Supplementary Information

Solvent-free hydroamination of phenylacetylene by plasmonic gold nanoparticles coupled with TiO_2 2D photonic layer on nanotube array

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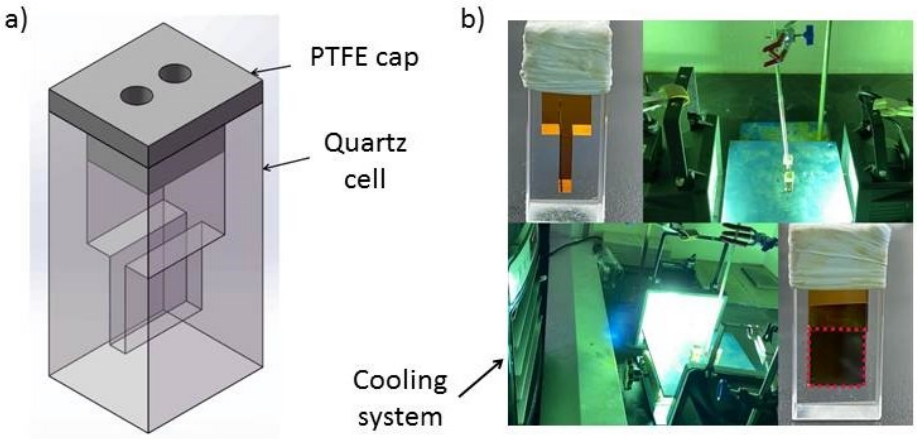
Reactor device (a) and experiment setup (b).



