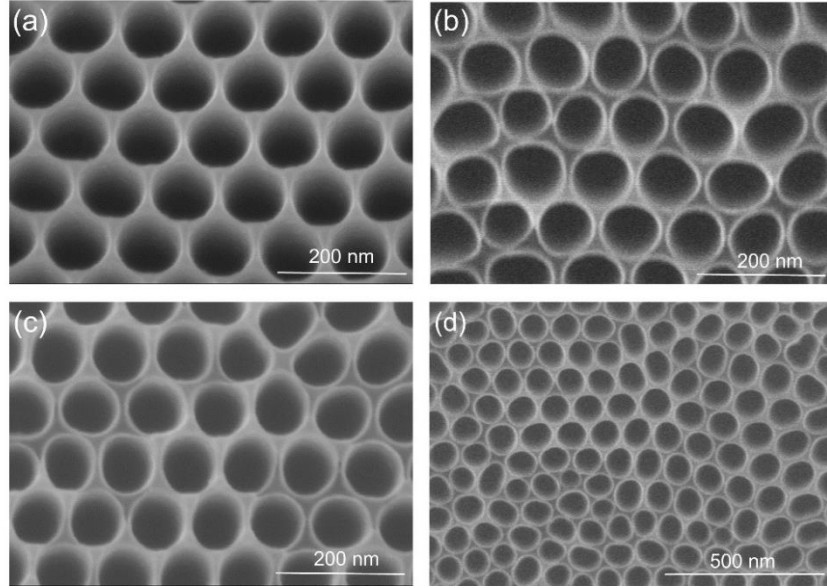


Figure S1 SEM images of pristine TiO₂ NT structures taken for one sample at different locations.

The SEM images in Fig. S1 show the morphology of the TiO₂ nanocavities used in the present work, taken for one sample at different locations. While the tube arrays show in general a high degree of self-ordering (a), some structural inhomogeneities (e.g. gaps between tubes, deviations from ideal hexagonal packing or variation in the nanotube diameter (b-d)) can be observed at specific points – likely at (or close to) grain boundaries of the parent polycrystalline Ti metal substrate.¹⁻³

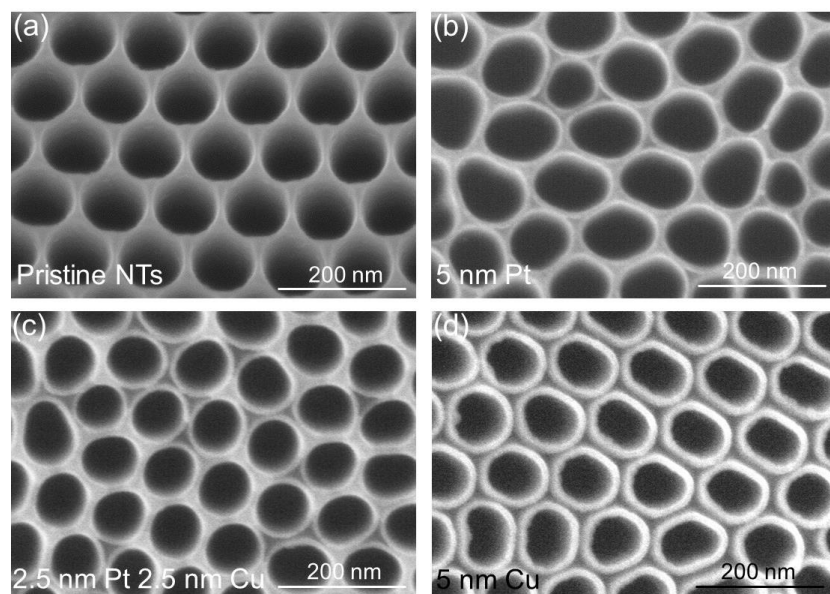


Figure S2 SEM images of different TiO_2 NT structures: (a) pristine; (b-d) sputter-coated with different metal films: (b) 5 nm Pt; (c) 2.5 nm Pt and 2.5 nm Cu; (d) 5 nm Cu.

