Supporting Information

Redox active Zn/ZnO duo generating superoxide ($\cdot O_2^-$) and H_2O_2 in all conditions for environmental sanitation

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Experimental Section

Materials

Tryptic soy broth (TSB) and yeast mould broth (YMB) powder were purchased from BD Diagnostics (Singapore) and used to prepare the broths according to the manufacturer's instructions. Gram-negative bacteria *E. coli* (ATCC No. 8739), Gram-positive bacteria *S. aureus* (ATCC No. 6538P), and fungi *C. albicans* (ATCC No. 10231) were purchased from ATCC (U.S.A) and re-cultured according to the suggested protocols. Zinc powders (<10 μm), Zinc oxide powder (~0.2-0.5 μm. Cat: 20553-2, Lot.: S15354-014.) were purchased from Sigma-Aldrich and used as received. $Zn(NO_3)_2.4H_2O$ and KOH were purchased from Merck. Reservoir water was collected from Pandan Reservior of Singapore, and sea water was collected from west coast of Singapore. Before use, the water was passed through 0.22 μm filter.

Sample preparation

Preparation of Zn/ZnO core/shell particles

Method A (Room temperature solution method):[1] 5 ml of 0.5 M $Zn(NO_3)_2$ aqueous solution and 5 ml of 4 M KOH were mixed, and then 1.0 g of Zn particles (pre-treated with 1 ml 1% HCl to remove the zinc oxide on surface) were added to the solution. After 2 h reaction at room temperature under gentle agitation, the product was separated by centrifugation, followed by washing 3 times with DI water and 2 times with ethanol. The prepared product was dried in vacuum oven, and stored at room temperature for future use.

Method B (Water cooking method): 2.0 g of Zn particles (1-10 μm) without pre-treatment were added in 10 ml of H_2O in a 15 ml sealed glass reactor. The reactor was heat up to 105 ^oC in a pre-heated oil bath for 10 hours under magnetic stirring.

Method C (Hydrothermal method): 1.3 g of Zn particles (0.02 mol, 1-10 μm) were washed with 1.3 ml 1% HCl. Aqueous solution of $Zn(NO_3)_2$ (0.001 mol) was added to $NH_3 \cdot H_2O$ (0.01 mol) solution. Precipitate formed immediately and then dissolved forming a transparent solution. Pre-treated Zn particles were added to the solution in a sealed reactor

and the volume of the mixture was made to 10 ml with water. Reaction was conducted at 100 ^{o}C in a water bath for 15 min under magnetic stirring.

Surface coating: 0.02 g of Zn particles, ZnO particles, Zn + ZnO mixture (0.01 g + 0.01 g), or 0.02 g Zn/ZnO core/shell particles were added in 200 µL ethanol and treated with ultrasonic for 5 min to obtain well-dispersed solutions. 100 µL of the solution was drop-coated onto a clean glass slide (2.5 × 2.5 cm). After evaporation of ethanol, the other 100 µL of particle solution was applied onto the slide. After drying, a smooth and condensed coating was formed on the glass slide. Each slide contains 0.02 g of powders on the surface.

Characterization of Zn/ZnO core/shell particles: The morphology of the core/shell structures was characterized by TEM (FEI Tecnai G^2 F20 electron microscope), SEM (JEOL JSM-7400E), and XRD (PANalytical X-ray diffractometer, X'pert PRO, with Cu Kα radiation at 1.5406 Å). Prior to SEM imaging, the samples were coated with thin Pt film using high resolution sputter coater (JEOL, JFC-1600 Auto Fine Coater). Coating conditions: (20 mA, 30 s).

Microbial growth conditions and antimicrobial test

Bacterial Culture: *E. coli* and *S. aureus* were cultured in TSB overnight in an incubator at 37 ˚C under constant shaking (300 rpm). *C. albicans* were grown in YMB at room temperature under constant shaking (300 rpm). Prior to each bacterial experiment, bacteria/fungus was refreshed from stock to 5 ml of respective nutrient broth. Cells were collected at the logarithmic stage of growth and the suspensions were adjusted to OD_{600} = 0.07 using TSB or YMB. This yielded a microbial stock solution with ~3 × 10^8 colony forming units (CFU) per mL.

JIS Z 2801 method for killing efficacy testing (Japanese industrial standard)[2]: The microbial stock solution (*E. coli* or *S. aureus*, 3 × 10^8 CFU/ml in TSB) was further diluted 100 times. And 100 µL of cell suspensions were placed on each surface. Experiments were carried out in triplicate at 37 °C. After incubation for 24 h, the respective cell suspensions were washed with 9.9 ml of TSB and then and plated on 1.5% LB agar plates after dilution. The plates were incubated for 24 h at 37 ˚C. Resulting colonies were counted and the number of colony forming units per mL was calculated. For *C. albicans*, YMB instead of TSB was used during the test.

Killing kinetics study[3]: The antibacterial activities of the samples was tested against *E. coli* and *S. aureus.* Cells were harvested from the stock solution by centrifugation at 3500 rpm for 5 min, washing twice with phosphate-buffered saline (PBS, pH 7.4) and diluting to the concentration of 10^6 CFU/ml. 5 mg of Zn/ZnO and ZnO were added in 450 µL PBS solution and then mixed with 50 µL of bacteria suspension. The mixture was incubated at 37 ^{o}C under constant shaking. At different time intervals (5 min, 20 min, 80 min, and 320 min), aliquots were taken out, serially diluted, and then dispersed onto LB agar. Colonies on agar were counted after incubation at 37 ^{o}C for 24 h. All of the experiments were performed in triplicate, and the results were presented as mean ± standard deviation.

Zone of inhibition test[3]: The antibacterial activities of the core/shell particles were evaluated using disk diffusion assay (Kirby Bauer Method). 100 µL of *E. coli* or *S. aureus*

(~10^8 CFU·mL^{-1}) were plated on LB agar. Zn, ZnO, Zn/ZnO core/shell particles (0.01 g), or Zn + ZnO (0.005 g + 0.005 g) were loaded on a sterile disk (diameter = 9 mm, specified for inhibition zone study). The disk was placed on the agar seeded with bacteria. After 24 h incubation at 37 °C, the diameters of the inhibition zones were measured.

Minimum inhibitory concentrations (MIC): MIC of Zn^{2+} was determined using a standard MIC assay in TSB at 37 °C against *E. coli* and *S. aureus*. For *Candida albicans*, YMB was used at 25 °C. The growth of bacteria was monitored with a microplate reader. The MIC was recorded as the lowest concentration of sample that inhibited 99% microbial growth of the test organism. Microbial cells cultured in broth medium were used as negative control. Each test was carried out in four replicates.

