Supporting Information

Text S1. Determination of TEM and FESEM-EDS

For electron-microscopic study, leaf tips (about 2–3 mm) were fixed in 2.5% (v/v) glutaraldehyde in 0.1 M sodium phosphate buffer (pH 7.4) overnight and then washed three times with buffer. The samples were post fixed in 1% (m/v) OsO_4 for 1 h and washed again three times with buffer. Thereafter, the samples were dehydrated in a graded series of ethanol (50, 60, 70, 80, 90, 95, and 100%, *v/v*) for 15–20 min each and then in absolute acetone for 20 min. After dehydration, the samples were embedded in Spurr's resin overnight and heated for 9 h at 70 °C. After that ultra-thin sections (80 nm) were cut and mounted on copper grids for transmission electron microscopy (TEM 1230EX, JEOL, Japan) at 60 kV. Three samples per treatment were used for ultrastructural observations studies. Moreover, the samples were examined by a field emission scanning electron microscope (FESEM-6301F) coupled with energy-dispersive spectroscopy (EDS). The electron beam energy was 10 kV and beam current was 80.0 μA. The samples were mounted onto a double-sided carbon tape on a single pin aluminum stab and sputter-coated with iridium on a rotation stage for 10 s using a sputter coater (Emitech K575X, Fall River, MA).

Text S2. The description of photosynthesis parameters

Six chlorophyll fluorescence parameters were examined as the results of the original fluorescence data, containing maximum quantum yield (F_v/F_m), actual photosynthetic rate (Y(II)), non-photochemical quenching (Y(NPQ)) related to all photo-protective mechanisms, non-photochemical quenching coefficient (qN), photochemical fluorescence quenching coefficient (qP)

in the puddle model, photochemical fluorescence quenching (qL) in the lake model.

F_v/F_m is calculated as following Eq. (1):

$$F_v/F_m=(F_m-F_0)/F_m=\triangle F/F_m \quad (1)$$

which indicates the maximum quantum efficiency of PSII. F_m presents complete reduction of photosystem II electron acceptor, and F_v refers to variable fluorescence. F_0 reflects the manufacture of maximal fluorescence, which can be induced by low irradiation followed by a saturating light pulse. Y(II) is deemed to be one of the most common parameters, which offers an immediate method to detect the photosystem II operating efficiency. Y(II) is calculated as following Eq. (2):

$$Y(II) = (F_m'-F_t)/F_m' \quad (2)$$

where F_m' shows the saturation pulse value with no dark adapting and F_t shows the fluorescence level reflecting photosynthetic activity. Photochemical quenching in the puddle model is calculated based on Eq. (5):

$$qP = (F_m'-F)/(F_m'-F_0') \quad (3)$$

which reflects the photosynthetic activity.

As a parameter of heat dissipation, NPQ presents a total combination of photo-protective mechanisms, and its calculation is following Eq. (3):

$$NPQ = (F_m-F_m')/F_m' \quad (4)$$

Also, Y(NPQ) presents heat dissipation, which is relative to total photo-protective mechanisms, which is calculated using Eq. (4):

$$Y(NPQ) =1-Y-Y(NO) \quad (5)$$

where the Y(NO) means all other combined total of non-photochemical quenching which are not related to photo-protective. qL is a parameter of photochemical quenching in lake model in PSII reaction, it was calculated as Eq. (6):

$$qL = qP*F_0'/F \quad (6)$$

qN presented the coefficient in non-photochemical fluorescence quenching, which is calculated by Eq. (7):

$$qN = (F_m-F_m')/(F_m-F_0) \quad (7)$$

Text S3. Assays of metabolites extraction and derivatization

Fresh rice leaves were immediately frozen in liquid nitrogen and freeze-dried, then grounded to powder and stored at −80 °C until further analysis.