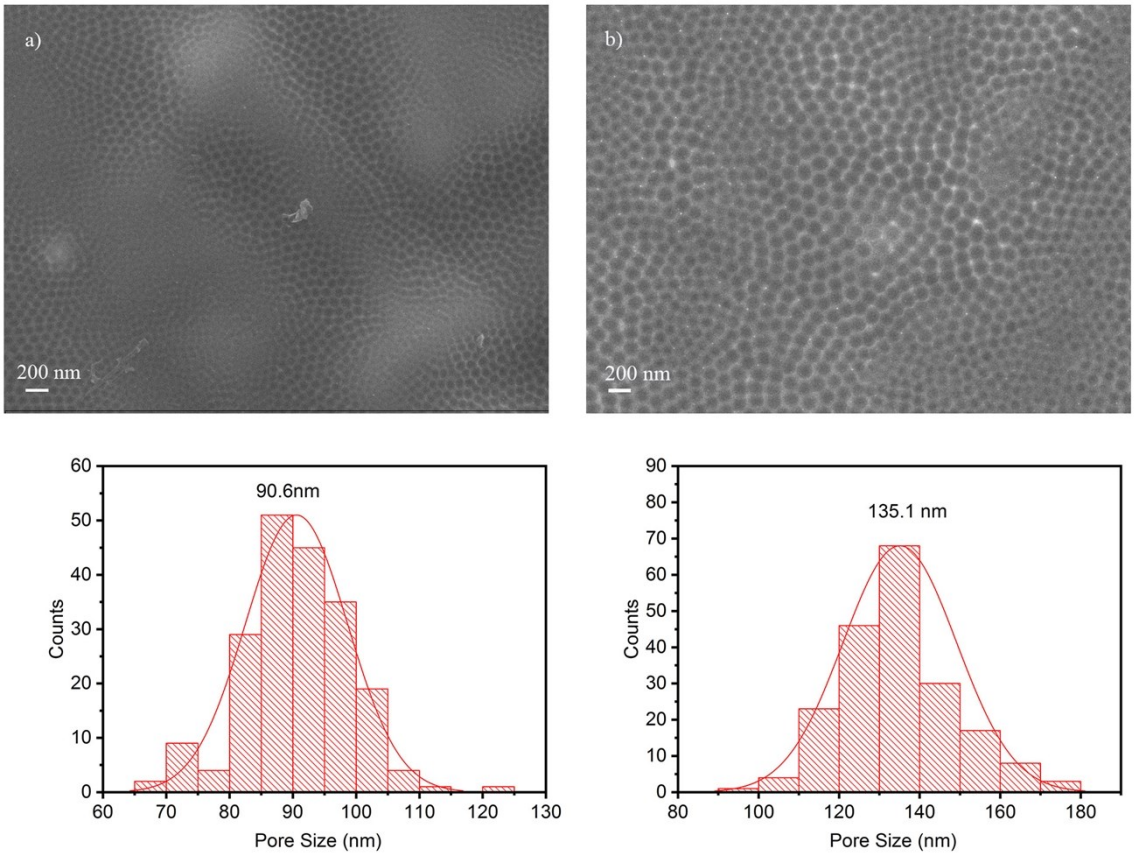


Fig. S1 SEM images of nano-imprints after removing TiO_2 NTs formed at a) 30 V and b) 50 V in first-step anodization.

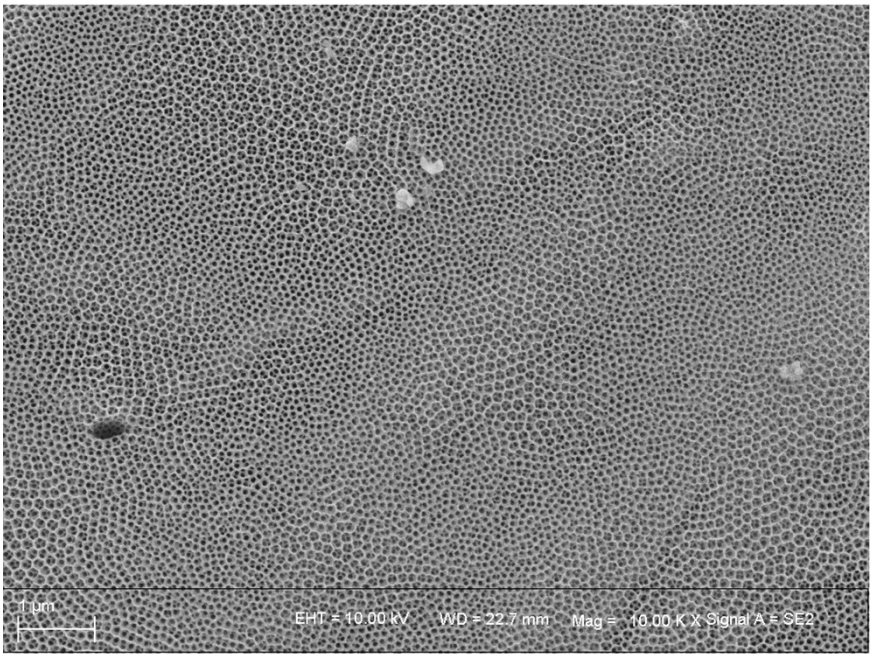


Fig. S2 An example of SEM image in large scale for TiO_2 PCNTs.