Killing mechanism study

Zn^{2+} release analysis: The release of zinc from the samples in different solutions was measured by Inductively Coupled Plasma Mass Spectrometry (ICP-MS, ELAN DRC-e, PerkinElmer Co., USA), using 10 ppb, 30 ppb and 50 ppb Zn^{2+} solution as standards. For the measurement, 0.01 g of particles was added into 1 ml of selected solution. At certain time points, 500 µL of the mixture was taken out and centrifuged (13500 g × 10 min) to remove the insoluble residues. 10 µL of supernatants were diluted with 2 mL 1% HNO_3 for ICP-MS measurements.

ROS testing

·O_2^- radical measurement by XTT: 0.01 g of samples was added into 1.5 ml centrifuge tubes. For the detection of ·O_2^-, 1 ml of 100 µM XTT solution in PBS was added to each tube, and the mixture was well mixed by vortex and kept in a 37 °C incubator in dark. At certain time point, the tube was centrifuged (16800 rpm × 5 min), and 100 µl of solution was transferred to 96-well plate for absorption measurement. Absorption at 470 nm was measured with a microplate reader (Tecan Multimode reader, Spark 10M).

·O_2^- radical measurement by Nitroblue tetrazolium (NBT) method: 0.1 g of Zn/ZnO was added into 5 ml of 1 mM NBT in water. UV absorption was monitored for up to 24 h.

OH· radical measurement: 1 ml of 10 µM HPF testing solution was added in each sample. And the solution was well mixed by vortex and kept in a 37 °C incubator in the dark. At certain time point, the solution was centrifuged (16800 rpm × 5 min), and 100 µl of solution was transferred to a black 96-well microplate for fluorescence testing. Fluorescence at 490 nm/515 nm was collected with a microplate reader (Tecan Multimode reader, Spark 10M).

Detection of H_2O_2[4]: Testing samples were kept in a 1.5 ml centrifuge tube. 1 ml of testing solution in water containing 5 µL of 5 mg/ml 2',7'-dichlorofluorescein diacetate in acetone was added to each tube. After incubation at room temperature in dark, 100 µL of the solutions were pipetted into a 96-well black microplate in triplicates. The fluorescence was recorded using a microplate reader (Tecan Multimode reader, Spark 10M) with excitation at 485 nm and emission at 538 nm.

Detection of H_2O_2 with phenol red method [5]: 0.01 g of ZnO or Zn/ZnO was added in a 25 ml of phenol red aqueous solution (5×10^{-5} M) which contains 0.025 M NaBr and 0.1 mM Na_2WO_4, and reacted in dark. After that, 100 µl of the solution was transferred into a 96-well plate, and the absorbance at 598 nm was measured (Tecan Multimode reader, Spark 10M).

Scavenger quenching experiments for $\cdot O_2^-$ radicals:[6] Before experiment, *E. coli* were grown in TSB at 37 °C on a shaking bed (300 rpm). After that, *E. coli* were collected by centrifuge, washed with PBS, and re-dispersed in PBS. The bacteria were diluted to ~10^5 CFU/ml before use.

In a 15 ml centrifuge tube, 1 mg Zn/ZnO core/shell particles was cultured in 10 ml PBS buffer solution containing ~10^5 CFU/ml *E. coli* and 1 mM TEMPO. *E. coli* with 1 mM TEMPO PBS solution was used as negative control and *E. coli* with 1 mg Zn/ZnO in 10 ml PBS solution was used as positive control. The solution was incubated under constant shaking (300 rpm) at 37 °C in the dark. At 1 hour intervals 100 µL of solution was taken out, serially diluted (1x, 10x and 100x), and 100 µL of each dilution was dispersed into LB agar plates. Colonies on the plates were counted after incubation at 37 °C for 24 h, and the number of colony forming units per mL was calculated. All of the experiments were performed in triplicate, and the results were presented as mean ± standard deviation.

Scavenger quenching experiments for H_2O_2[6]: Before experiment, *E. coli* were grown in TSB solution at 37 °C on a shaking bed at 300 rpm. After that, *E. coli* were collected by centrifugation. The cells were washed with pH 7.4 PBS and re-dispersed in PBS.

In a 15 ml centrifuge tube, 1 mg of Zn/ZnO core/shell particles was cultured in 10 ml of PBS buffer solution which contains ~10^5 CFU/ml *E. coli* and 1 mg/ml of catalase (2950 unit/mg). *E. coli* mixed with 1 mg/ml catalase PBS solution was used as negative control while *E. coli* mixed with 1 mg Zn/ZnO PBS solution was used as positive control. The solution was incubated under constant shaking (300 rpm) at 37 °C in dark. At 1 hour intervals 100 µL of solution were taken out, serially diluted (1x, 10x and 100x), and 100 µL of each dilution was dispersed on LB agar. Colonies were counted after incubation at 37 °C for 24 h, and the number of colony forming units per mL was calculated. All of the experiments were performed in triplicates. The results were presented as mean ± standard deviation.

Materials safety study

Hemolysis assay: Fresh rat red blood cells were diluted with PBS buffer to give a cell suspension (4 % in volume). The cell suspension (100 µL) was introduced to each well of a 96-well plate and 100 µL of Zn/ZnO suspension was then added to the well. Triton X-100 (0.2 %) was used as positive control. The red blood cells in PBS were used as negative control. The plates were incubated for one hour at 37 ˚C. The 96-well plates were centrifuged at 2200 rpm for 5 min. Aliquots (100 µL) of the supernatant were transferred to a new 96-well plate. Hemoglobin release was measured at 576 nm using a microplate reader (Tecan Multimode reader, Spark 10M). Absorbance of the wells containing red blood cells lysed with 0.1 % Triton X-100 was taken as 100% hemolysis. Percentage of hemolysis was calculated using the following formula: Hemolysis (%) = [($OD_{576\ nm}$ in the sample - $OD_{576\ nm}$ in PBS)/($OD_{576\ nm}$ in 0.1 % Triton X-100 - $OD_{576\ nm}$ in PBS)] × 100. The data were expressed as mean and standard deviation of four replicates and the tests were repeated 3 times.

Ames test (Genotoxicity and mutagenic potential test): It was conducted via an external testing service (PWG Genetics Pte. Ltd, Singapore), according to guidelines specified in national and international regulatory authority test guidelines of OECD GLP, OECD TG 471, ISO 10993-12:2012 and ISO 10993-3:2014.