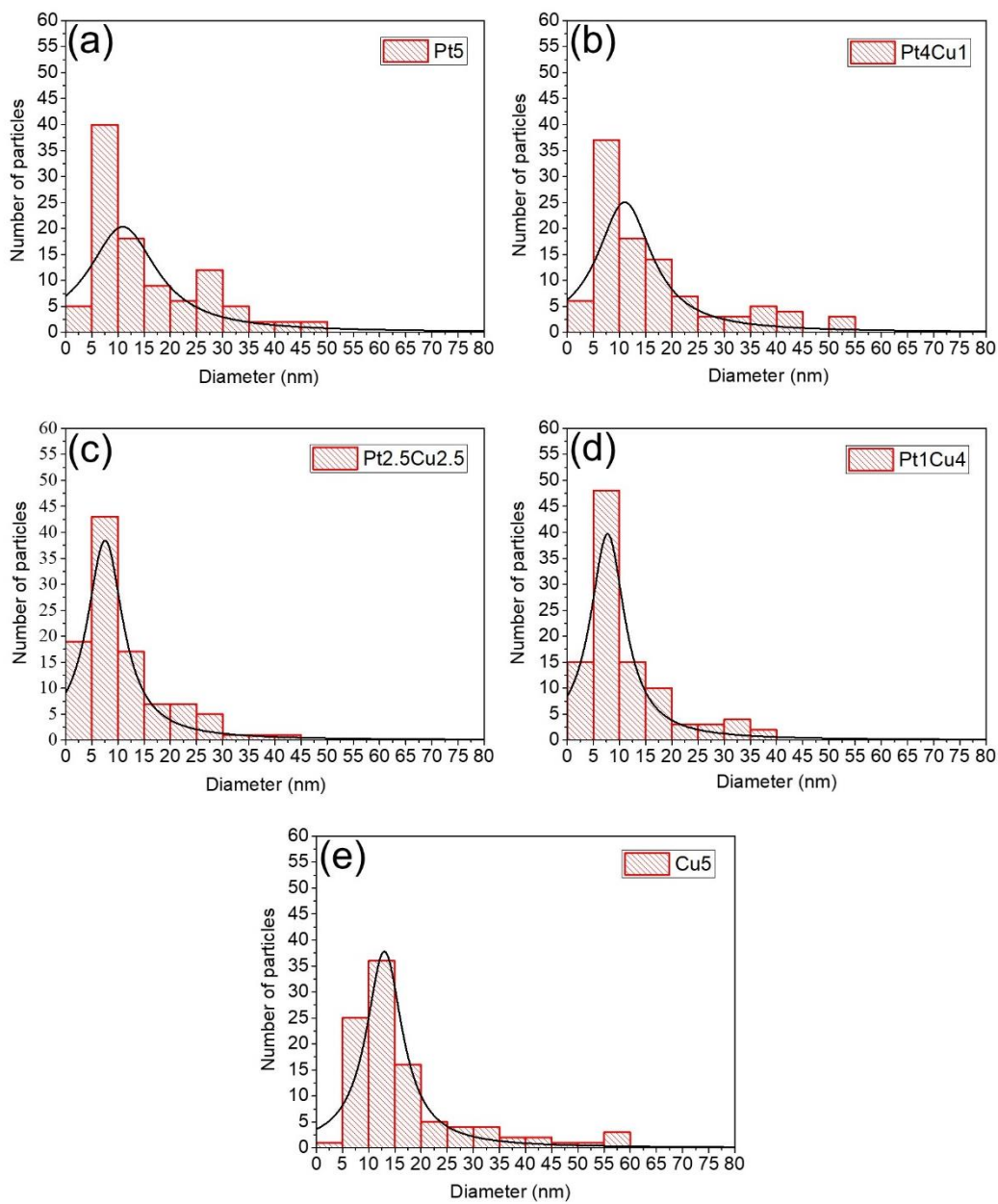


Figure S3 Particle size distribution for samples (a) Pt5, (b) Pt4Cu1, (c) Pt2.5Cu2.5, (d) Pt1Cu4 and (e) Cu5.