The extraction solution was a single-phase solvent methanol: chloroform: water mixture (2 mL, 5:2:2, v/v/v) containing 20 mg/L ribitol as internal standard. 10.0 mg of rice leaf powder were mixed with 2 ml extraction solution in a sample. The metabolites were extracted by an ultrasonic method for 40 min at room temperature. Then the extraction solution was centrifuged twice at 10, 000 g for 10 min. Lately, 400 μL of the supernatant was transferred to a 2 mL Eppendorf tube and freeze-dried.

For derivatization, 60 μL of O-methoxyamine hydrochloride in pyridine (20 mg/L) was added to the dried samples. After vortexed for 1 min, the mixture was incubated at at 37 °C for 90 min. Then 80 μL of MSTFA was added, the samples were incubated at 37 °C for 30 min to silylated.

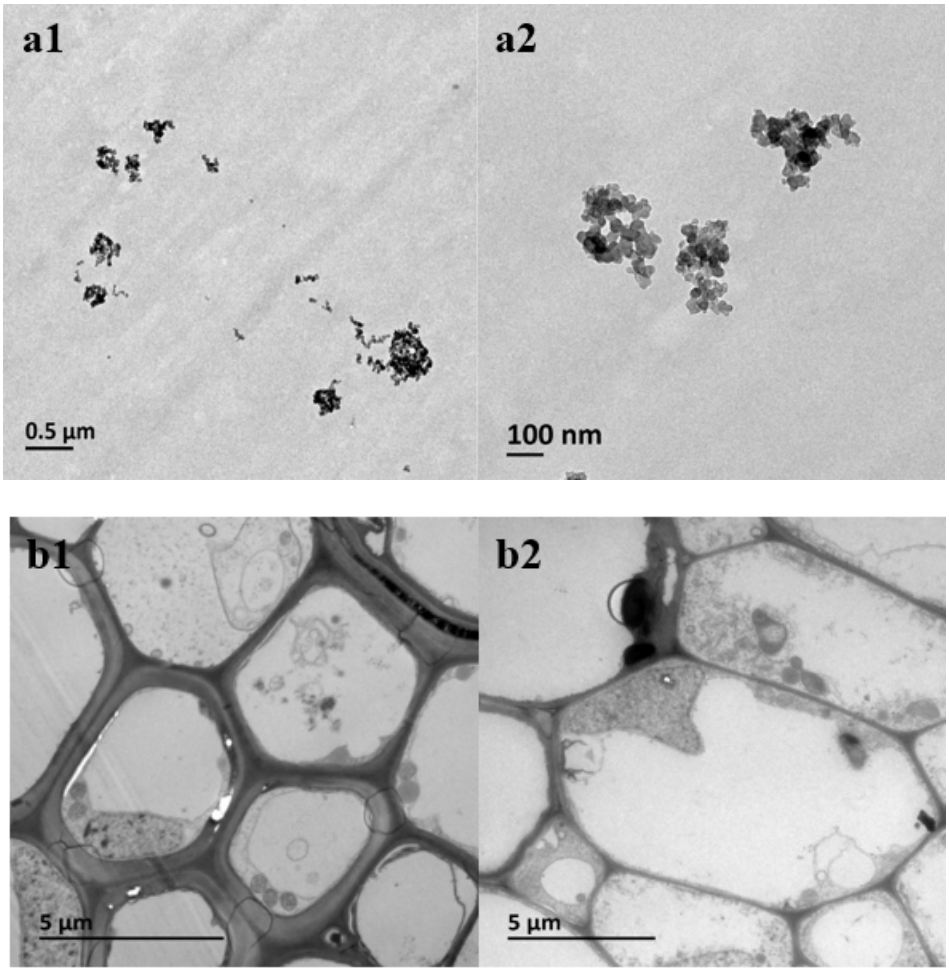

Fig. S1. The TEM images of nano-TiO_2 in the treatment group of 100mg/L (a1 and a2) with 12,000X and 50,000X, respectively. The TEM images of root (b1) and leave (b2) of rice in 100mg/L exposure with 5,000X and 4,000X, respectively.