Application Study

Water disinfection

Before experiment, *E. coli* and *S. aureus* were grown in TSB solution at 37 ^{o}C on a shaking bed at 300 rpm. After that, bacteria were collected by centrifugation (3500 rpm × 5 min). After washing with sterilized water twice, the bacteria was re-dispersed in water and diluted to ~10^5 CFU/ml before use.

10 mg Zn/ZnO core/shell particles was cultured in 10 ml sterilized water containing ~10^5 CFU/ml bacteria in a 15 ml centrifuge tube. The solution was incubated under constant shaking (300 rpm) at 37 ^{o}C in dark. At 1 hour intervals 100 μL of solution was taken out and serially diluted (1x, 10x and 100x). 100 μL of each dilution was dispersed on LB agar. Colonies were counted after incubation at 37 ^{o}C for 24 h, and the number of colony forming units per mL was calculated. All of the experiments were performed in triplicates. The results were presented as mean ± standard deviation.

To find out the lowest effective concentration, Zn/ZnO solutions with concentration from 0.1 mg·L^{-1} to 100 mg·L^{-1} were prepared and each solution contains ~10^5 CFU/ml bacteria. The solution was incubated under constant shaking (300 rpm) at 37 ^{o}C in dark. At 3 hour and 24 h, 100 μL of solution was taken out and serially diluted (1x, 10x and 100x). 100 μL of each dilution was dispersed on LB agar. Colonies were counted after incubation at 37 ^{o}C for 24 h, and the number of colony forming units per mL was calculated.

Dye degradation:

Methylene blue degradation under dark: Zn/ZnO 0.2 g, methylene blue: 10 mg.L^{-1}, 100 ml, room temperature; stirred under dark.

Antibacterial paint:

Zn/ZnO core/shell particles was mixed with Nippon water-based polyacrylic acid (PAA) emulsion paint at different concentrations (0%, 1%, 3% and 5%, wt %). 0.8 g of paint was coated onto each testing surface (polycarbonates, 5 cm × 5 cm). The surface was dried in a 60 ^{o}C oven overnight before test.

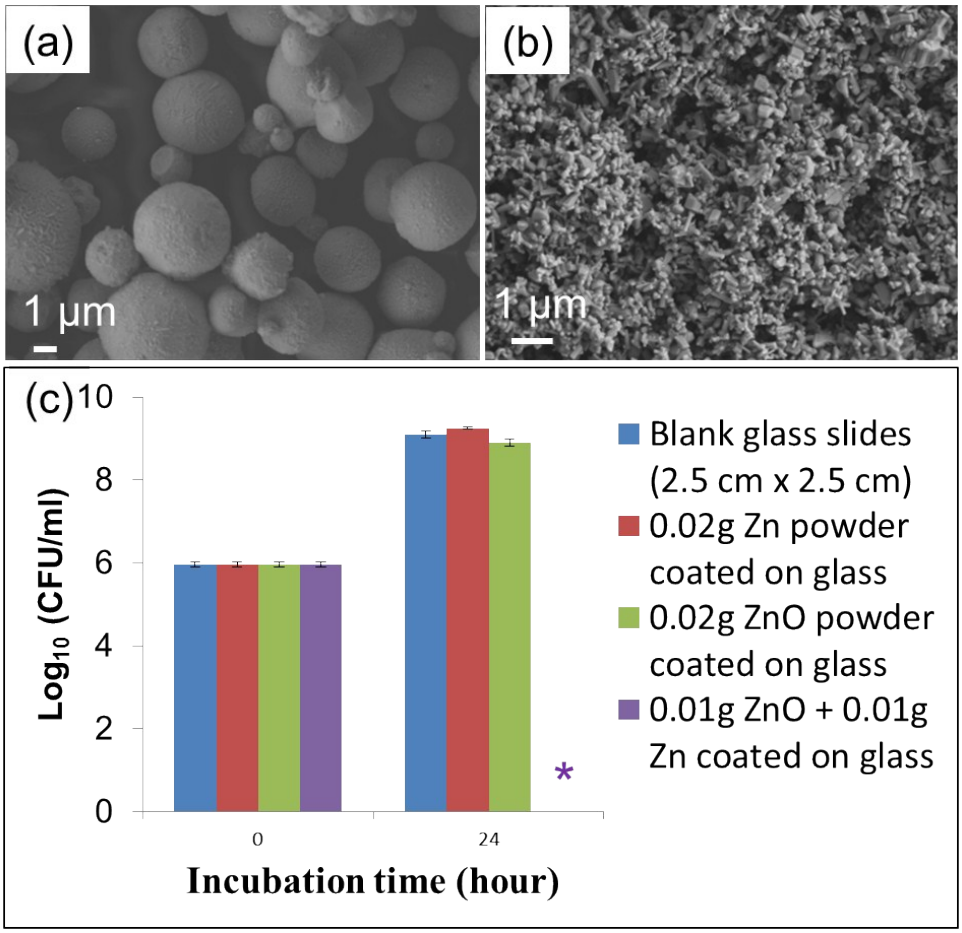

Figure S1: SEM image of (a) Zn particles and (b) ZnO particles. (c) Antibacterial property test of glass surface coated with different particles (against *E. coli*, ATCC8739). The antibacterial property was evaluated by JIS Z 2801/ISO 22196 method. * indicates that no colony was observed. The data are expressed as mean ± S.D. of 3 replicates.

