Supporting Information

Vertical 3D Printed Pd/TiO_2 Arrays for High Efficiency Photo-assisted Catalytic Water Treatment

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Keywords: 3D printing, TiO_2, Hierarchical vertical array, Catalytic water treatment, 4-nitrophenol

Supplementary Figures:

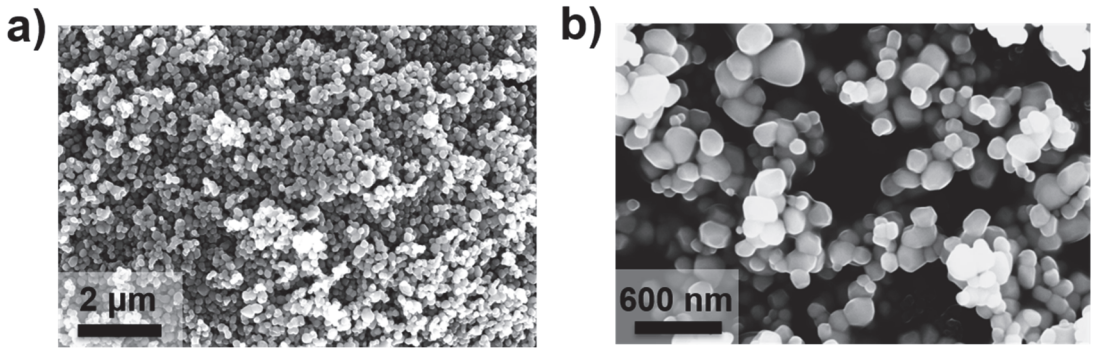

Figure S1. SEM images of raw TiO_2 particles with submicron diameters.

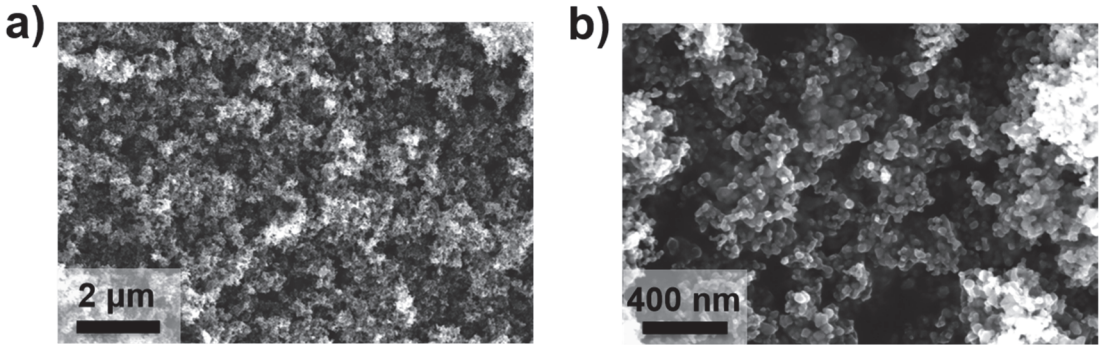

Figure S2. SEM images of raw TiO_2 nanoparticles.

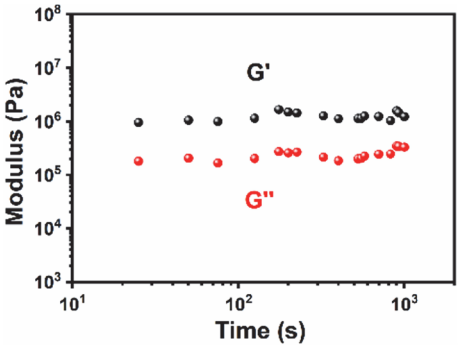

Figure S3. Dynamic modulus (G′ and G″) evolution as a function of time for the TiO_2 ink with a solid content of 56 wt%.

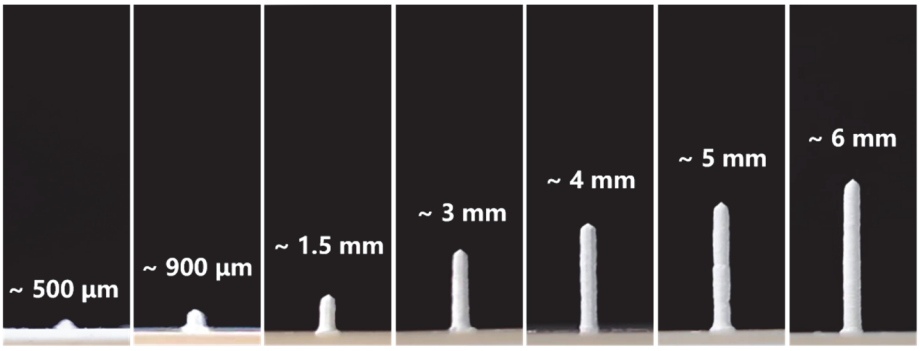

Figure S4. Optical images of TiO_2 vertical pillars with different heights, demonstrating the flexibility and controllability of vertical 3D printing.