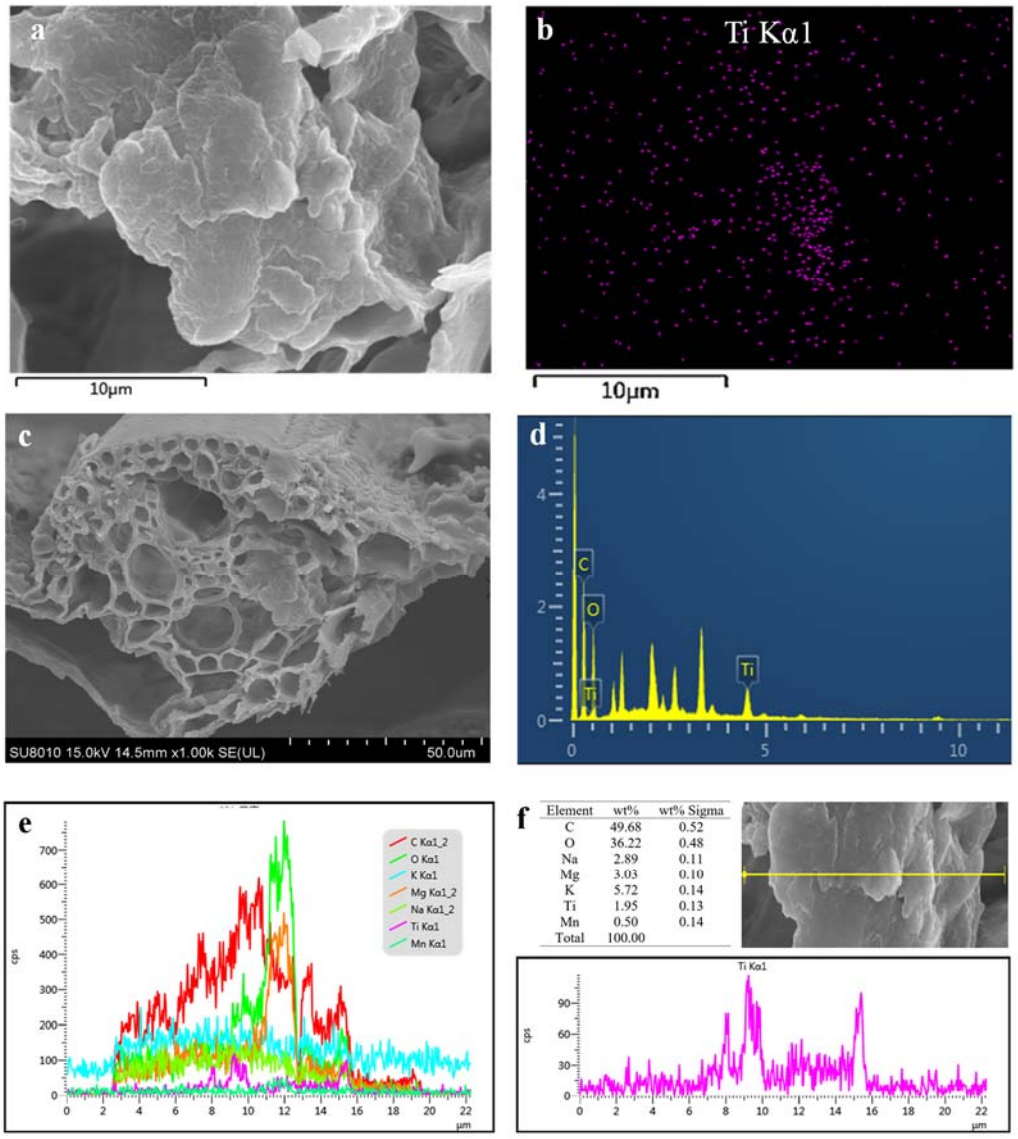

Fig. S2. The FESEM images of nano-TiO_2 in the treatment group of 100 mg/L (a and c). The EDS results (d, e, f) and the EDS layered image (b).