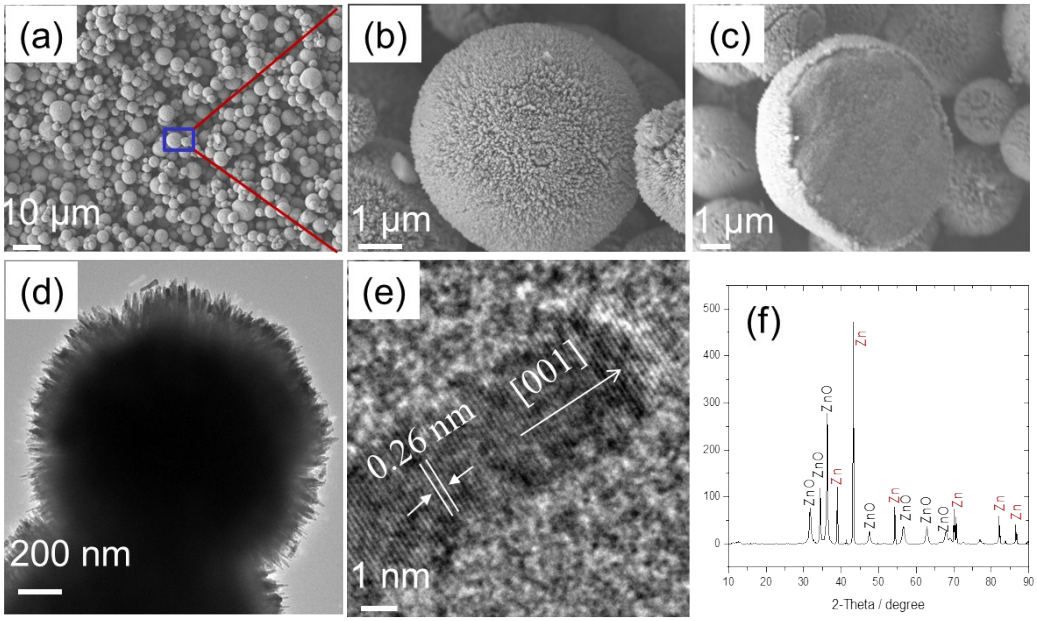

Figure S2: SEM images (a, b and c), TEM image (d) of Zn/ZnO core/shell particles; HRTEM image (e) of ZnO pillars on Zn/ZnO core-shell particles; and (f) XRD pattern of Zn/ZnO core/shell particles.

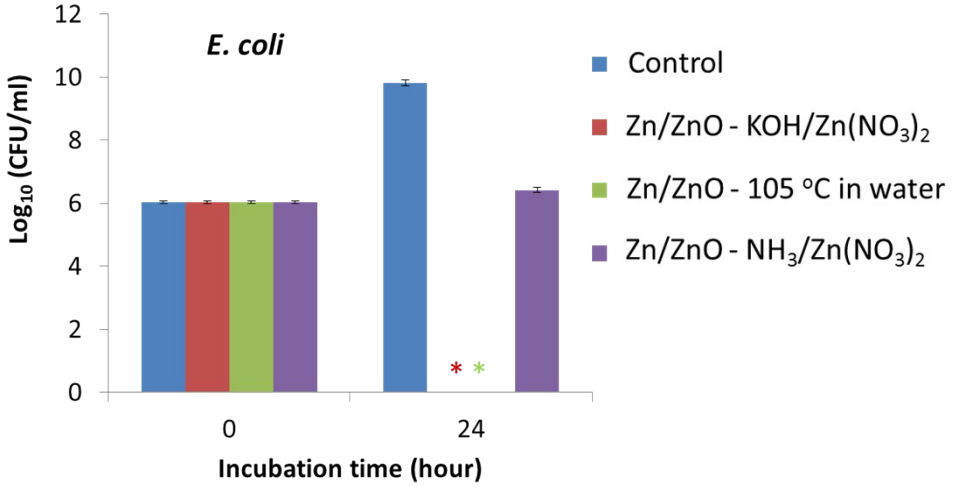

Figure S3: Antibacterial property test of glass surface coated with different Zn/ZnO particles (against *E. coli*, ATCC8739). The antibacterial property was evaluated by JIS Z 2801/ISO 22196 method. * indicates that no colony was observed.

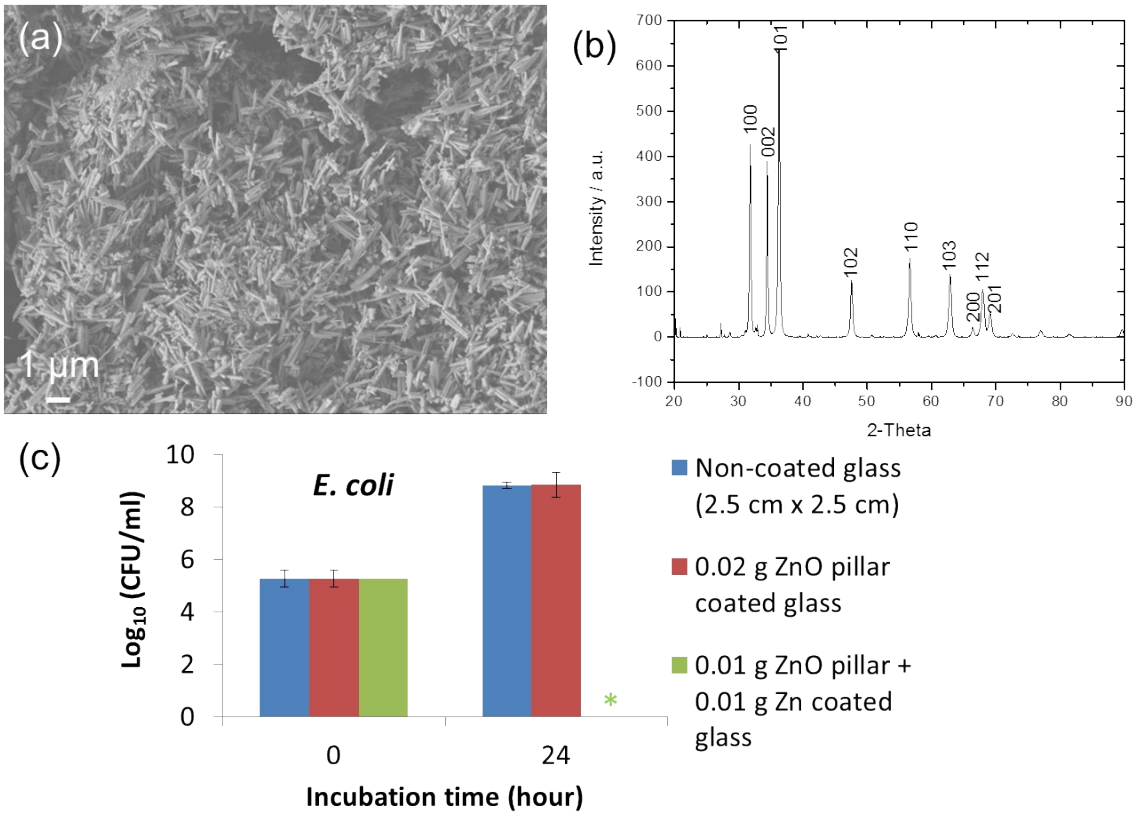

Figure S4: (A) SEM image of ZnO pillars; (B) XRD pattern of ZnO pillars; and (C) Antibacterial properties of glass surface (2.5 cm × 2.5 cm) without and with ZnO pillars coating. The antibacterial property of the surfaces was evaluated by JIS Z 2801/ISO 22196 method. * indicates that no colony was observed. The data are expressed as mean ± S.D. of 3 replicates.

