**Supplementary Information**

# Photocatalytic Degradation-based Efficient Elimination of Pesticides using Ruthenium/Gold Metal Nanoparticle-anchored Zirconium Dioxide

Anuj Chauhan,[a] Namasivayam Dhenadhayalan,[a,*] Jen-Chen Yeh,[a] and King-Chuen Lin[a,b,*]

[a] Department of Chemistry, National Taiwan University, Taipei-10617, Taiwan.

[b] Institute of Atomic and Molecular Sciences, Academia Sinica, Taipei-10617, Taiwan.

*Correspondence should be addressed.

E-mail: ndhena@gmail.com (Namasivayam Dhenadhayalan); Tel.: +886-2-33668289.

E-mail: kclin@ntu.edu.tw (King-Chuen Lin); Fax: +886-2-23621483; Tel.: +886-2-33661162.

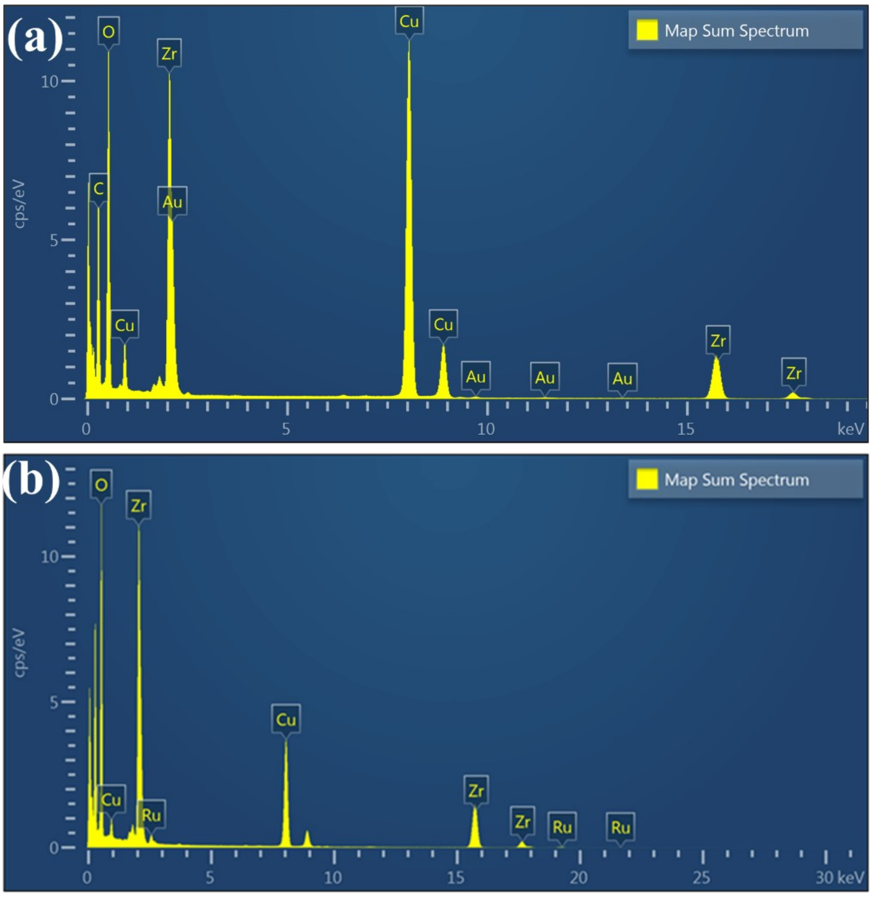



**Fig. S1**. EDX spectra of (a) $ZrO_2$@Au and (b) $ZrO_2$@Ru.

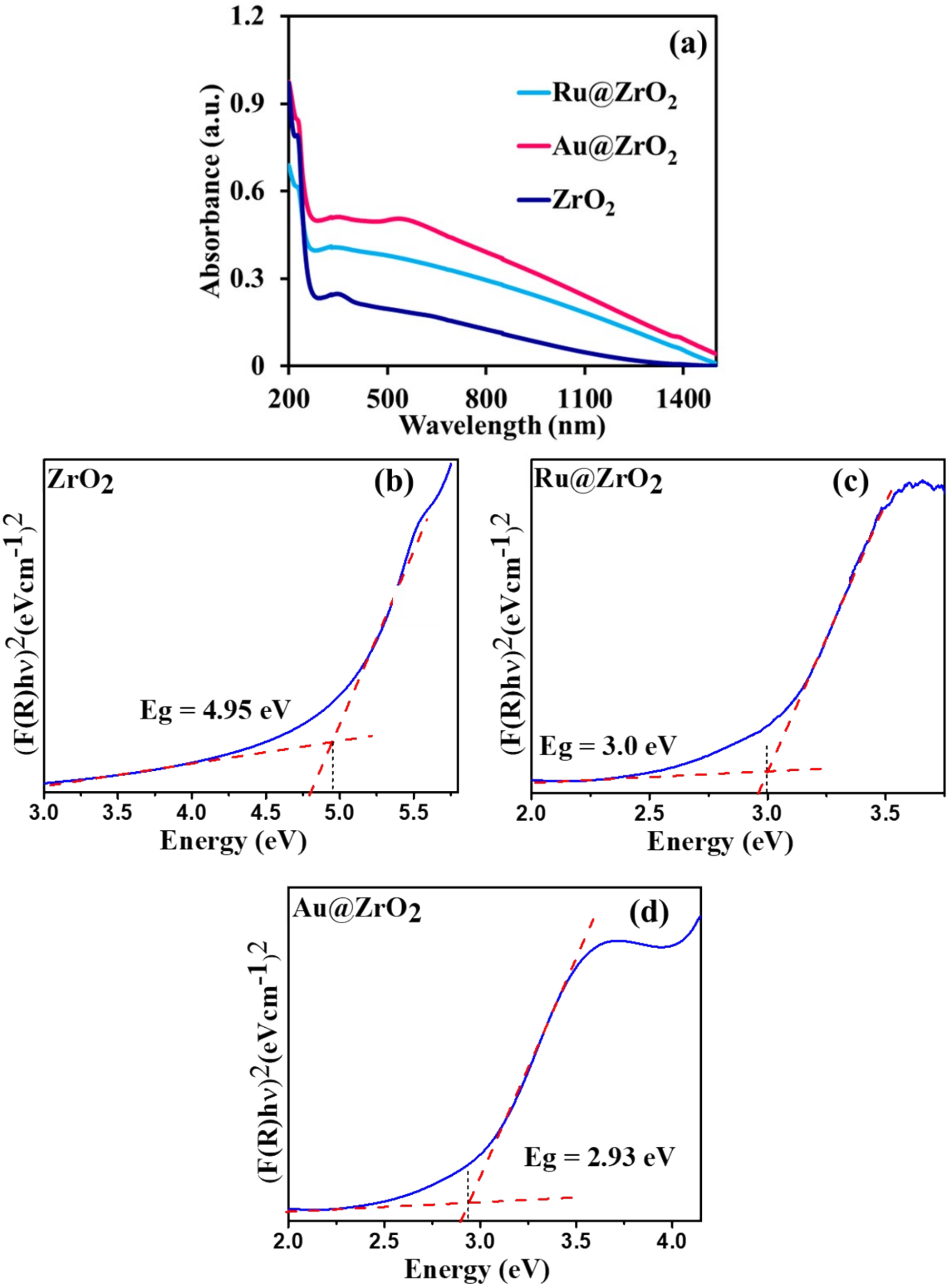



**Fig. S2.** (a) UV-visible diffuse absorption spectra of the nanohybrids. Tauc plots of (b) $ZrO_2$, (c) $ZrO_2$@Ru, and (d) $ZrO_2$@Au.