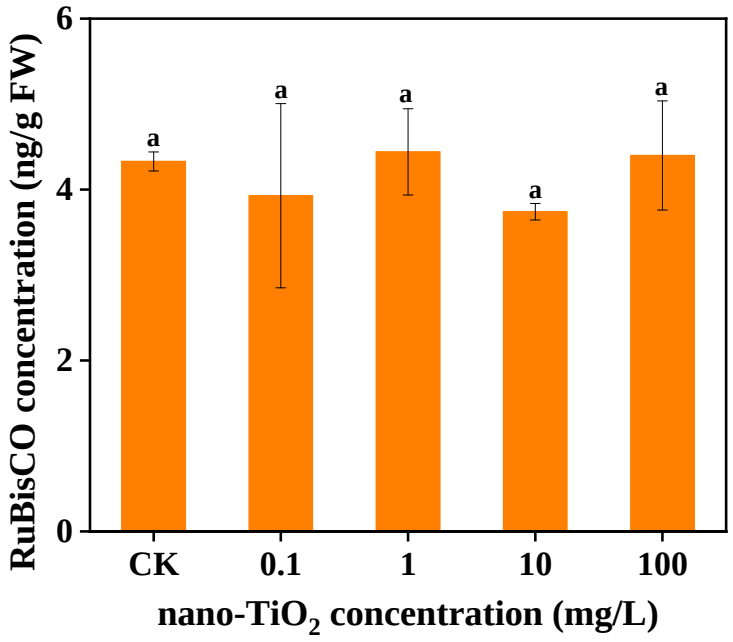

Fig. S3. RuBisCO content of rice leaves after exposure to nano-TiO_2 for 21-day. Values are presented as means ± SE (n = 3). Points denoted by different lower case letters on each bar differ significantly at $p < 0.05$. The same upper case or lower case letter is not significantly different for a particular dose

Table S1. The list of identified metabolites of rice

Name	0.1mg/L	1mg/L	10mg/L	100mg/L
1,2-Ethandimine	0.6534 *	0.3330	0.3186	
1-Monopalmitin	1.0020	1.0147	0.9728	0.9679
2-Butenedioic acid	0.5134	0.4416	0.3996	0.8629*
2-Keto-l-gluconic acid	1.2199	1.3088	1.2408	1.4613
3-Methylpiperazine-2,5-dione	0.1962	0.1031	0.1746	0.1706
3-Pentenenitrile	0.0297	0.0161	0.0368	0.0233
4-Aminobutanoic acid	4.4439**	4.3873**	3.8488**	4.5655**
4-Coumaric acid	0.8834	0.8833	1.0258*	0.9870
4-Hydroxybutanoic acid	0.3607	0.2264	0.3864*	0.3731
9,12-Octadecadienoic acid	1.9395*	2.1838	2.0690	1.4755**
Aucubin	0.2498	0.2836	0.2911	
Azelaic acid	0.6719	0.6453	0.6832	0.7318
Benzoic acid	0.1237		0.1384	0.1697
Boric acid	2.0536	1.7650	1.0395	1.7482
Butanedioic acid	1.8938	1.6912*	1.9607	2.2083
Campesterol	1.9043	2.0970	2.0983	2.1674
Citric acid	9.1848**	8.7808**	8.9971**	9.9749
D-(+)-cellobiose	2.1678	2.1722	3.4465*	2.5675
D-(+)-galactopyranose	0.1169	0.1597		0.1430
D-(+)-galacturonic acid	1.9527	2.0217	1.9756	1.9607
D-(+)-talose	47.2880	47.6889	38.3052**	38.0571**
D-(+)-turanose	0.5259*	0.7510*	0.5493*	0.2858*
D-(+)-xylose	1.9971	2.2340	2.0541	1.3799
D-allose	15.3130	15.7789	14.0262**	14.6771**
D-arabinose	1.1813	1.5819	1.2236	1.5078
D-erythro-pentitol	0.1500	0.1613	0.1523	
D-fructose	61.6904	63.6884	50.8176**	49.1599**

