

## Supporting Information

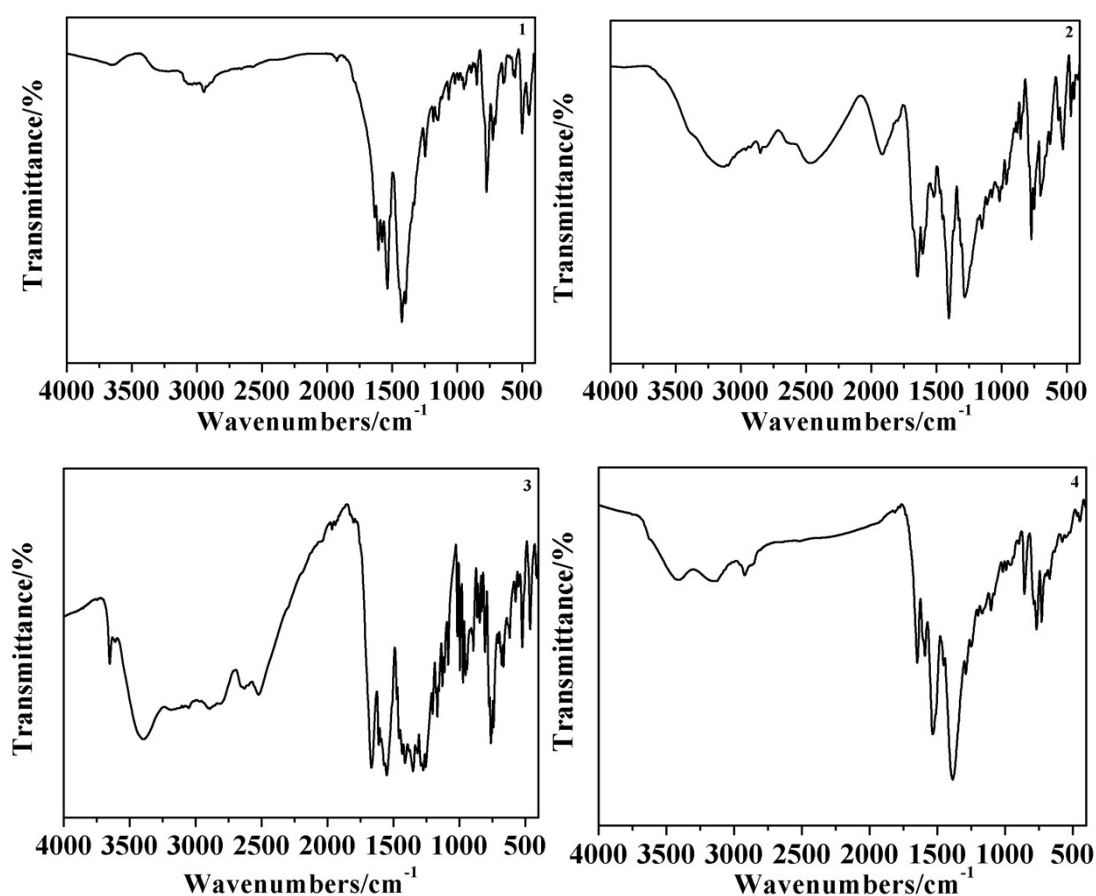


Fig. S1. IR spectra of complexes 1 (a), 2 (b), 3 (c) and 4 (d).