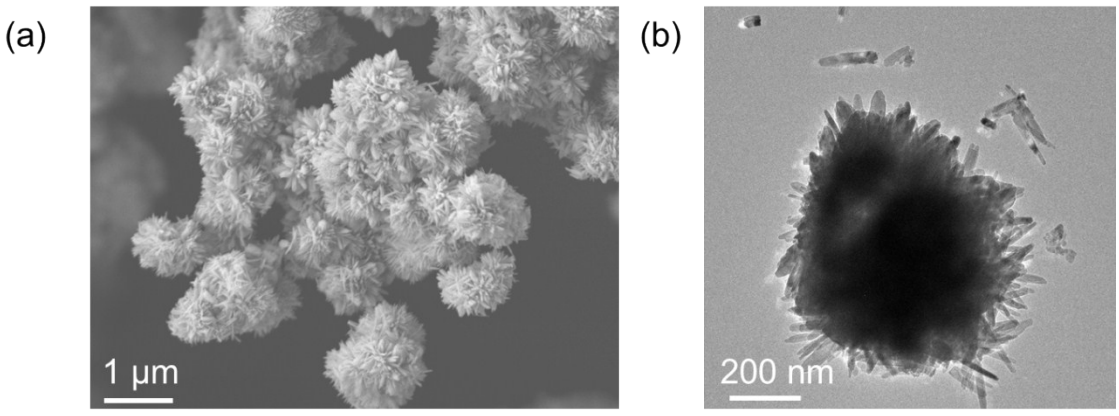

Figure S5: (a) SEM and (b) TEM image of Zn/ZnO core/shell particles prepared from smaller size of Zn.

Table S1: Zone of inhibition test results.

	E. coli (diameter)	***S. aureus*** (diameter)
Zn	10 mm	11 mm
ZnO	10 mm	10 mm
ZnO + Zn	13 mm	13 mm
Zn/ZnO	13.5 mm	14 mm

Table S2: Minimum inhibitory concentrations (MIC) of Zn against different bacteria. Values are in mg/mL.

	E. coli	***S. aureus***	***C. albicans***
$Zn(NO_3)_2$	3.1*	>50*	0.8

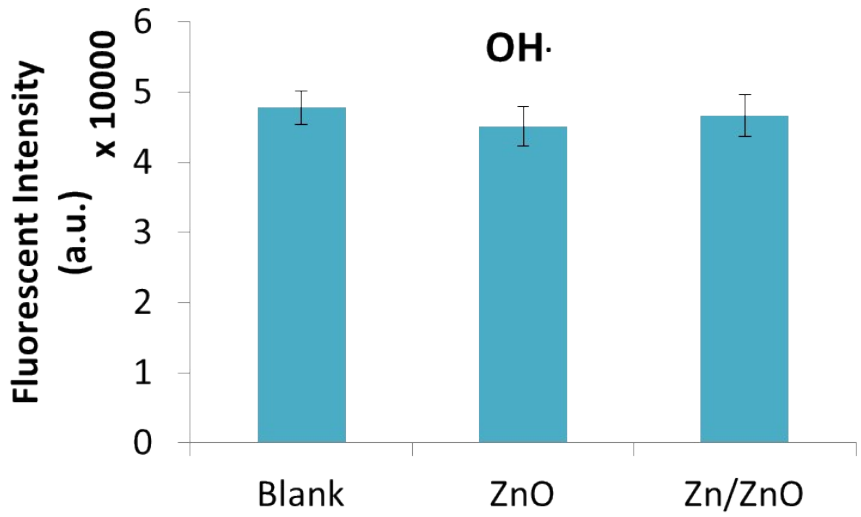

Figure S6: Release of OH· radicals in water in dark after 24 h.

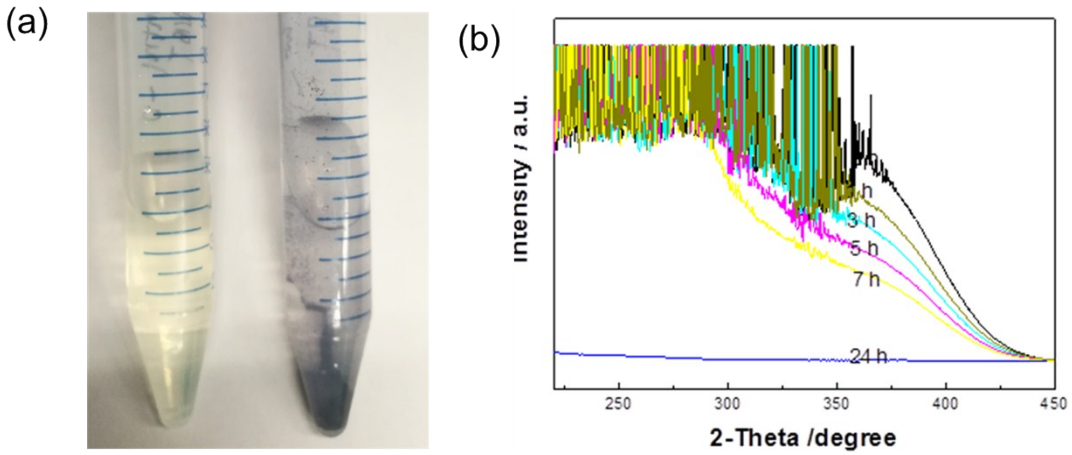

Figure S7: a) 1 mM NBT in water without and with 0.1 g of Zn/ZnO after 24 h. After 24 h, NBT solutions with 0.1 g Zn/ZnO completely lose the color of NBT. b) The absorption spectrum of NBT with 0.1 g Zn/ZnO continue to decrease, and come to zero after 24 h, indicating the continuous generation of $\cdot O_2^-$ by Zn/ZnO and react with NBT. NBT = Nitroblue tetrazolium.