D-galactose	2.5874*	2.3673	3.3406	4.1571
D-glucoin acid	1.1876	0.4225	0.9509	1.4218*
D-lactose	1.1275	1.5433	1.2929	1.3931
D-mannitol	0.6057	0.7166	1.1821**	0.4816
D-ribose	1.8066	1.3377	1.6211	1.1370
D-xylofuranose	1.3173		0.7054	1.5572
Erythrono-1,4-lactone	0.3804	0.3585	0.3482	0.3283
Ethanolamine	3.4981	3.2483	3.3432	2.4893
Ferulic acid	0.6652	0.7958*	0.7939*	0.7661
Galactoside	0.5229	0.4007	0.3310	0.5476
Glyceric acid	1.7973**	2.2076	1.7884**	2.3497
Glyceryl-glycoside	1.8290**	1.2377**	1.8389**	1.6476**
Glycolic acid	0.6940	0.6601	0.6769	0.7654
Heptadecanoic acid	0.1989		0.3856	
Hydracrylic acid		0.1528	0.2105	0.1438
Isonicotinic acid		0.1720	0.1807	
Itaconic acid	0.2733	0.4319	0.5942**	0.6507**
Lactic acid	2.8802**	2.9402**	2.1931**	3.7807
Lactulose	0.2952	0.6037	0.3181	0.3258
L-alanine	0.8789	0.7274	1.0661	1.0544
L-aspartic acid	0.8051	0.4840	1.0980	1.8293
L-fucose		0.0328	0.5932	1.5150
L-glutamic acid	1.4993	1.9599	1.9738	
L-isoleucine	0.1940	0.3108	0.1119	0.1272
L-leucine	0.0906	0.1601	0.0966	0.1107
L-norvaline	0.0931		0.3133	0.3248
L-serine	1.4800	1.6726	1.5785	1.4138
L-threonic acid	3.9881	4.1565	3.8424	4.3929*
L-threonine	0.3889	0.4792*	0.3246	0.5134**

L-valine	0.2894	0.4856*	0.2890	0.2560
Malic acid	13.4410**	14.3380**	15.0350**	16.9478
Maltose	5.7784	5.8820	2.4798**	3.2034**
Maleic acid			0.2089	0.2227
Myo-inositol	7.1385**	7.2428**	6.7891*	6.7493*
N-acetyl glucosamine	0.0947	0.0878	0.1023	0.0912
Oxalic acid	0.2407		0.2218	0.1728
Palmitic acid	7.8231	7.8875	8.3949*	7.9340
Pentaric acid	3.7796	3.1160*	4.4796*	4.5791
Phosphoric acid	24.2575**	22.4100**	24.0711**	22.5914**
Phthalic acid	3.0760	5.9068	3.4769	4.4980
Proline	3.0229	3.1861	3.6319	3.5889
Putrescine	1.8796**	2.1643**	1.1258	1.1141
Quininic acid	4.2066**	5.1267**	3.7364**	2.9063
Rhamonse	0.8632*	0.7983*	0.5728	0.5510
Ribonic acid	0.6883	0.6404	0.5195	0.6076
Shikimic acid	4.9014*	5.5961**	4.9736**	4.2905
Stearic acid	2.7922	2.9615	3.1923**	2.9374
Stigmast-5-ene	2.2018	2.3158	2.2788	2.3548
Stigmasterol	2.7639	2.9373	2.9432	3.0636**
Sucrose	57.1546**	55.9755**	51.9403	39.9889**
Alpha-d-glucopyranoside	0.0731	0.1050	0.0847	0.1462
Alpha-linolenic acid	2.7344	3.3139*	3.4339**	2.3494**
Alpha-mannobiose	0.8033	1.2026	1.1237	1.0259
Beta-alanine	0.3237	0.3270	0.3358	0.3135
Beta-d-(+)-talopyranose	0.2126	0.1941	0.1982	0.1759
Beta-gentiobiose	1.2891	1.3484	0.9157	1.0394

* significant difference when $p < 0.05$

** significant difference when $p < 0.01$