Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.


# Supplementary Information

**Hybrid materials of ZnO nanostructures with reduced graphene oxide and gold nanoparticles: Enhanced photodegradation rates in relation to their composition and morphology**

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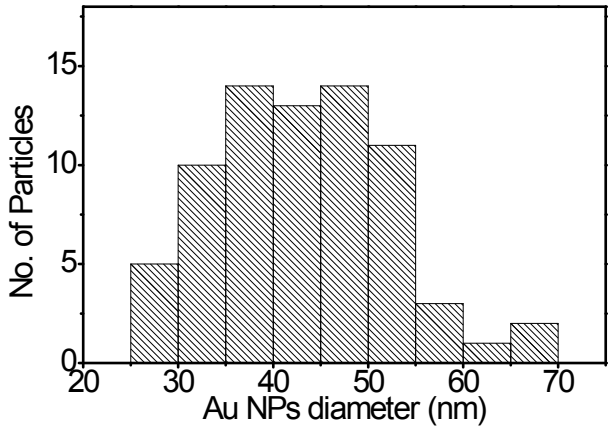


Figure S1. Au particle size distribution obtained from backscattered SEM images

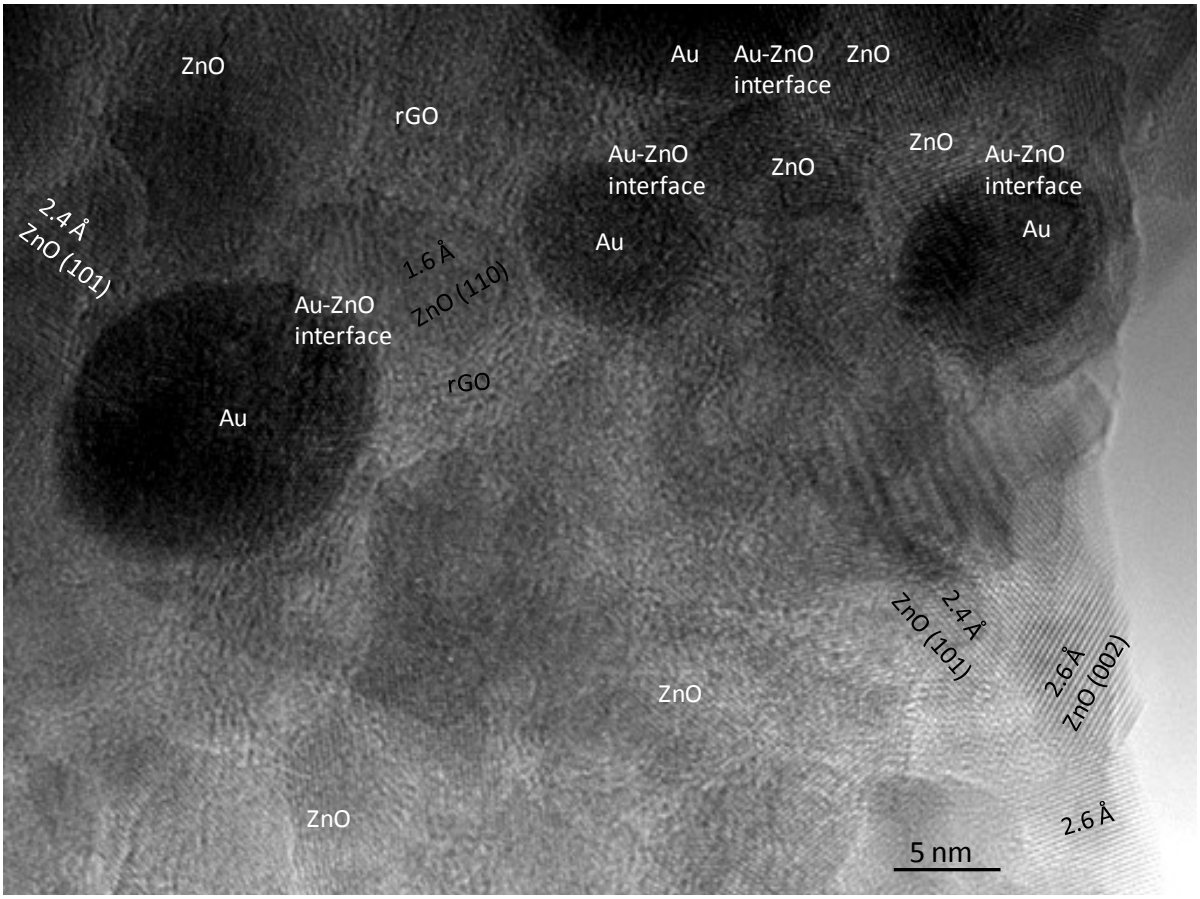


Figure S2: High resolution TEM of rGO-Au-ZnO NPs prepared by solution phase method showing the interfaces of lattice resolved Au NPs, ZnO NPs and rGO.

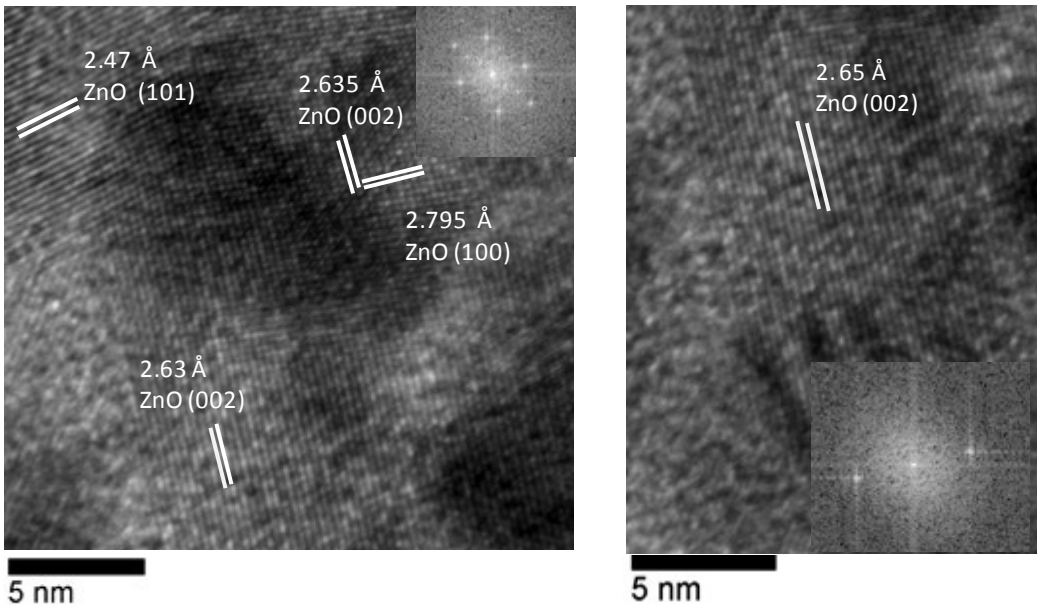


Fig. S3. Additional HRTEM images of rGO-ZnO NRs showing (002) planes along rod axis and other planes where rods overlap.