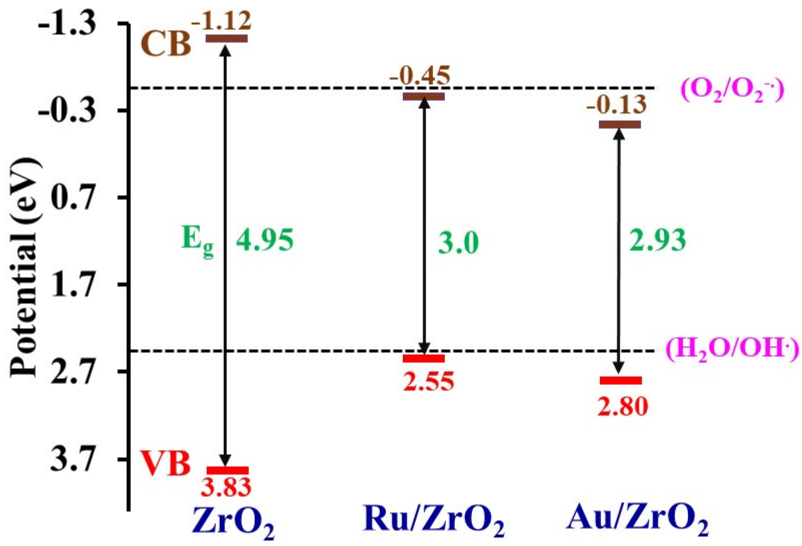



**Fig. S3.** Conduction band and valence band positions of $ZrO_2$, $ZrO_2$@Au, and $ZrO_2$@Ru.

To simplify the mechanism of the photocatalytic behaviour of the composite, it is required to find out the position of the conduction band (CB) and valence band (VB) potentials. These positions were calculated using the following equations:[S1,S2]

$$E_{CB} = \chi - E_e - \frac{1}{2}E_g \quad (1)$$

$$E_{VB} = E_{CB} + E_g \quad (2)$$

$$\chi = \left[\chi(A)^a \chi(B)^b \chi(C)^c \chi(D)^d\right]^{\frac{1}{a+b+c+d}} \quad (3)$$

Where $E_{CB}$ is the CB position, $E_{VB}$ is the VB position, $\chi$ is the electronegativity of the semiconductor, (a, b, c, d) are the number of elements present in the composite, $E_e\ (4.5\ eV)$ is the energy of free electrons vs. hydrogen, and $E_g$ is the bandgap of the nanomaterial.

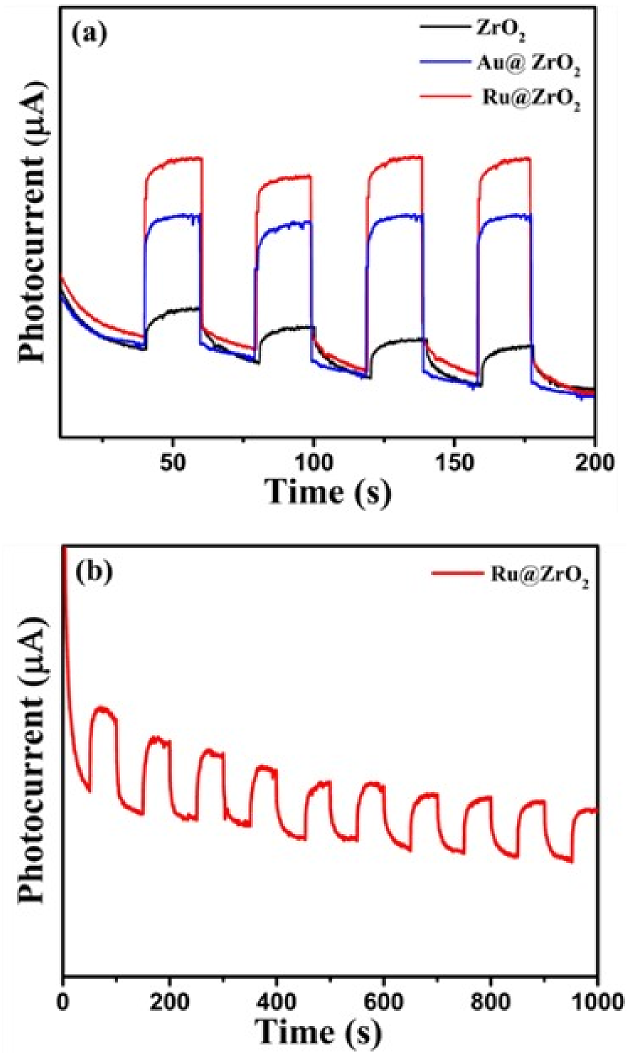



**Fig. S4.** (a) Photocurrent response of $ZrO_2$, $ZrO_2$@Au, and $ZrO_2$@Ru. (b) Photocurrent stability test of $ZrO_2$@Ru.