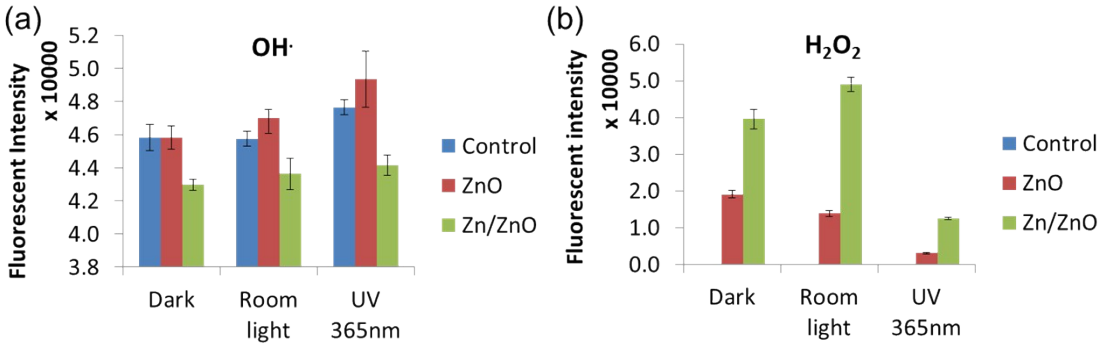

Figure S8. Radicals in dark, room light and UV for 24 h. The data are expressed as mean ± S.D. of 3 replicates.

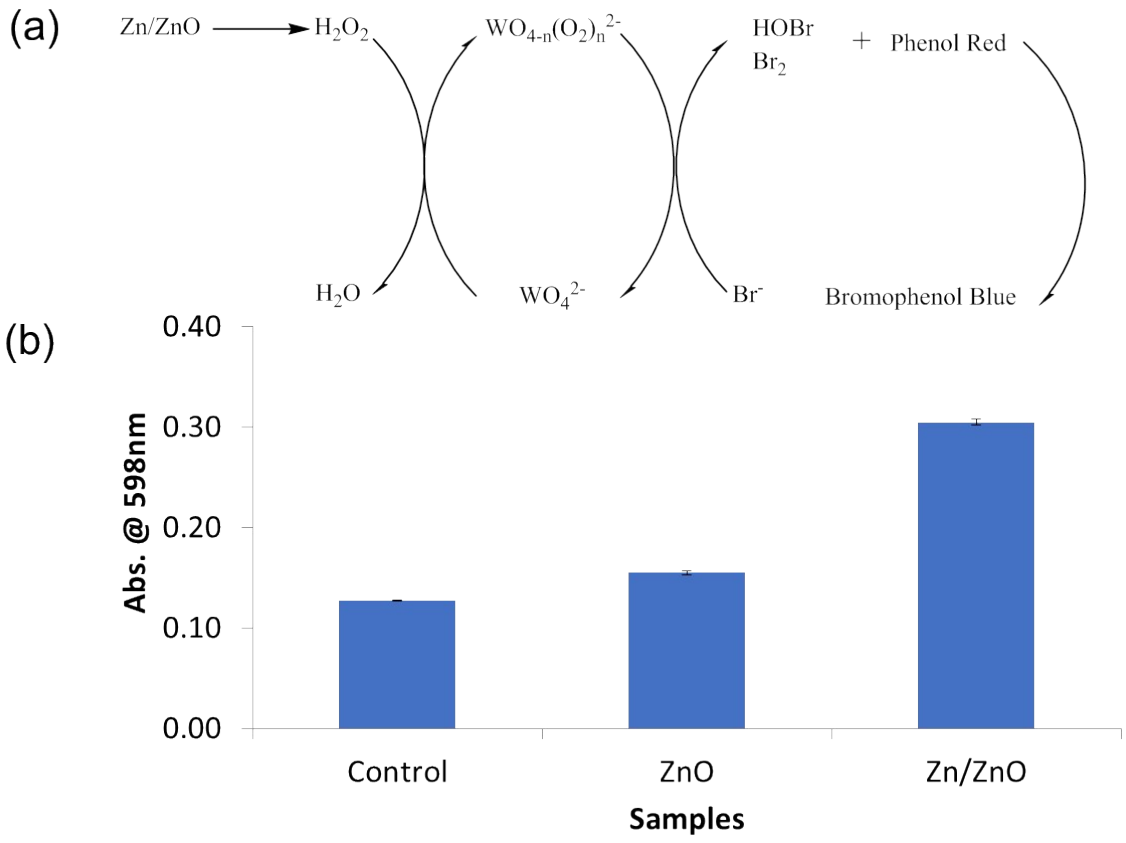

Figure S9. The detection of H_2O_2 with phenol red method. In the existence of WO_4^{2-} catalyst and Br^-, H_2O_2 generated from Zn/ZnO or ZnO oxidize Br^- into HOBr / Br_2 species, and the later turn phenol red into bromophenol blue.[5] (a) Scheme of testing principles, and (b) the H_2O_2 level from different samples.

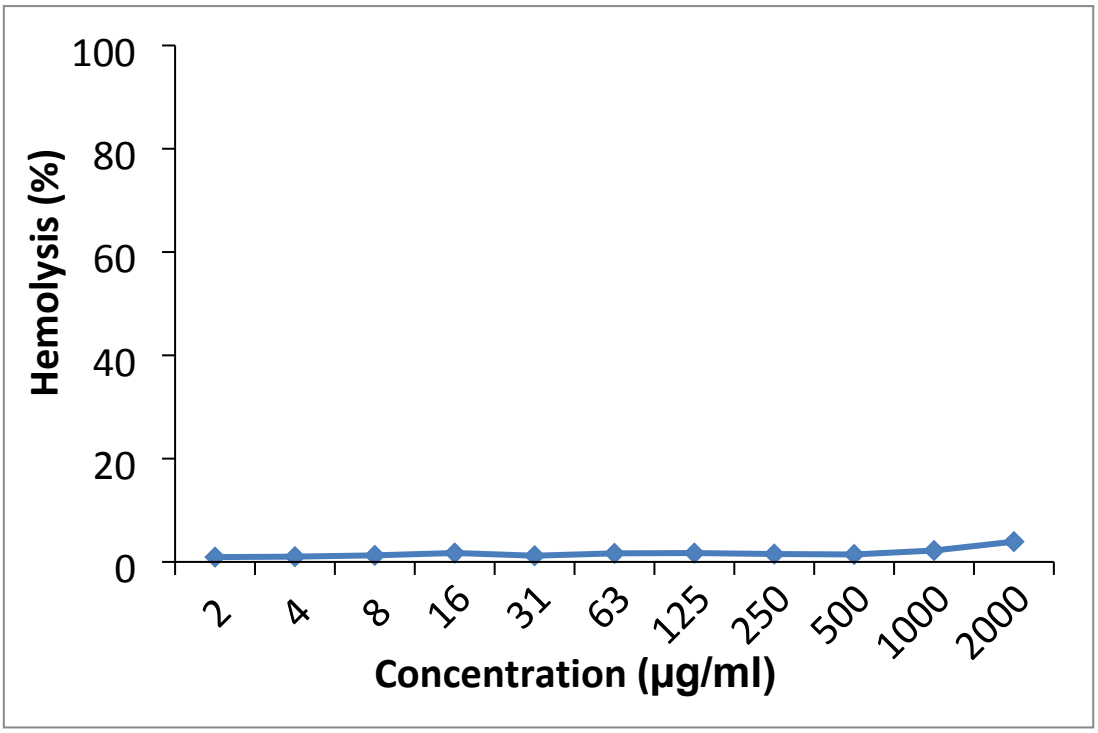

Figure S10. Hemolysis study of Zn/ZnO core/shell particles on rat red blood cells.