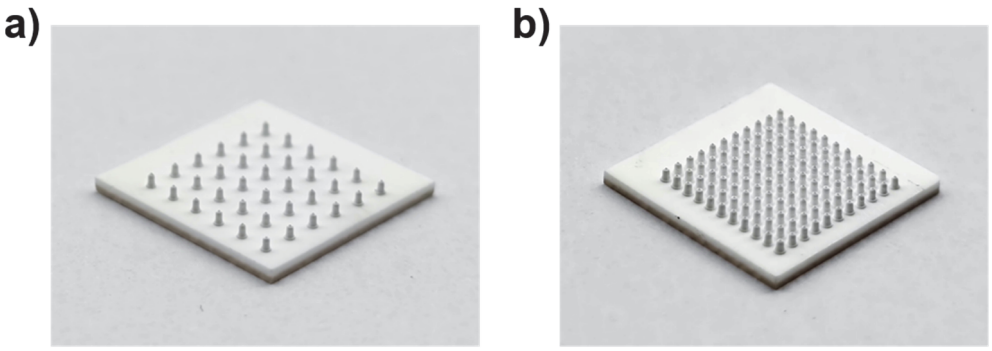

Figure S5. Optical images of TiO_2 pillar arrays with different packing densities.

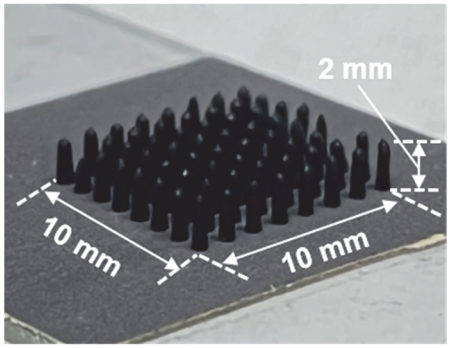

Figure S6. Photograph of a vertically printed graphene array.

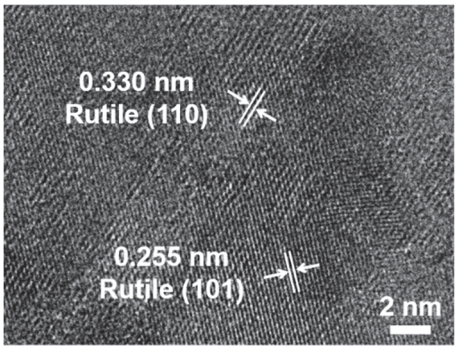

Figure S7. The lattice fringe spacing of a TiO_2 nanorod.

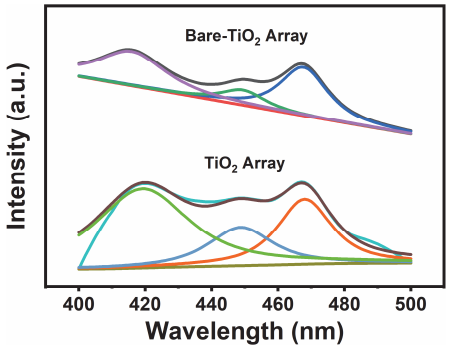

Figure S8. Photoluminescence spectra of the bare-TiO_2 array and hierarchical TiO_2 array.

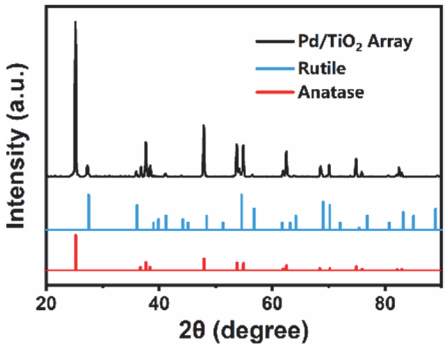

Figure S9. XRD patterns of Pd/TiO_2 array in contrast to rutile TiO_2 and anatase TiO_2.