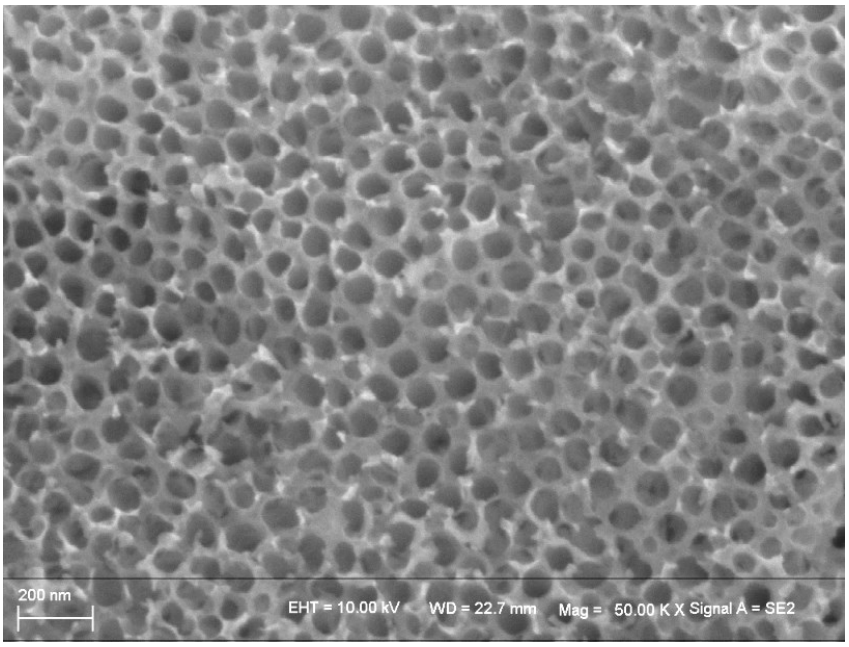


Fig. S3 SEM image of TiO_2 NTs formed with applied potential 50 V for 1 h.

Table. S1 The summary of XRD analysis for TiO_2 NTs, TiO_2 PCNTs, Au/TiO_2 NTs and Au/TiO_2 PCNTs.

Catalyst	Intensity ratio of (004)/(101)	Peak area of (004)/(101)	Peak area ratio of (004)/(101)
TiO_2 NTs	1.08	137474/79002	1.74
TiO_2 PCNTs	1.32	254258/88178	2.88
Au/TiO_2 NTs	1.03	129785/81012	1.60
Au/TiO_2 PCNTs	1.17	228440/87248	2.62

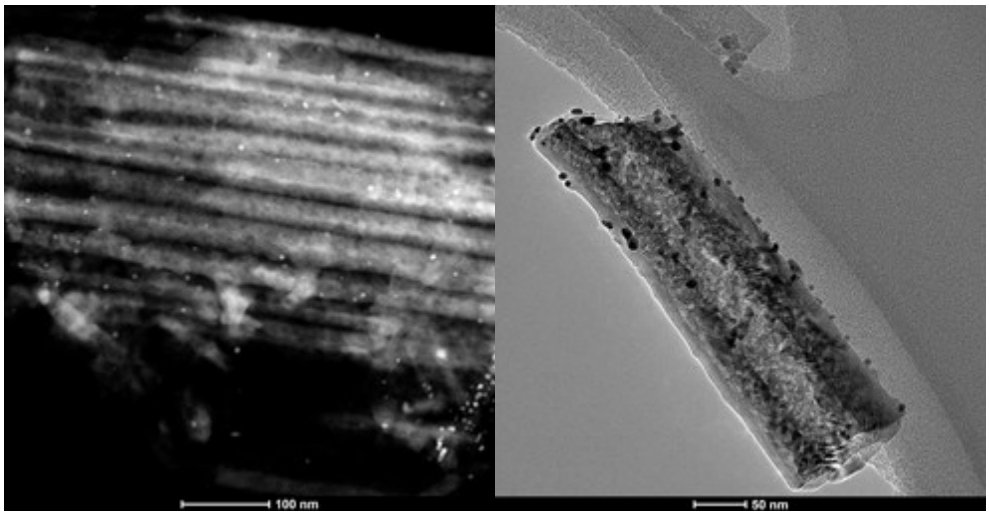
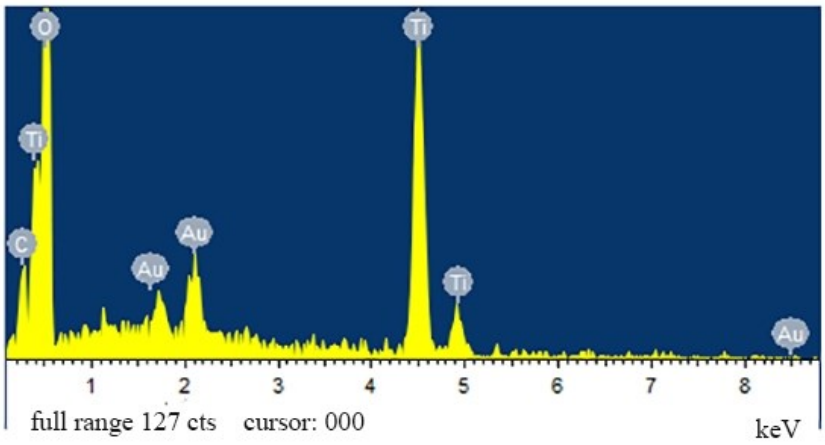