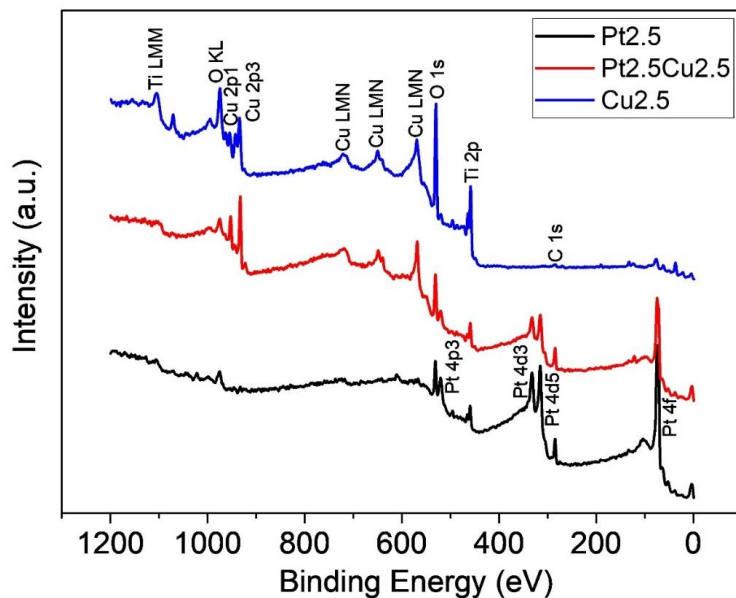


Figure S4 XPS surveys for samples Pt2.5, Pt2.5Cu2.5 and Cu2.5.

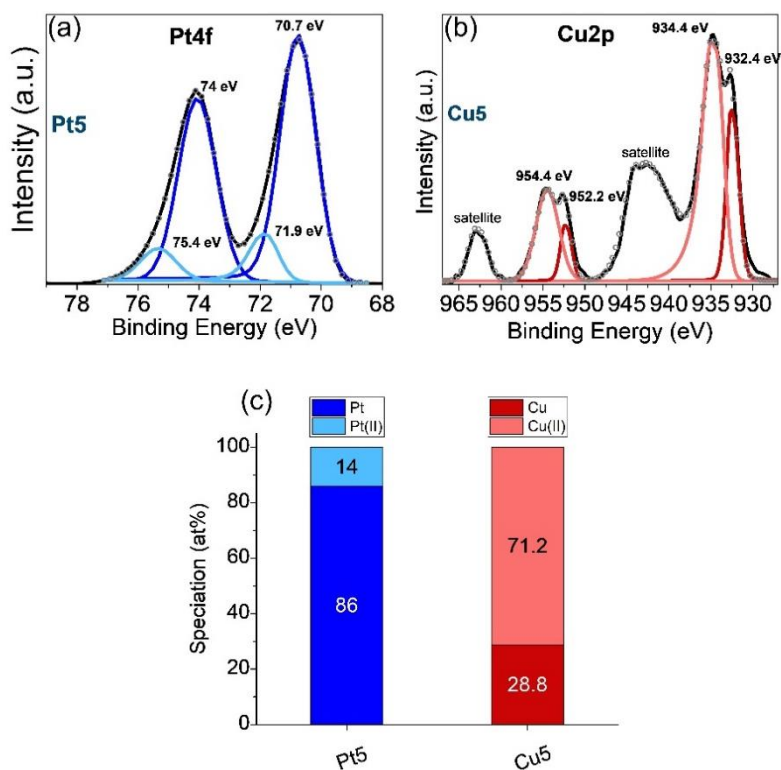


Figure S5 XPS spectra for (a) Pt 4f region of samples Pt5, (b) Cu 2p region of samples Cu5, (c) Pt and Cu speciation determined by fitting the spectra in (a,b).

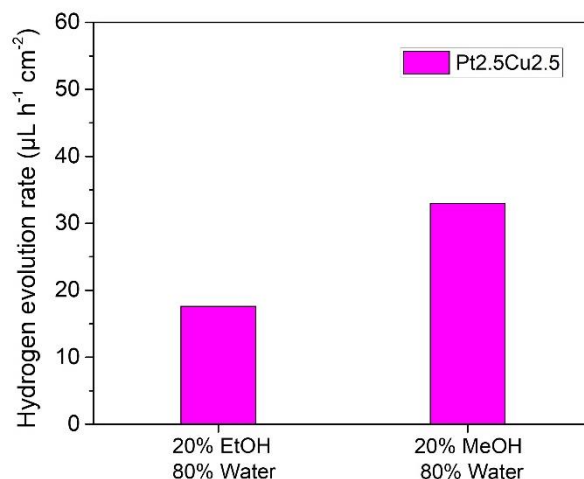


Figure S6 Photocatalytic H₂ evolution rate under UV light illumination measured for sample Pt_{2.5}Cu_{2.5} in different alcohol-water mixtures.