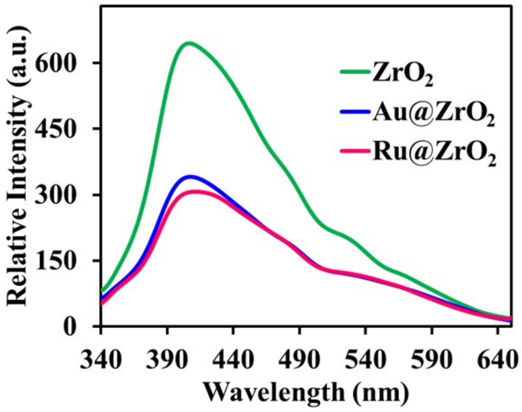



**Fig. S5**. Photoluminescence emission spectra of $ZrO_2$, $ZrO_2$@Au, and $ZrO_2$@Ru.

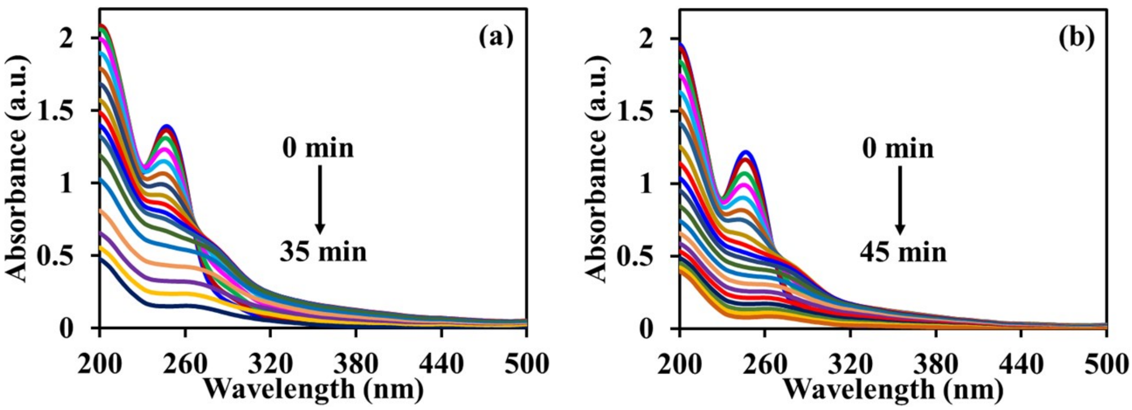



**Fig. S6.** Time-dependent absorption spectra of DI with the presence of 0.02 mg/mL (a) $ZrO_2$@Ru and (d) $ZrO_2$@Au.

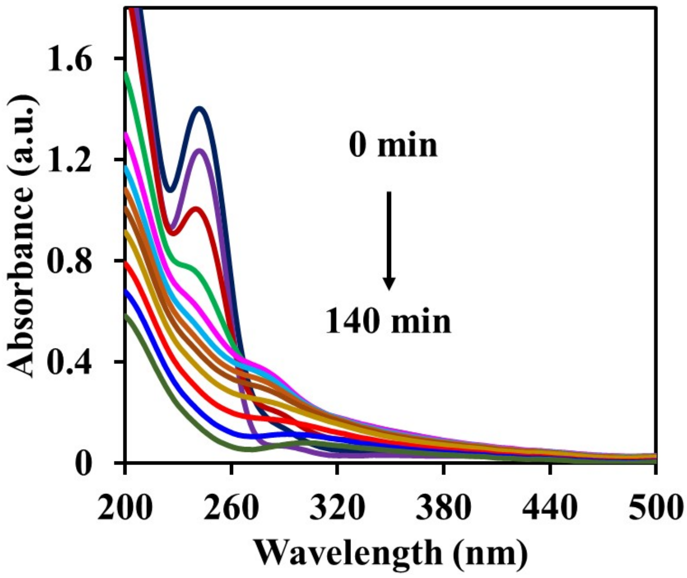



**Fig. S7.** Time-dependent absorption spectra for the photodegradation of DI without photocatalyst.

**Table S1**. The reported data for the photocatalytic degradation of DI and MP.

| Pesticides | Photocatalyst | Time (min) | Rate constant ($min^{-1}$) | Ref. |
|---|---|---|---|---|
| DI | P-25 $TiO_2$ | 120 | 0.1111 | 54 |
| | $Bi_2W_2O_9$ | 180 | ~0.0045 | 55 |
| | $CuS/Bi_2W_2O_9$ | 180 | ~0.0150 | 55 |
| | Ag/ZnO | 90 | 0.0370 | 56 |
| | $ZrO_2$@Ru | 13 | 0.2506 | This work |
| | $ZrO_2$@Au | 18 | 0.1766 | This work |
| MP | N-doped $TiO_2$ | 60 | - | 57 |
| | Ag-$TiO_2$ | 420 | 0.0069 | 58 |
| | La/$TiO_2$ | 120 | - | 59 |
| | $Fe_3O_4$@$SiO_2$@$TiO_2$ | 30 | 0.0659 | 60 |
| | Pd@ZnONSt | 110 | 0.0635 | 61 |
| | Ag-$TiO_2$ (4% Ag) | 60 | 0.0344 | 62 |
| | ZnO/CuO | 60 | 0.0331 | 63 |
| | Cu(II)/MCM-41 | 240 | 0.0053 | 64 |
| | Ni(II)/MCM-41 | 240 | 0.0061 | 64 |
| | $ZrO_2$@Ru | 35 | 0.0762 | This work |
| | $ZrO_2$@Au | 60 | 0.0456 | This work |