Fig. S4 TEM images of Au/TiO_2 PCNTs.



Element	Weight percent	Atom percent
C K	3.03	6.49
O K	39.99	64.18
Ti K	53.99	28.94
Au M	2.99	0.39
Total	100.00	

Fig. S5 SEM-EDS mapping of Au atom percent analyzed from top view.

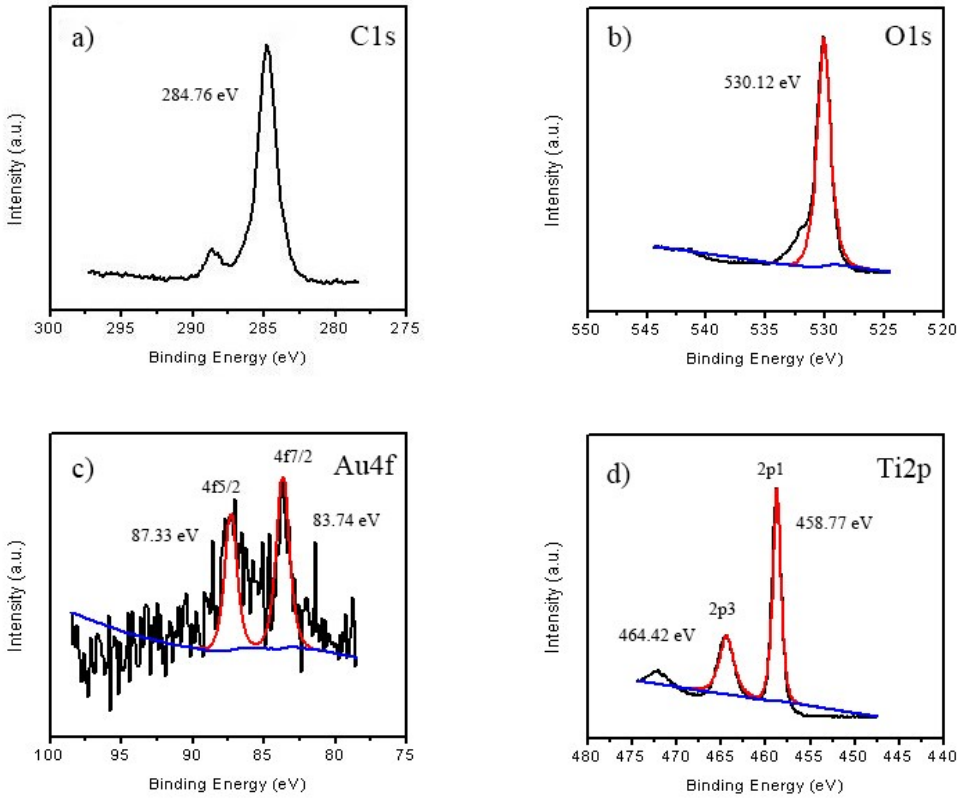


Fig. S6 XPS of a) C1s, b) O1s, c) Au4f and d) Ti2p for Au/TiO_2 PCNTs scratched off from Ti foil surface.