The H₂ evolution activity of the PtCu-TiO₂ system was measured not only in 20% MeOH-water mixtures but also in a 20% EtOH aqueous solution for comparison.

We observed a substantially higher activity (~ 2 times higher) in methanol-water mixtures than in the presence of ethanol, despite using the same concentration for the different hole scavengers. These results are well in line with the findings of Al-Azri et al.⁵ The effect of different sacrificial agents on the photocatalytic H₂ evolution rate has been also studied in other works – examples are refs.⁶⁻⁹ In general, it was found that for a given photocatalyst (e.g. Pt-TiO₂), the ability of the scavenger in capturing valence band holes depends primarily on factors such as the scavenger redox potential and its polarity. The more negative its redox potential and the higher its polarity, the better the hole capturing efficacy.⁵ A more negative redox potential provides larger thermodynamic driving force for the oxidation of the scavenger via VB holes. The redox potential of methanol ($E^{\circ}_{\text{ox}} = 0.016 \text{ V}_{\text{NHE}}$) is more negative than that of ethanol ($E^{\circ}_{\text{ox}} = 0.084 \text{ V}_{\text{NHE}}$), which explains the higher photocatalytic rate measured with methanol. The polarity affects the scavenger oxidation rate by influencing its adsorption kinetics on the photocatalyst surface.

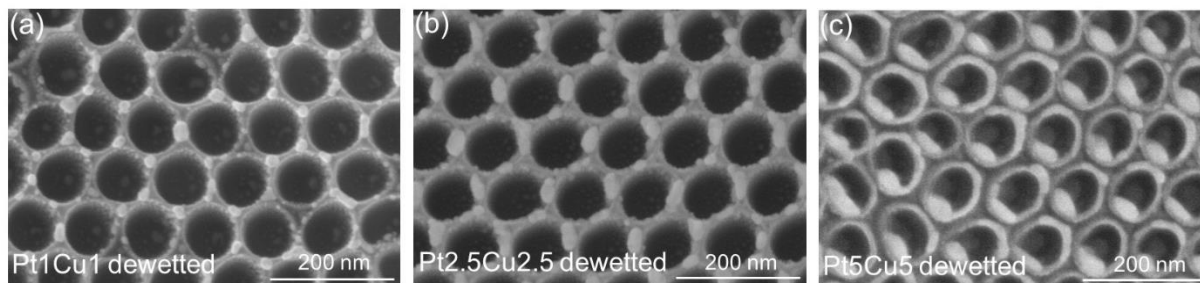


Figure S7 SEM images of different TiO₂ nanotube arrays decorated with NPs dewetted from (a) 1 nm Pt – 1 nm Cu, (b) 2.5 nm Pt – 2.5 nm Cu and (c) 5 nm Pt – 5 nm Cu.

The dewetted metal nanoparticles feature a certain size distribution (Fig. 1, S3 and S6) and their size depends on the location at which they form due to various factors. As outlined in previous work⁴ on solid state dewetting of thin metal films, inherent mechanism and its occurrence specifically on TiO₂ NT surfaces, a most relevant factor determining the particle size and distribution is the initial thickness of the sputtered metal film. Due to the porous morphology of the NT substrate and the directionality of the film deposition technique used, the formed metal films are typically slightly thicker at the tube top rims and at the tube bottoms. The metal films are on the other hand slightly thinner at the inner surface of the NT side walls. Bearing in mind that the thinner the film the smaller the dewetted particles (and vice versa, i.e. the thicker the film the bigger the particles), particles formed at the surface of the NT side walls are smaller, and are bigger when formed at the tube top rims and in the tube bottoms – this specific size distribution of the dewetted particles is evident from the SEM images in Fig. 1 and S6.

Another factor can be related to the distribution of species from the anodizing electrolyte (e.g. F or P species) adsorbed/incorporated in specific zones of the NT structure.¹ Such species may provide different surface chemistry at specific locations of the oxide substrate and hence different wettability properties inducing different dewetting modes for the metal film. These features however play likely a minor role compared to fluctuations of the metal film thickness.