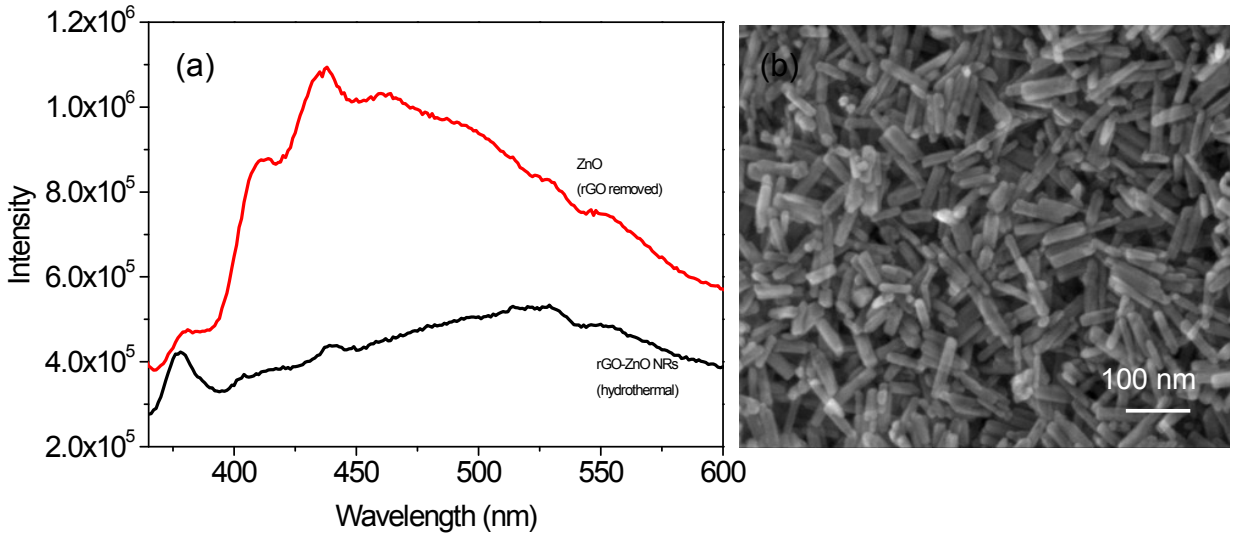


Figure S4: (a) PL spectra of rGO-ZnO NRs prepared by hydrothermal method before and after removing rGO by heating in air. (b) FESEM image of ZnO NRs after removing rGO.

Table S1: Elemental composition from EDS analysis of ZnO and its hybrids

| | ZnO NPs solution phase | | rGO-ZnO NPs solution | | rGO-Au-ZnO NPs solution | | rGO-ZnO NRs hydrothermal | |
|---|---|---|---|---|---|---|---|---|
| | Wt% | At% | Wt% | At% | Wt% | At% | Wt% | At% |
| Zn L | 70 | 37 | 33 | 9 | 39 | 16 | 73 | 38.5 |
| O K | 30 | 63 | 20 | 21 | 13 | 20 | 22 | 47.5 |
| C K | ---- | ---- | 47 | 70 | 28 | 61 | 5 | 14 |
| Au M | ---- | ---- | ---- | ---- | 20 | 3 | ---- | ---- |

Table S2. Rate constants for photodegradation by ZnO systems reported in the literature