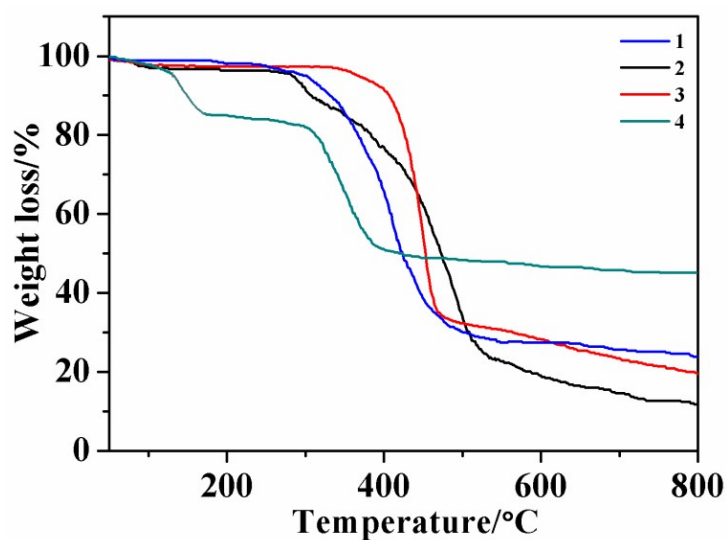
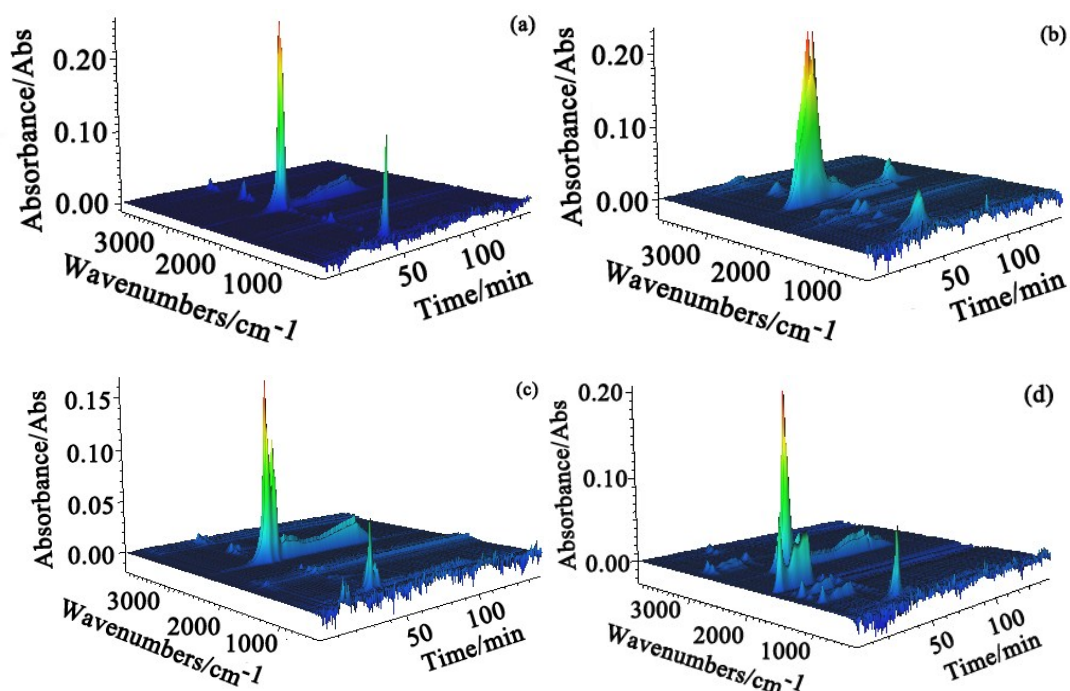