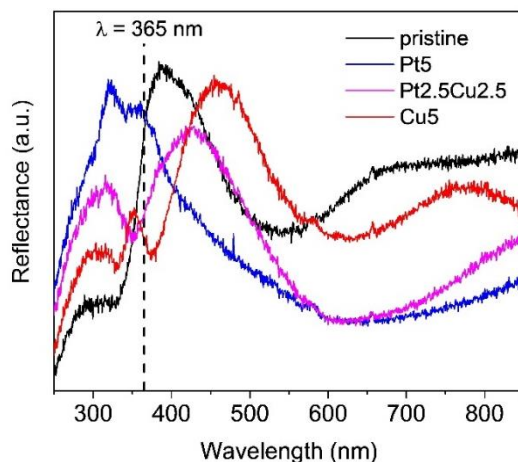
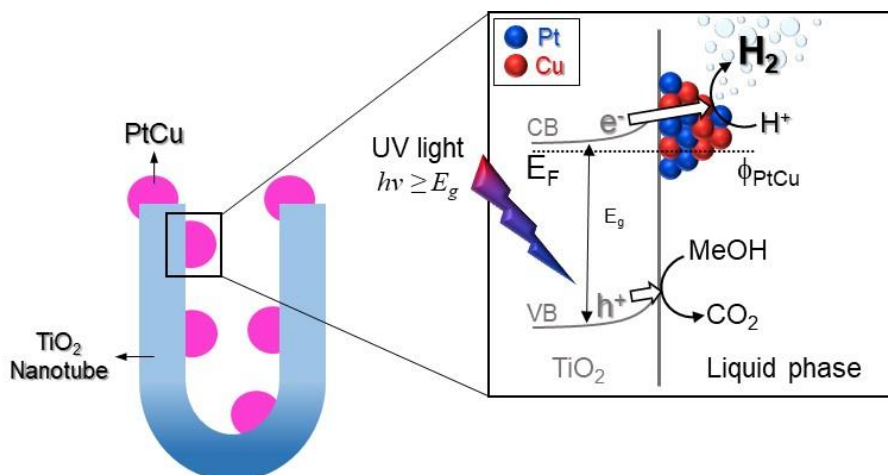


Figure S8 UV-Vis reflectance spectra of pristine TiO₂ NTs and of Pt-, Cu- and PtCu-decorated TiO₂ nanotubes.



Scheme S1 Charge carrier generation (in TiO₂), trapping (in the PtCu NPs) and transfer (to H⁺ for H₂ evolution).

The enhanced photocatalytic activity of TiO₂ NTs decorated with dewetted-alloyed PtCu NPs is ascribed to the electronic interaction between Pt and Cu atoms in the bimetallic NPs¹⁰ – such interaction can lead to a net increase of the electron density on Pt, enhancing the trapping efficiency of photo-generated electrons from the TiO₂ CB, decreasing charge recombination in the semiconductor and consequently improving the photocatalytic H₂ evolution rate.

at% (XPS)					
Sample	Ti	O	C	Pt	Cu
Pt2.5	7.9	25.2	46.6	20.3	-
Pt2.5Cu2.5	7.0	26.2	45.5	9.5	11.8
Cu2.5	15.1	66.2	9.4	-	9.3

Table S1 Surface atomic concentration for samples Pt2.5, Pt2.5Cu2.5 and Cu2.5 determined from XPS data.

Sample Pt5				
Atom	<i>n</i>	<i>r</i> (Å)	<i>r</i> ₀ (Å)	σ^2 (Å ²)
Pt1	12	2.762(5)	2.774	0.0054(5)
Pt2	6	3.94(5)	3.924	0.009(5)
Pt3	24	4.79(4)	4.805	0.012(4)
Sample Pt2.5Cu2.5				
Atom	<i>n</i>	<i>r</i> (Å)	<i>r</i> ₀ (Å)	σ^2 (Å ²)
Pt1	12	2.71(1)	2.774	0.0061(5)
Pt2	6	3.94(3)	3.924	0.006(2)

Table S2 Results of fitting of EXAFS data at the Pt L₃-edge.

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