| S. NO | Catalyst system | Catalyst (Wt) | Dye ,Conc. | UV / visible, Power | Rate | References |
|---|---|---|---|---|---|---|
| 1 | i. rGO-Au-ZnO NPs<br>ii. rGO-ZnO NPs<br>iii. rGO-ZnO NRs<br>iv. ZnO NPs | 10 mg | 50 mL, 40 μM Rhodamine B (RB) solution (19 ppm) | 200 W UV spot light source - 365 nm (intensity 110 mW/cm$^2$) & distance between Lamp and Vessel 4.5 cm | i) 97% degradation in 40 min, 0.065 min$^{-1}$<br>ii) 0.046 min$^{-1}$<br>iii) 0.033 min$^{-1}$<br>iv) 0.0135 min$^{-1}$ | **This Work** |
| 2 | Ag/ZnO/rGO composite (NPs) | 11.25 mg | 30 mL, 15 mg L$^{-1}$ Methylene orange (MO) & ratio dye : catalyst ,1 :25 | 365 nm (8W) & distance between Lamp and Vessel 5 cm | 94% degradation in 68 min | Sanjit Sarkar, CrystEngComm, 2013, 15, 7606–7614. |
| 3 | G/ZnO/Au | 200 mg (4 mg/mL) | 5 mM, 50 mL Nitro Benzene | 500 W UV-visible lamp ( used filter to get <420 nm) | Reduction of Nitrobenzene to Aniline 97.8% in 140 min | Prathik Roy et al., Environ. Sci. Technol. 2013, 47, 6688−6695. |
| 4 | rGO/ZnO NPs | 200 mg (4 mg/mL) | 50 mL, 6 ppm RB | Simulated sun light (UV & visible light) – Flux intensity 300 W/m$^2$ | Degradation completes in 60 min | Jinfeng Wang et al., ACS Appl. Mater. Interfaces 2012, 4, 3084−3090. |
| 5 | rGO/ZnO NPs | 60 mg (1g/L) | 60 mL of 10 mg/L Cr (VI) solution | 500 W (High pressure Hg lamp) – 365 nm | 96% removal in 60 min | Xinjuan Liu et al., Chem. Eng. J. 2012, 183, 238–243. |
| 6 | rGO-ZnO NPs ($GHZ_{1.2}$) | 50 mg | 100 mL, 10 μM solution Methylene Blue (MB) | 11 W UV lamp (λ = 254 nm) & 175 W metal halide lamp (λ > 420 nm)light intensity 0.93 and 2.5 mW/cm$^2$ | Visible light -0.60632 h$^{-1}$ &<br>UV light-0.18948 min$^{-1}$ | Xiaojuan Bai et al., Langmuir 2013, 29, 3097−3105. |
| 7 | rGO/ZnO NPs | 6 mg | 60 mL, 0.125 mg/mL MB (7.5 mg) | UV illumination (254 nm) intensity ~ 3 mW/cm$^2$ | 70% in 50 min | Long Zhang et al., Physica E 2013, 47, 279–284. |
| 8 | rGO-ZnO NPs | 50 mg | 50 mL, 10 μM solution (RB &MB) | 300 W (High pressure Hg lamp)-(λ>365 nm) & visible light source 300 W (High pressure Hg lamp)-(λ>400 nm with filter) | Complete degradation in 60 min | Baojun Li et al., J. Mater. Chem. 2011, 21, 3346–3349. |
| 9 | ZnO/graphene | 50 mg | 40 mL, 10 mg/L RB solution | 15 W UV light tube (365 nm) & for Visible light 150 W Xenon lamp (filters) | 100% degradation in 60 min | Qi Zhang et al., J. Mater. Chem., 2012, 22, 11778–11784. |
| 10 | rGO/ZnO NRs | 30 mg | 60 mL, 5 ppm conc. Cr(VI) | 300 W Xe arc lamp (visible light > 400 nm) | 0.17 h$^{-1}$ | Xiaoyang Pan et al., Phys. Chem. Chem. Phys., 2014, 16, 5589-5599. |
| 11 | rGO-ZnO NRs | 15 mg | 70 mL, 100 ppm MB | 300 W Xe arc lamp ( 365 ±15 nm) | Complete degradation in 40 min | Zhang Chen et al., CrystEngComm, 2013, 15, 3022–3030. |
| 12 | GNP/ZnO NRs | 10 mg | 80 mL, 20 mg/L MO solution | 300 W arc lamp ( 365 ±15 nm) | 0.0622 min$^{-1}$ | Fangxing Xiao et al., J. Mater. Chem. 2012, 22, 2868–2877. |
| 13 | i)ZnO NRs-rGO-CNTs<br>ii) pure ZnO | 100 mL ,1.5 mg/L | 100 mL, 5 mg/L MB solution | 500 W (High pressure Hg tube)-365 nm | i)0.011 min$^{-1}$<br>ii) 0.00442 min$^{-1}$ | Tian Lv et al., Catal. Sci. Technol. 2012, 2, 2297–2301. |
| 14 | rGO/ZnO nanopyramids | 25 mL, 0.25 mg/mL | 25 mL, 30 μM Malachite green (MG) solution | UV lamp (365 nm) | 78% degradation in 90 min | Natalie P. Herring et al., J. Nanopart. Res. 2012, 14, 1277. |