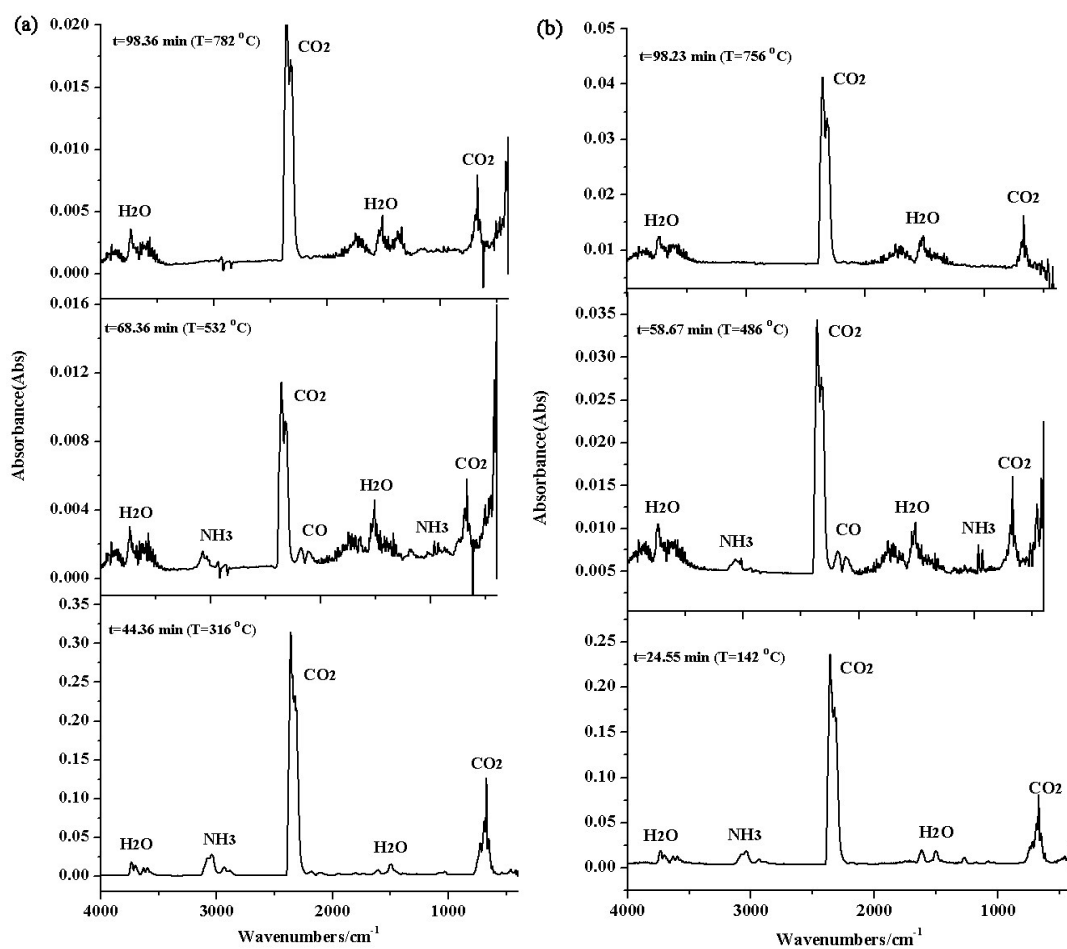
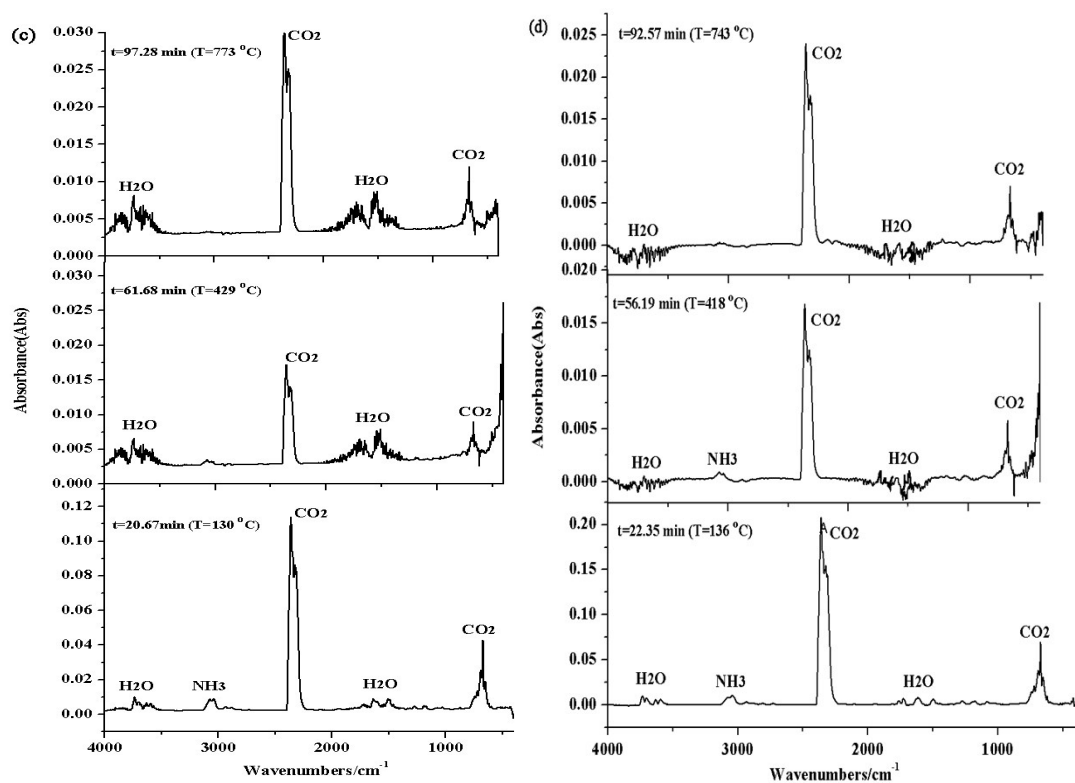