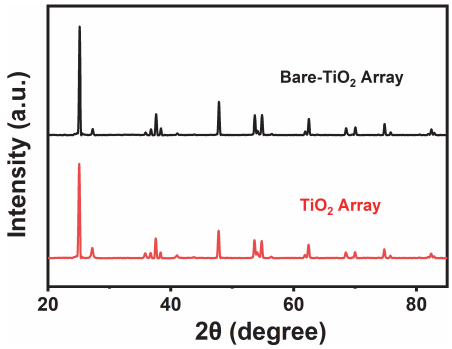

Figure S10. XRD patterns of vertically printed TiO_2 pillar array without (top) and with (bottom) nanorods.

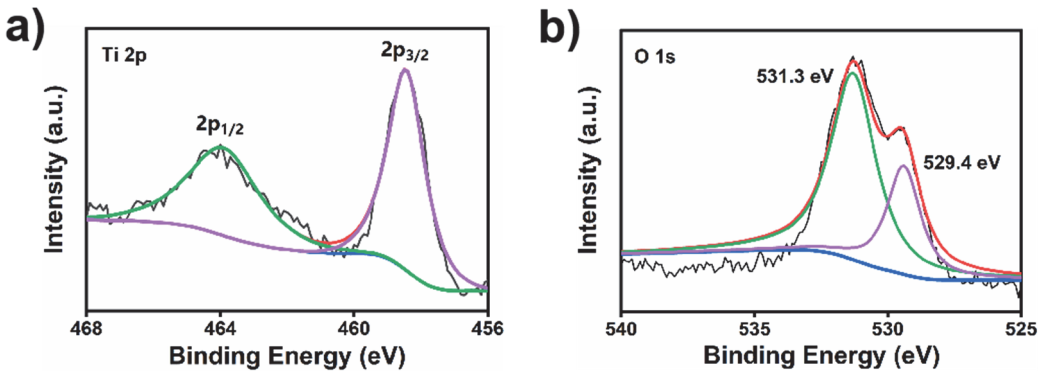

Figure S11. XPS survey spectra of Ti 2p peaks and O 1s peaks.

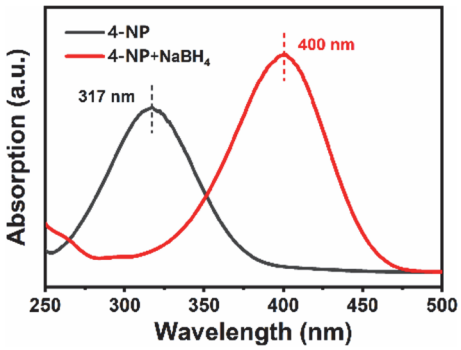

Figure S12. UV–vis spectra of pure 4-NP aqueous solution as well as the mixed solution of 4-NP and $NaBH_4$. The addition of $NaBH_4$ enabled the absorption peak to redshift from 317 nm to 400 nm.

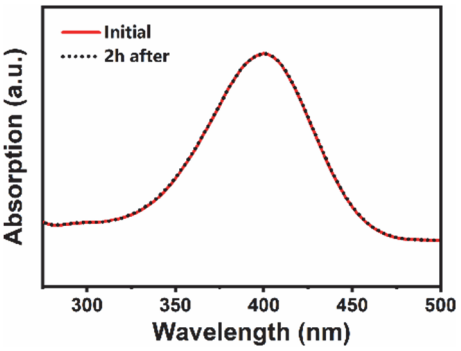

Figure S13. UV–vis spectra of the mixed solution of 4-NP and $NaBH_4$ in the absence of catalysts, initially and being placed in dark conditions for 2 hours.

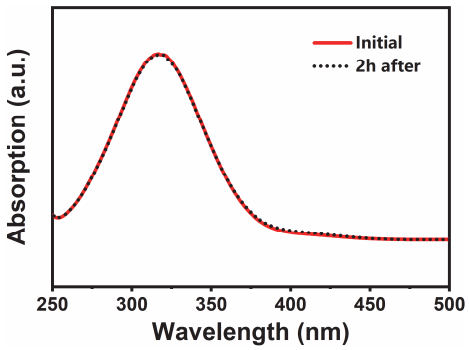

Figure S14. UV–vis spectra of the 4-NP solution with catalysts in the absence of $NaBH_4$, initially and being placed in dark conditions for 2 hours.