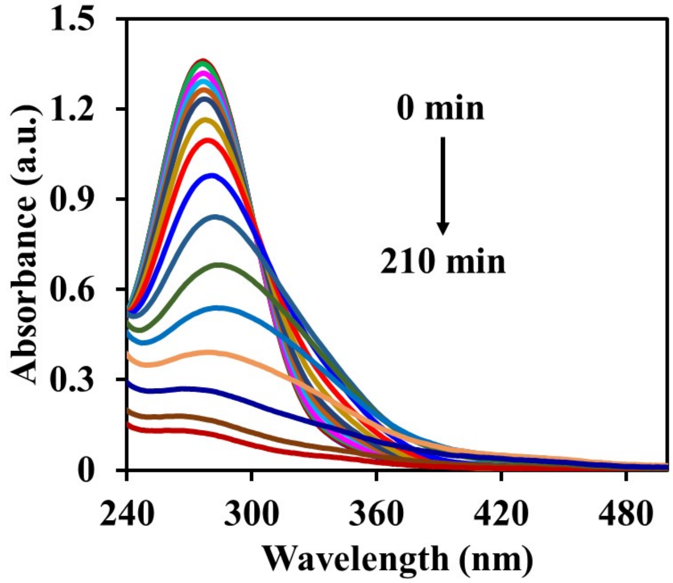



**Fig. S8.** Time-dependent absorption spectra for the photodegradation of MP without photocatalyst.

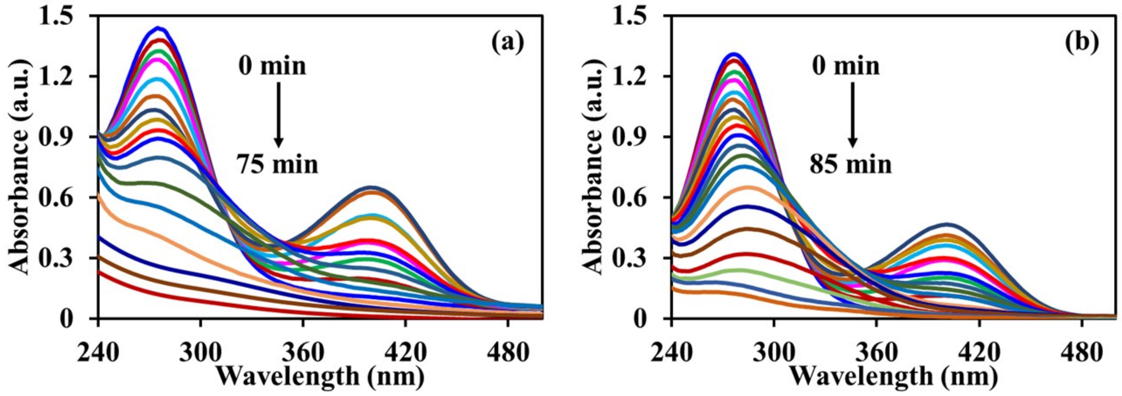



**Fig. S9.** Time-dependent absorption spectra of MP with presence of (a) $ZrO_2$@Ru and (d) $ZrO_2$@Au (0.02 mg/mL).