Fig. S2. TG curves of 1-4.

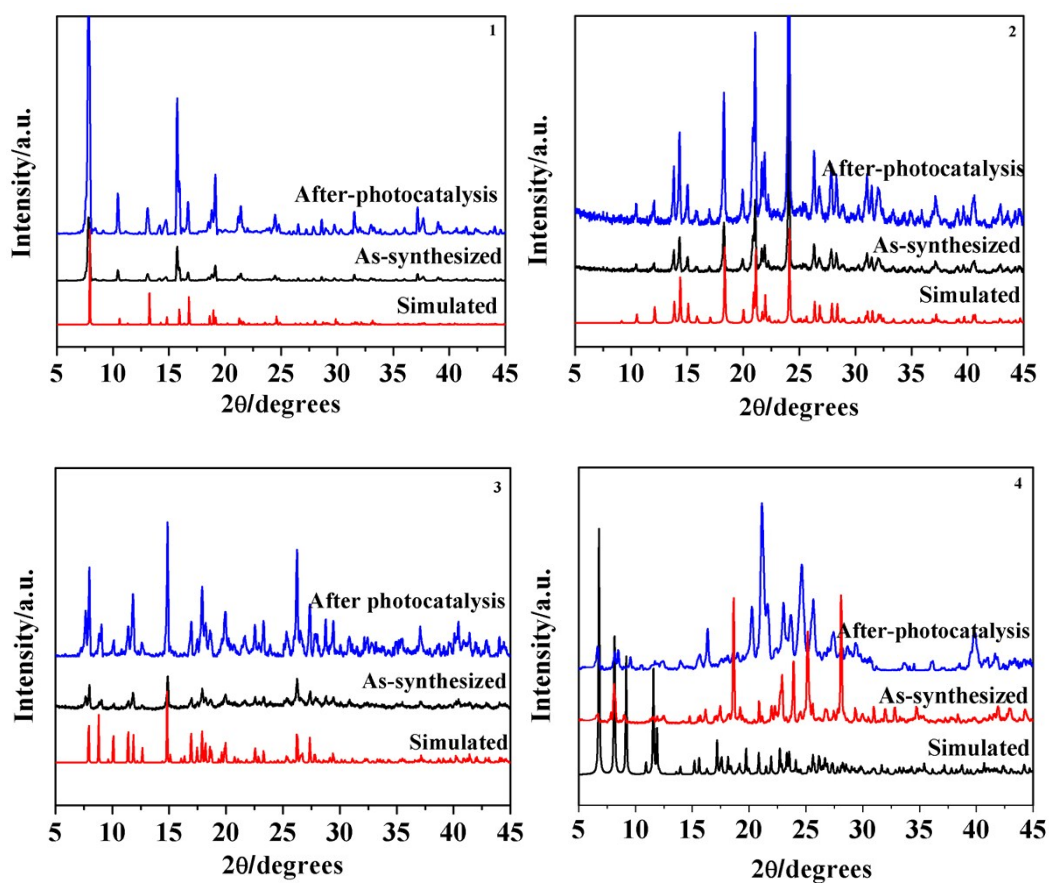


**Fig. S3.** Three-dimensional IR accumulation spectra of gaseous **1** (a), **2** (b), **3** (c) and **4** (d).

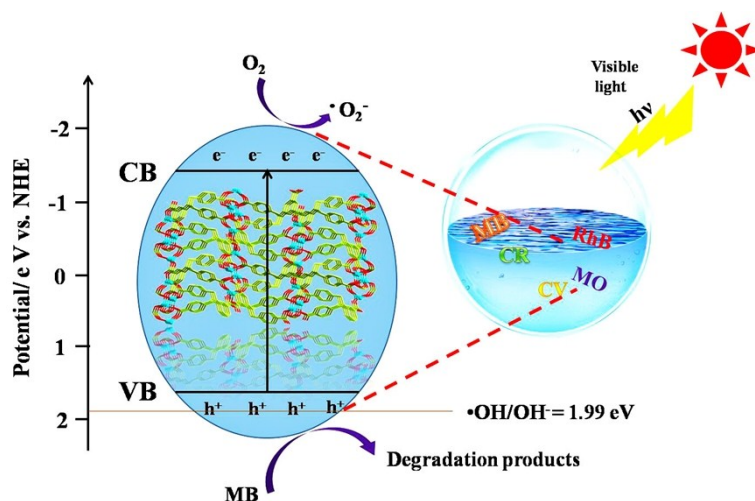




**Fig. S4.** FTIR spectra of gaseous products of 1-4 at different temperature.



**Fig. S5.** The simulated and experimental PXRD patterns of 1-4.



**Fig. S6.** Possible mechanism for the photo-induced charge transfer route of photocatalyst.

**Table S1** Select bond lengths(Å) and angels(°) for **1-4**

| Complex 1                                                                                                                                           |            |                                              |            |                                              |            |
|-----------------------------------------------------------------------------------------------------------------------------------------------------|------------|----------------------------------------------|------------|----------------------------------------------|------------|
| Zn(1)-O(2) <sup>#3</sup>                                                                                                                            | 1.924(3)   | Zn(1)-O(5) <sup>#1</sup>                     | 1.924(3)   | Zn(1)-O(8) <sup>#2</sup>                     | 1.932(4)   |
| Zn(2)-O(6) <sup>#2</sup>                                                                                                                            | 1.925(3)   | Zn(2)-O(7) <sup>#1</sup>                     | 1.945(3)   | Zn(2)-O(4) <sup>#4</sup>                     | 1.948(3)   |
| O(2) <sup>#3</sup> -Zn(1)-O(5) <sup>#1</sup>                                                                                                        | 99.09(16)  | O(2) <sup>#3</sup> -Zn(1)-O(8) <sup>#2</sup> | 104.49(17) | O(5) <sup>#1</sup> -Zn(1)-O(8) <sup>#2</sup> | 124.69(18) |
| O(2) <sup>#3</sup> -Zn(1)-O(1)                                                                                                                      | 124.27(16) | O(5) <sup>#1</sup> -Zn(1)-O(1)               | 106.06(16) | O(8) <sup>#2</sup> -Zn(1)-O(1)               | 100.52(16) |
| O(6) <sup>#2</sup> -Zn(2)-O(3)                                                                                                                      | 100.95(15) | O(6) <sup>#2</sup> -Zn(2)-O(7) <sup>#1</sup> | 124.83(17) | O(3)-Zn(2)-O(7) <sup>#1</sup>                | 103.38(15) |
| O(6) <sup>#2</sup> -Zn(2)-O(4) <sup>#4</sup>                                                                                                        | 117.67(17) | O(3)-Zn(2)-O(4) <sup>#4</sup>                | 110.38(15) | O(7) <sup>#1</sup> -Zn(2)-O(4) <sup>#4</sup> | 98.69(15)  |
| Symmetry code: <sup>#1</sup> -x+5/2, y-1/2, -z+3/2; <sup>#2</sup> x+1/2, -y+1/2, z+1/2; <sup>#3</sup> -x+2, -y, -z+2; <sup>#4</sup> -x+3, -y, -z+1. |            |                                              |            |                                              |            |