Table S3*:* In this assay, *S. typhimurium* and *E. coli* were used as the testing bacteria. Four strains of *S. typhimurium* (TA98, TA100, TA1535, TA1537) and two strains of *E. coli* (wp2 [pKM101], wp2 [uvrA]) were prepared for this assay. All strains were tested in triplicate with the test article extracted at 37 ± 1°C for 72 ± 2 hours in phosphate buffered saline and DMSO; extraction was conducted at an approximate ratio of 2 g test article to 10 mL of extraction vehicle. None of the samples yielded a ⩾ 2.0-fold induction over the solvent derived baseline, while positive controls on all test conditions showed a > 2.0 well count on revertants, marking the strains as active and validating the test.

TA98

	With Zn/ZnO						Without Zn/ZnO				
	Platet 1	**Plate 2**	**Plate 3**	**Mean**	**StDev**		**Plate 1**	**Plate 2**	**Plate 3**	**Mean**	**StDev**
Saline	0	3	2	1.67	1.25	**Saline**	1	2	4	2.33	1.25
TA Saline	2	1	1	1.33	0.47	**TA Saline**	0	3	5	2.67	2.05
DMSO	2	3	3	2.67	0.47	**DMSO**	4	5	4	4.33	0.47
TA DMSO	4	1	1	2.00	1.41	**TA DMSO**	1	3	3	2.33	0.94
Positive	48	48	48	48.00	0.00	**Positive**	46	44	47	45.67	1.25

TA100

	With Zn/ZnO						Without Zn/ZnO				
	Platet 1	**Plate 2**	**Plate 3**	**Mean**	**StDev**		**Plate 1**	**Plate 2**	**Plate 3**	**Mean**	**StDev**
Saline	8	4	3	5.00	2.16	**Saline**	4	4	6	4.67	0.94
TA Saline	7	6	5	6.00	0.82	**TA Saline**	7	5	8	6.67	1.25
DMSO	8	8	7	7.67	0.47	**DMSO**	8	6	7	7.00	0.82
TA DMSO	9	7	8	8.00	0.82	**TA DMSO**	4	8	7	6.33	1.70
Positive	48	48	47	47.67	0.47	**Positive**	48	48	48	48.00	0.00

TA1535

	With Zn/ZnO						Without Zn/ZnO				
	Platet 1	**Plate 2**	**Plate 3**	**Mean**	**StDev**		**Plate 1**	**Plate 2**	**Plate 3**	**Mean**	**StDev**
Saline	1	1	3	1.67	0.94	**Saline**	1	3	3	2.33	0.94
TA Saline	2	0	0	0.67	0.94	**TA Saline**	2	1	3	2.00	0.82
DMSO	3	3	1	2.33	0.94	**DMSO**	2	2	0	1.33	0.94
TA DMSO	3	3	0	2.00	1.41	**TA DMSO**	2	3	1	2.00	0.82
Positive	38	30	31	33.00	3.56	**Positive**	48	47	48	47.67	0.47

TA1537

	With Zn/ZnO						Without Zn/ZnO				
	Platet 1	**Plate 2**	**Plate 3**	**Mean**	**StDev**		**Plate 1**	**Plate 2**	**Plate 3**	**Mean**	**StDev**
Saline	2	1	1	1.33	0.47	**Saline**	1	3	2	2.00	0.82
TA Saline	3	2	0	1.67	1.25	**TA Saline**	1	2	1	1.33	0.47
DMSO	1	1	2	1.33	0.47	**DMSO**	0	2	0	0.67	0.94
TA DMSO	1	2	0	1.00	0.82	**TA DMSO**	3	0	0	1.00	1.41

Positive	23	26	24	24.33	1.25	**Positive**	41	46	44	43.67	2.05

***E. coli* (mix)**

With Zn/ZnO						Without Zn/ZnO					
	Platet 1	**Plate 2**	**Plate 3**	**Mean**	**StDev**		**Plate 1**	**Plate 2**	**Plate 3**	**Mean**	**StDev**
Saline	4	6	6	5.33	0.94	**Saline**	8	11	11	10.00	1.41
TA Saline	4	3	5	4.00	0.82	**TA Saline**	10	10	10	10.00	0.00
DMSO	5	5	2	4.00	1.41	**DMSO**	11	8	6	8.33	2.05
TA DMSO	7	2	5	4.67	2.05	**TA DMSO**	10	6	8	8.00	1.63
Positive	22	32	27	27.00	4.08	**Positive**	34	32	42	36.00	4.32