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|---|---|---|---|---|---|---|
| 15 | rGO-ZnO Hollow sphere | 20 mg | 100 mL, 10 μM solution of MB | 500 W Hg lamp (5 cm distance) | Complete degradation in 90 min | Qiu-Ping Luo et al., J. Phys. Chem. C 2012, 116, 8111−8117. |
| 16 | i)ZnO NPs<br>ii) ZnO NPs – Carbon fibers (4:1)<br>iii) ZnO NPs - Carbonfibers (8:1) | 100 mg | 100 mL, 10 mg/L RB | 50 W (High pressure Hg tube) – 313 nm | i)0.02187 $min^{-1}$<br>ii) 0.05350 $min^{-1}$<br>iii) 0.07533 $min^{-1}$ | Jingbo Mu et al., ACS Appl. Mater. Interfaces 2011, 3, 590–596. |
| 17 | Au/ZnO Nano composite | 100 mg | 50 mL, 20 μM RB solution | Direct SUN light (~50000 lx) | 0.0291 $min^{-1}$ | Chanchal Modal et al., New J. Chem. 2014, 38, 2999—3005. |
| 18 | Au/ZnO NRs | 30 mg | 40 mL, 20 μM RB solution | 300 W (High pressure Hg lamp) – 365 nm | 100% degradation in 15 min | Qian Wang et al., Environ. Sci. Technol. 2009, 43, 8968–8973. |
| 19 | Au-ZnO Nano pyramids | 30 mg | 1 mL, 1 mmol/L RB | 300 W Xenon lamp | 100% degradation in 10 min | Peng Li et al., J. Am. Chem. Soc. 2011, 133, 5660–5663. |
| 20 | Ag-ZnO NRs<br>(5 wt % of Ag on ZnO) | 30 mg | 90 mL, 50 μM MO solution | 4*4 W fluorescent Hg lamps (365 nm) | 100% degradation in 30 min | Yuanhui Zheng et al., Inorg. Chem. 2007, 46, 6980-6986. |
| 21 | Au NPs-ZnO Nanosheet | Not given | 15 ppm of MO | 365 nm _Intensity 150 $mW/Cm^2$ | 75% degradation in 240 min | Yu-Hsiang Sung et al., Phys. Chem. Chem. Phys., 2012, 14, 14492–14494. |
| 22 | i)ZnO Nano fibers<br>ii) Ag – ZnO Nano fibers (7.5% of Ag) | 10 mg | 10 mL, 25 μM RB solution | 8 W (low pressure Hg tube) – 254 nm | i)0.0025 $min^{-1}$<br>ii) 0.024 $min^{-1}$ | Dandan Lin et al., Chem. Mater. 2009, 21, 3479–3484. |
| 23 | ZnO NPs (25 nm) | 10 mg | 100 mL (1.5mg) of 15 mg $L^{-1}$ MB | UV A tubes – 365 nm (0.3 mW $Cm^{-2}$) | 0.0275 $min^{-1}$ | Anna Mclaren et al., J. Am. Chem. Soc. 2009, 131, 12540–12541. |
| 24 | i). ZnO (THF) Cauliflower<br>ii). ZnO (Decane) Truncated hexagonal conical<br>iii). ZnO (Acetone) Nano spherical<br>iv). ZnO (Ethanol) NRs<br>v). ZnO (water) Tubular<br>vi). ZnO (Tolune) Hour glass like<br>vii) Commercial ZnO | 50 mg | 50 mL, 15 ppm Phenol solution | Six 15 W UV lamps (254 nm) | i) 0.1469 $min^{-1}$<br>ii) 0.0867 $min^{-1}$<br>iii) 0.0385 $min^{-1}$<br>iv) 0.0468 $min^{-1}$<br>v) 0.0651 $min^{-1}$<br>vi) 0.0518 $min^{-1}$<br>vii) 0.0182 $min^{-1}$ | Linping Xu et al., Chem. Mater. 2009, 21, 2875–2885. |
| 25 | ZnO NRs & ZnO nano crystals | 20 mg | 50 mL, 50 μM MO solution | 300 W (High pressure Hg lamp) – 365 nm | Complete degradation in 60 min | Yuanhui Zheng et al., Inorg. Chem. 2007, 46, 6675-6682. |
| 26 | i). ZnO NPs<br>ii) ZnO NRs<br>iii) ZnO NWRs<br>iv) ZnO undeveloped NRs | 20 mg | 100 mL, 10 μM RB solution | 125 W UV lamp | I) 0.07205 $min^{-1}$<br>ii) 0.0491 $min^{-1}$<br>ii) 0.0614 $min^{-1}$<br>iv) 0.0466 $min^{-1}$ | Li Wang et al., Inorg. Chem. 2008, 47, 1443-1452. |