| Complex 2                                                                                                                                           |            |                                              |            |                                              |            |
| Mn-O(7) <sup>#5</sup>                                                                                                                               | 2.134(2)   | Mn-O(1) <sup>#4</sup>                        | 2.061(2)   | Mn-O(1W)                                     | 2.092(2)   |
| Mn-O(4) <sup>#6</sup>                                                                                                                               | 2.1849(17) | O(5)-Mn-O(1) <sup>#4</sup>                   | 122.63(10) | O(5)-Mn-O(1W)                                | 121.58(11) |
| O(1) <sup>#4</sup> -Mn-O(1W)                                                                                                                        | 115.72(11) | O(5)-Mn-O(7) <sup>#5</sup>                   | 102.46(10) | O(1) <sup>#4</sup> -Mn-O(7) <sup>#5</sup>    | 85.18(9)   |
| O(1W)-Mn-O(7) <sup>#5</sup>                                                                                                                         | 84.18(9)   | O(5)-Mn-O(4) <sup>#6</sup>                   | 84.14(10)  | O(1) <sup>#4</sup> -Mn-O(4) <sup>#6</sup>    | 95.54(9)   |
| Symmetry code: <sup>#4</sup> x-1/2, -y+3/2, z-1; <sup>#5</sup> x, y+1, z-1; <sup>#6</sup> -x+2, -y+1, z-1/2.                                        |            |                                              |            |                                              |            |
| Complex 3                                                                                                                                           |            |                                              |            |                                              |            |
| Cd-O(1W)                                                                                                                                            | 2.229(2)   | Cd-O(2) <sup>#1</sup>                        | 2.234(2)   | Cd-O(4) <sup>#2</sup>                        | 2.2700(19) |
| Cd-O(2W)                                                                                                                                            | 2.291(2)   | Cd-O(3) <sup>#2</sup>                        | 2.488(2)   | Cd-O(5)                                      | 2.515(2)   |
| Cd-O(1) <sup>#1</sup>                                                                                                                               | 2.704(2)   | O(1W)-Cd-O(2) <sup>#1</sup>                  | 98.90(8)   | O(1W)-Cd-O(4) <sup>#2</sup>                  | 161.72(8)  |