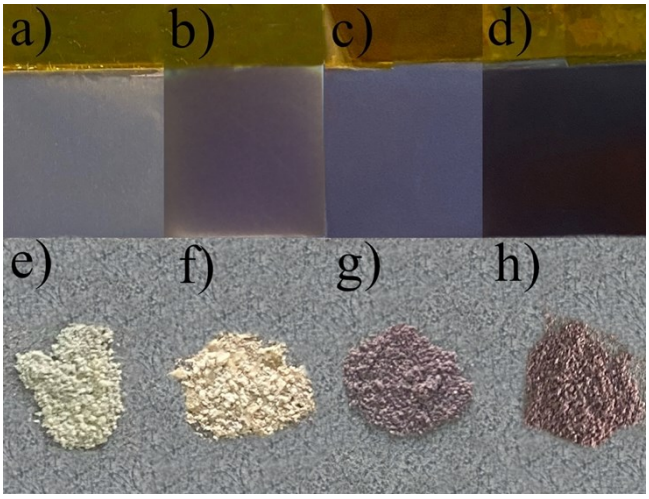


Fig. S7 Digital photograph of the prepared samples and scratched powder from Ti foil. a, e) TiO_2 NTs; b, f) TiO_2 PCNTs; c, g) Au/TiO_2 NTs; d, h) Au/TiO_2 PCNTs.

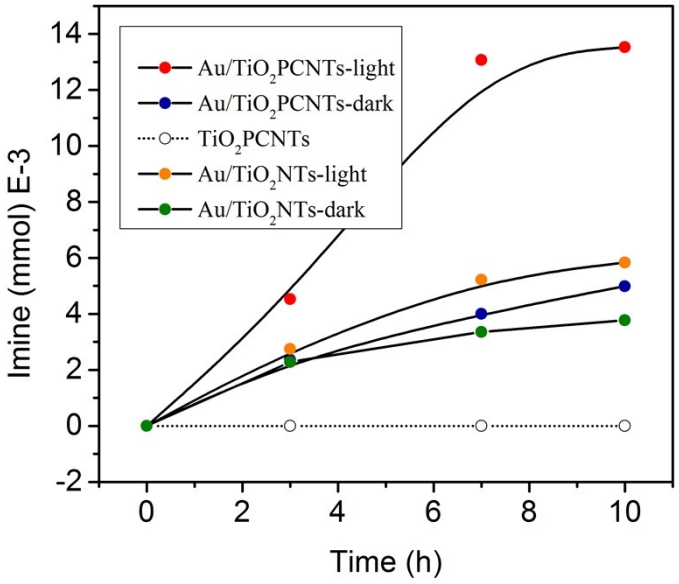


Fig. S8 Imine product yields for hydroamination of phenylacetylene with aniline.

Table. S2 The summary of Au content in Au/TiO_2 NTs and Au/TiO_2 PCNTs tested by ICP.

Samples	Entry	Raw data (μg) per slice	Average value (μg) per slice	Content (mmol) per slice
Au/TiO_2 NTs	1	1.960	5.059	$2.568*10^{-5}$
	2	4.257		
	3	8.961		
Au/TiO_2 PCNTs	1	7.296	8.737	$4.435*10^{-5}$
	2	8.261		
	3	10.654		

Table. S3 The comparison of activity for hydroamination of phenylacetylene with aniline over different catalysts.

Catalyst	**Reaction condition**	**Yield (mmol)**	**TON[a]**	**TOF (h^{-1})**	**Ref**
Au/TiO_2 PCNTs	visible light, 55 °C	13.1×10^{-3}	294.8	42.1	This work
Au_n-SiO_2@ICRM	Room temperature	0.215	43	1.79	1
Au/TiO_2+H_3PO_4·$12WO_3$	80 °C	0. 92	460	38.3	2
Au/C	100 °C	0.5~0.7	24~35	1~1.5	3
Au/TiO_2(B)_N	visible light, 40 °C	0.4	104	4.16	4
Au-Ch(I)SiO_2	100 °C	0.92	83.6	3.8	5
AuCo/ZrO_2	visible light, 80 °C	0.95	187.2	7.8	6

[a] TON is calculated on the mole of Au content.