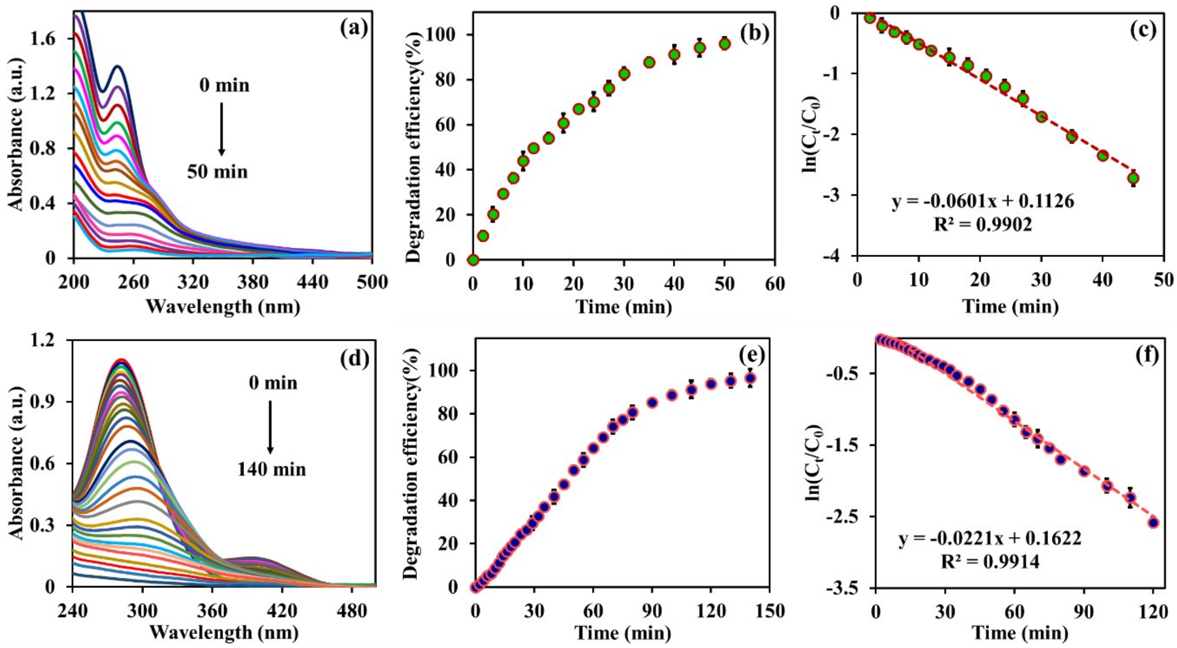



**Fig. S10**. Time-dependent absorption spectra of (a) DI and (d) MP in the presence of bare $ZrO_2$ (0.2 mg/mL). Plot of degradation efficiency versus time for (b) DI and (e) MP. Plot of $\ln(C_t/C_0)$ versus time for (c) DI and (f) MP.