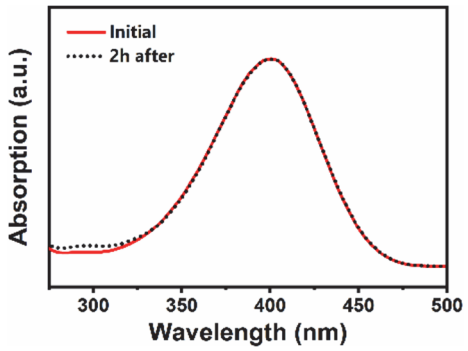

Figure S15. Under light irradiation, comparison of UV–vis spectra of the mixed solution of 4-NP and $NaBH_4$ at the initial time and after 2 hours in the absence of catalysts.

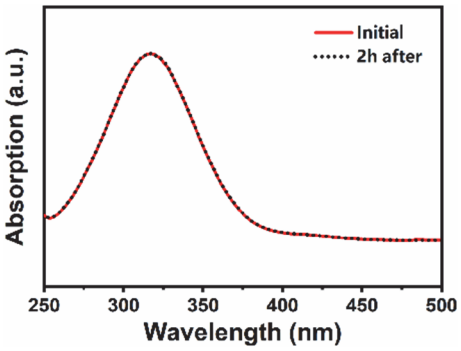

Figure S16. Under light irradiation, comparison of UV–vis spectra of the 4-NP solution with catalysts at the initial time and after 2 hours in the absence of $NaBH_4$.

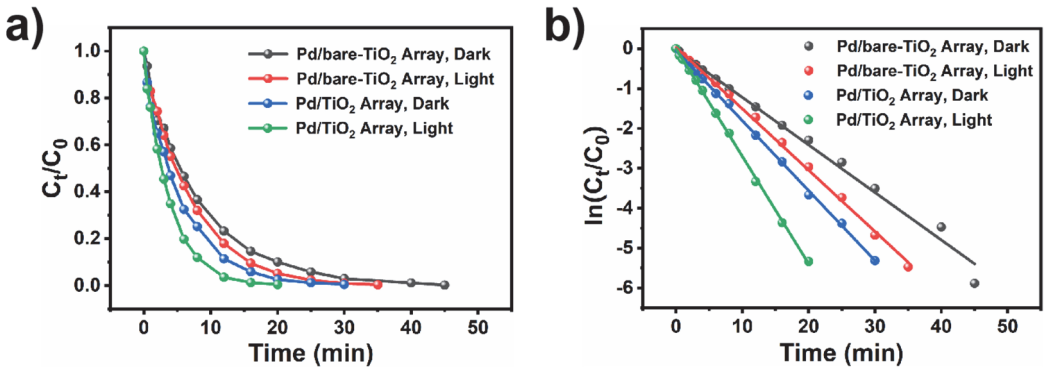

Figure S17. (a) Plots of C_t/C_0 vs the reaction time for the catalytic reduction of 4-NP to 4-AP using the Pd/bare-TiO_2 array and hierarchical Pd/TiO_2 array under light and dark conditions. b) Plots of $\ln[C_t/C_0]$ vs the reduction time.

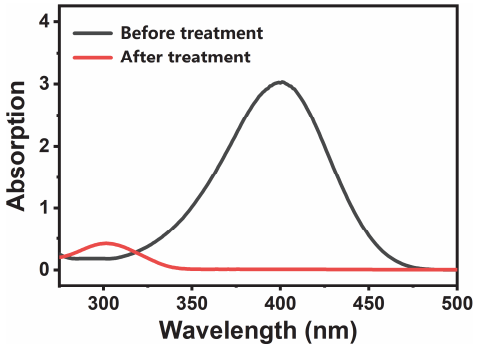

Figure S18. Comparison of UV–vis absorption spectra of reaction solutions before and after treatment.

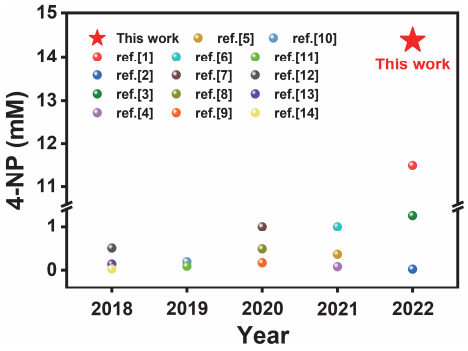

Figure S19. Comparison of the 4-NP concentration treated in this work with other works reported in recent years (non-exhaustive survey).[1-14]

Supplementary videos:

Video S1. Dynamic display of the flow state when fluid passes through the TiO_2 vertical array (MP4).