|                                                                          |           |                                           |           |                             |          |
|--------------------------------------------------------------------------|-----------|-------------------------------------------|-----------|-----------------------------|----------|
| O(2) <sup>#1</sup> -Cd-O(2W)                                             | 123.17(7) | O(4) <sup>#2</sup> -Cd-O(3) <sup>#2</sup> | 54.87(6)  | O(2) <sup>#1</sup> -Cd-O(5) | 79.11(7) |
| O(4) <sup>#2</sup> -Cd-O(5)                                              | 84.45(7)  | O(2W)-Cd-O(5)                             | 157.03(7) | O(3) <sup>#2</sup> -Cd-O(5) | 76.17(6) |
| Symmetry code: <sup>#1</sup> -x+1/2, y-1/2, z ; <sup>#2</sup> x+1, y, z. |           |                                           |           |                             |          |

| Complex 4                                                                                                    |           |                                              |          |                                              |          |
|--------------------------------------------------------------------------------------------------------------|-----------|----------------------------------------------|----------|----------------------------------------------|----------|
| Pb(1)-O(6) <sup>#2</sup>                                                                                     | 2.387(7)  | Pb(1)-O(5) <sup>#2</sup>                     | 2.517(8) | Pb(1)-O(7) <sup>#3</sup>                     | 2.602(7) |
| Pb(2)-O(8) <sup>#1</sup>                                                                                     | 2.299(12) | Pb(2)-O(7) <sup>#1</sup>                     | 2.698(8) | O(6) <sup>#2</sup> -Pb(1)-O(2)               | 75.4(3)  |
| O(2)-Pb(1)-O(1)                                                                                              | 52.5(2)   | O(6) <sup>#2</sup> -Pb(1)-O(5) <sup>#2</sup> | 53.8(2)  | O(6) <sup>#2</sup> -Pb(1)-O(7) <sup>#3</sup> | 77.9(3)  |
| O(8) <sup>#1</sup> -Pb(2)-O(4)                                                                               | 96.4(4)   | O(8) <sup>#1</sup> -Pb(2)-O(1W)              | 74.8(4)  | O(1W)-Pb(2)-O(3)                             | 114.0(4) |
| O(1W)-Pb(2)-O(7) <sup>#1</sup>                                                                               | 128.0(4)  | O(4)-Pb(2)-O(7) <sup>#1</sup>                | 119.5(3) | O(8) <sup>#1</sup> -Pb(2)-O(7) <sup>#1</sup> | 54.6(4)  |
| Symmetry code: <sup>#1</sup> -x+2, -y+2, -z+2; <sup>#2</sup> -x+1, -y, -z+1; <sup>#3</sup> -x+2, -y+1, -z+2. |           |                                              |          |                                              |          |