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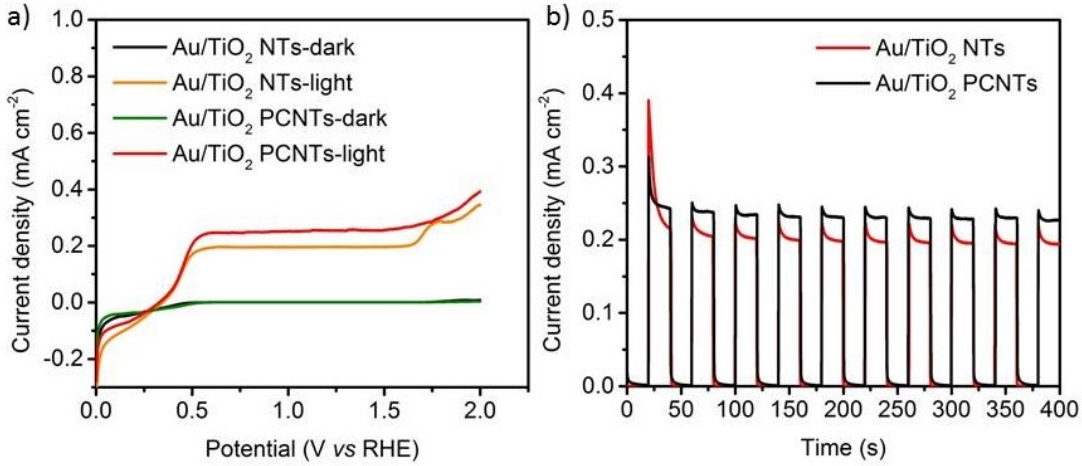

Fig. S9 a) The LSV and b) I-t curves at 1.23 V *vs.* RHE for Au/TiO_2 NTs and Au/TiO_2 PCNTs under light and in the dark. The test was conducted in 1.0 M KOH aqueous solution, Xe lamp with light filter (> 400 nm).

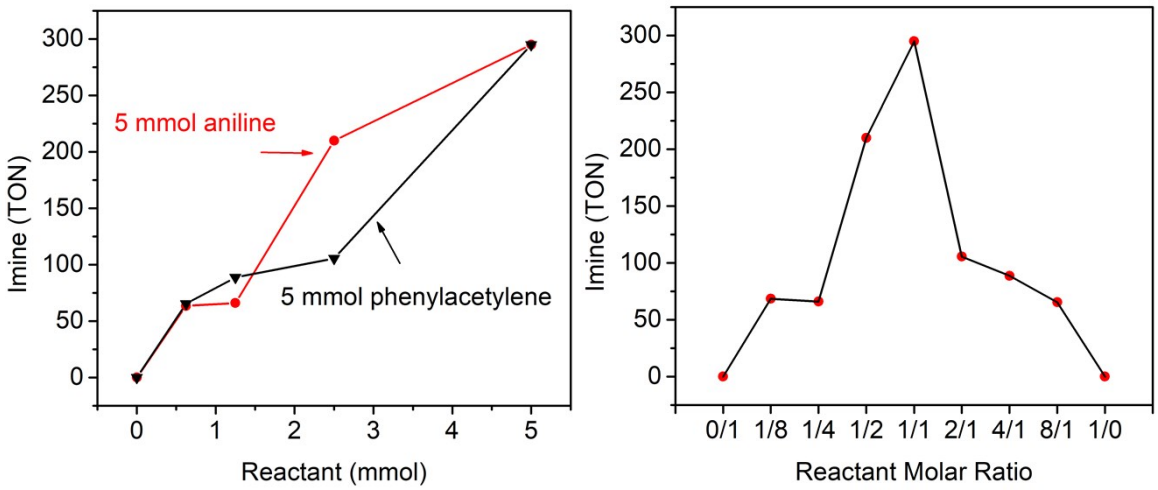

Fig. S10 The influence of reactant molar ratio on the imine yield (TON) for Au/TiO_2 PCNTs.