Video S2. Dynamic display of the experimental device for the rapid and efficient treatment of 4-NP wastewater by hierarchical Pd/TiO_2 vertical arrays (Double speed video) (MP4).

Supplementary tables:

Table S1. G-code of the vertical 3D printing protocol.

1	Line Speed	1.2			
2	Z Clearance Setup	20	1		
3	Call Subroutine	70	8	95	10001
4	Call Subroutine	70	8.5	95	10001
5	Call Subroutine	70	9	95	10001
6	Call Subroutine	70	9.5	95	10001
7	Call Subroutine	70	10	95	10001
8	Call Subroutine	70	10.5	95	10001
9	Call Subroutine	70	11	95	10001
10	Call Subroutine	70	11.5	95	10001
11	Call Subroutine	70	12	95	10001
12	Call Subroutine	70	12.5	95	10001
13	Call Subroutine	70	13	95	10001
14	Call Subroutine	70	13.5	95	10001
15	Call Subroutine	70	14	95	10001
16	Call Subroutine	70	14.5	95	10001
17	Call Subroutine	70	15	95	10001
18	Call Subroutine	70	15.5	95	10001
19	Call Subroutine	70	16	95	10001
20	Call Subroutine	70	16.5	95	10001
21	Call Subroutine	70	17	95	10001
22	Call Subroutine	70	17.5	95	10001
23	Call Subroutine	70	18	95	10001
24	End Program				
25	Label No	1			
26	Line dispense Setup	0.2	0.5	0	0
27	Line Start	70	8	85	
28	Line End	70	8	84.2	
29	Line Start	70.5	8	85	
30	Line End	70.5	8	84.2	
31	Line Start	71	8	85	
32	Line End	71	8	84.2	
33	Line Start	71.5	8	85	

34	Line End	71.5	8	84.2	
35	Line Start	72	8	85	
36	Line End	72	8	84.2	
37	Line Start	72.5	8	85	
38	Line End	72.5	8	84.2	
39	Line Start	73	8	85	
40	Line End	73	8	84.2	
41	Line Start	73.5	8	85	
42	Line End	73.5	8	84.2	
43	Line Start	74	8	85	
44	Line End	74	8	84.2	
45	Line Start	74.5	8	85	
46	Line End	74.5	8	84.2	
47	Line Start	75	8	85	
48	Line End	75	8	84.2	
49	Line Start	75.5	8	85	
50	Line End	75.5	8	84.2	
51	Line Start	76	8	85	
52	Line End	76	8	84.2	
53	Line Start	76.5	8	85	
54	Line End	76.5	8	84.2	
55	Line Start	77	8	85	
56	Line End	77	8	84.2	
57	Line Start	77.5	8	85	
58	Line End	77.5	8	84.2	
59	Line Start	78	8	85	
60	Line End	78	8	84.2	
61	Line Start	78.5	8	85	
62	Line End	78.5	8	84.2	
63	Line Start	79	8	85	
64	Line End	79	8	84.2	
65	Line Start	79.5	8	85	
66	Line End	79.5	8	84.2	
67	Line Start	80	8	85	
68	Line End	80	8	84.2	
69	End Program				

Table S2. The comparison of TOF value of 4-NP catalytic reduction by Pd/TiO_2 array with that of Pd-based catalysts reported in literature in the past five years (non-exhaustive survey).

Sample	4-NP (mM)	TOF (min^{-1})	Reference
Pd/3D-AC	14.38	1.68	15
Pd-D-SCG	0.12	1.53	16
CS-CNTs-PdNPs	0.067	0.035	17
Pd/LDHs	1.30	3.42	18
PNIPAM-Pd	0.147	6.7	19
MNPs-PDDA-HA/Pd	0.1	2.18	20
Pd@PPM2	0.1	0.99	21
Pd/TiO_2	14.38	2.69	22
Pd@CHI	0.013	0.42	23
Pd/PNGO	0.19	6.115	24
Pd@polyCD	0.0056	0.0316	25
Pd/CNSs	0.09	2.63	26
Pd/TiO_2	14.38	8.00/12.17	This work

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