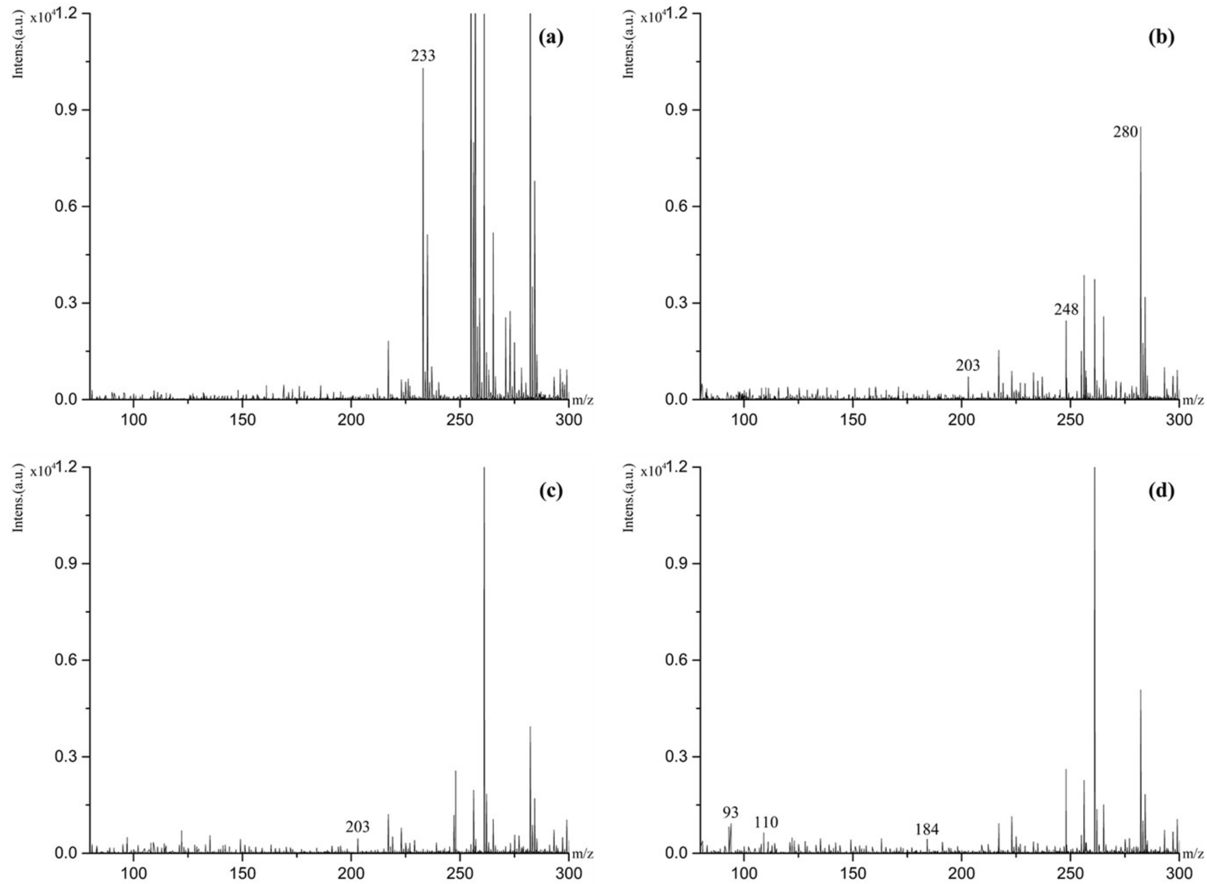



**Fig. S11.** ESI-MS spectra for photocatalytic degradation of DI with the presence of $ZrO_2$@Ru (0.02 mg/mL). (a) without irradiation (b) 5 min, (c) 15min, and (d) 35 min (end of the reaction).

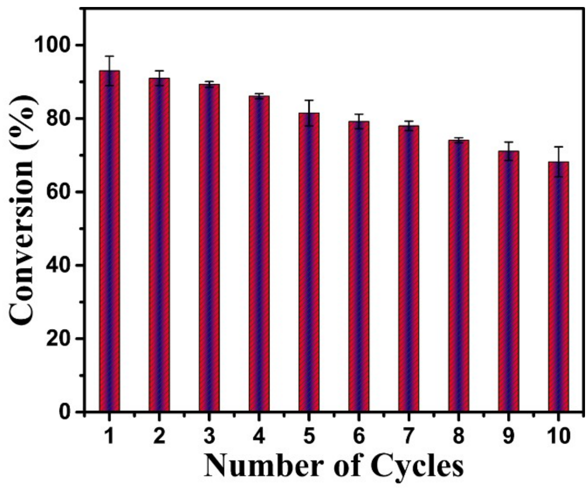
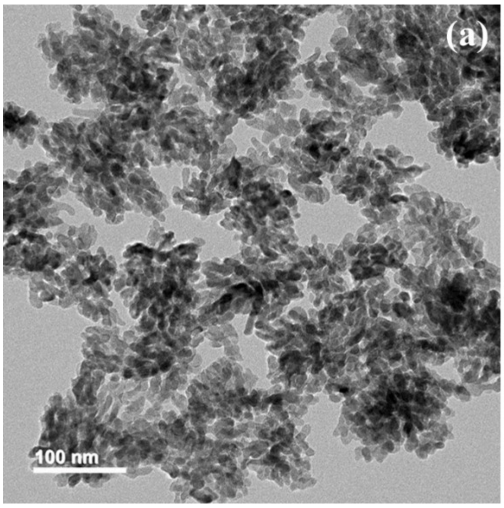