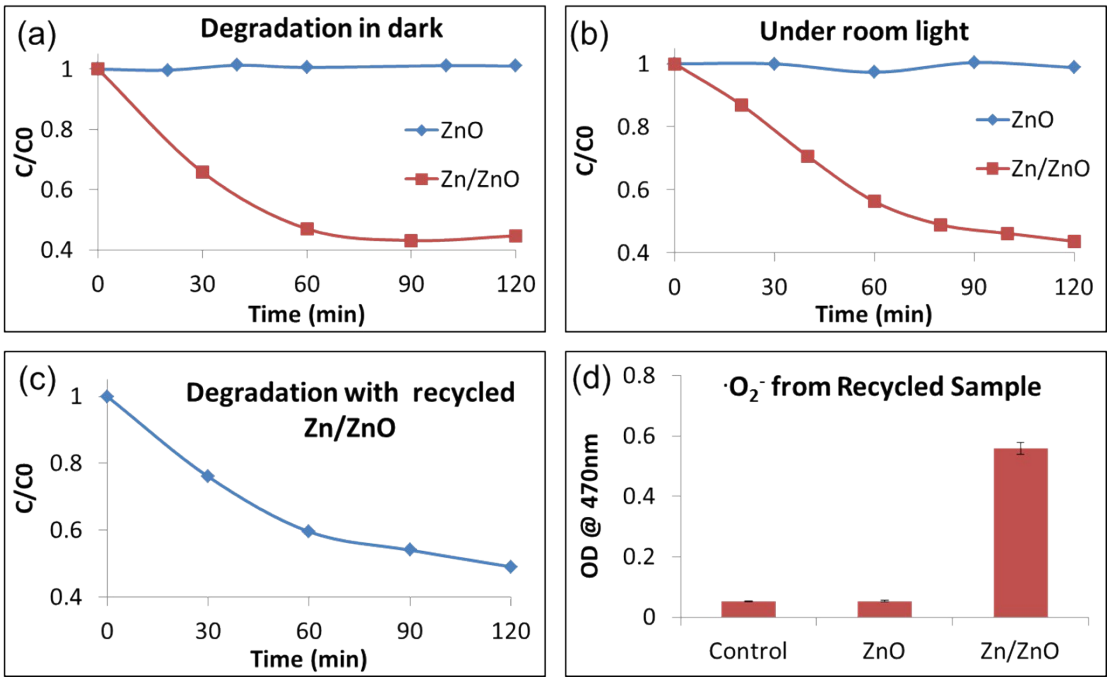

Figure S11. Methylene blue degradation experiments. Reaction conditions: Zn/ZnO and ZnO, 0.2 g; methylene blue: 10 mg/L, 100 ml; room temperature in the dark under magnetic stirring.

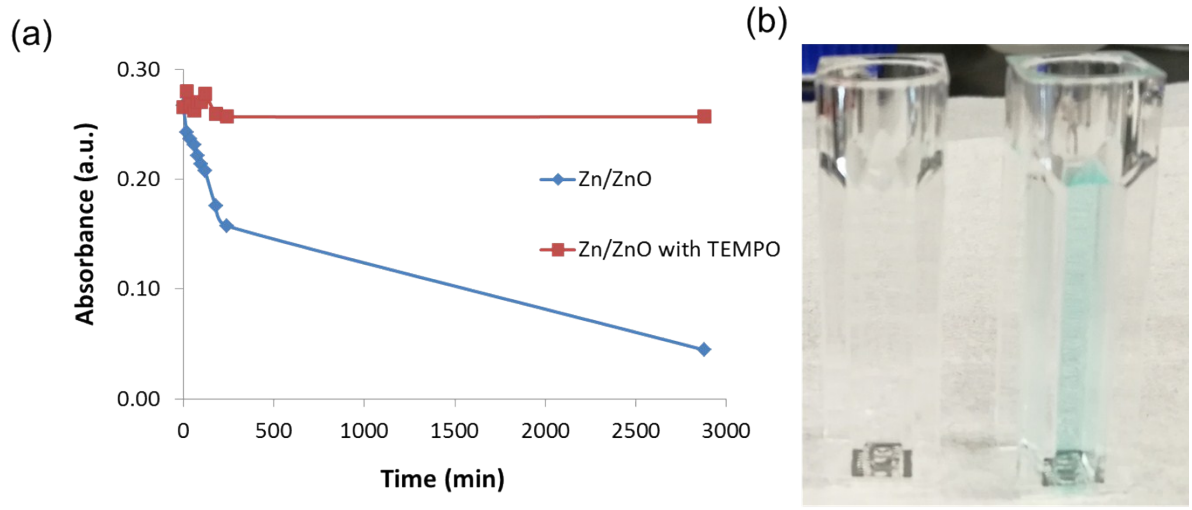

Figure S12. (a) Methylene blue degradation by Zn/ZnO without and with $\cdot O_2^-$ capturing agent TEMPO; and (b) Methylene blue degradation by Zn/ZnO after 48 h without and with $\cdot O_2^-$ capturing agent TEMPO. Reaction conditions: methylene blue: 1 mg/L, 100 ml; Zn/ZnO, 0.2 g; TEMPO: 5 mmol/L; room temperature in the dark under magnetic stir at 600 rpm. Absorbance measured at 663.5 nm

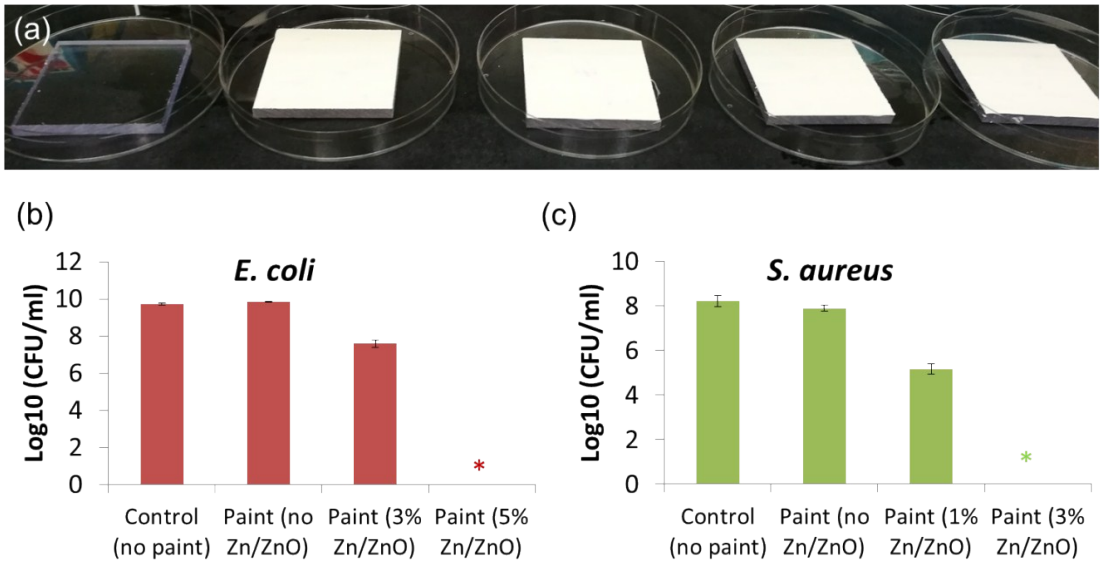

Figure S13. (a) Polycarbonate plates (5 cm × 5 cm) without painting, and painting with 0%, 1%, 3%, 5% Zn/ZnO in the paint, respectively. (b and c) Antibacterial properties of surface coated with paint with and without Zn/ZnO in the paints. The antibacterial property of the surfaces was evaluated by JIS Z 2801/ISO 22196 method. * indicates that no colony was observed. The data are expressed as mean ± S.D. of 3 replicates.

References

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