**Fig. S12.** Conversion efficiency of $ZrO_2$@Ru towards the degradation of DI.



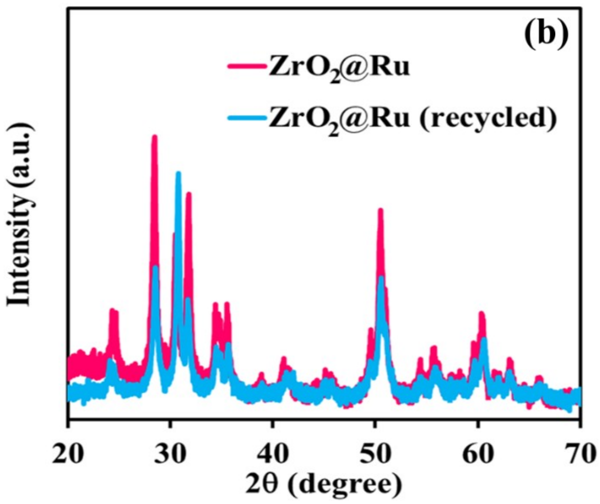




**Fig. S13.** (a) FETEM image and (b) XRD pattern of recycled $ZrO_2$@Ru.

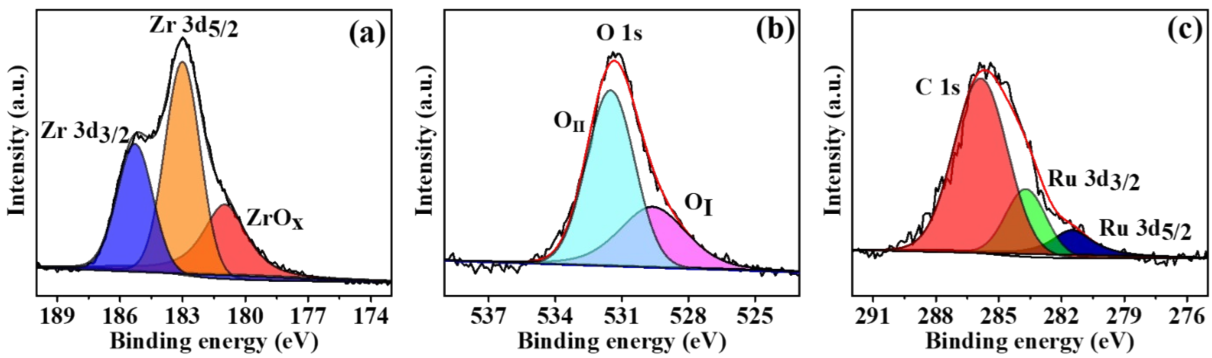



**Fig. S14**. Deconvoluted XPS spectra of recycled $ZrO_2$@Ru. [(a) Zr 3d, (b) O 1s, (c) Ru 3d].

## References


S1. I. Ahmad, M. S. Akhtar, E. Ahmad and M. Ahmad, *J. Mater. Sci.: Mater. Electron.*, 2020, 31, 1084–1093.

S2. Y. Q. Liang, Z. D. Cui, S. L. Zhu, Z. Y. Li, X. J. Yang, Y. J. Chen and J. M. Ma, *Nanoscale*, 2013, 5, 10916-26.