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Supporting information

Ru loaded mesoporous WO_3 microflowers for dual applications: enhanced H_2S sensing, and sunlight driven photocatalysis

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Supporting information SI-1

Synthetic protocol

In a typical experiment, WO_3 powders were prepared as follows: sodium tungstate powder (8.15 g) was dissolved in distilled water (100 ml). This Na_2WO_4 solution was acidified to pH range of 1-1.5 using H_2SO_4 (3 mol/l) solution resulted in white precipitate. After addition of 6.3 g of $H_2C_2O_4$, in an obtained mixture, a translucent, homogeneous sol was formed. This sol was diluted to 200 mL and added (0.3 g) Rb_2SO_4. WO_3 sol was transferred to 250 ml autoclave, sealed, and maintained at 180°C for 4, 12, 18, 24 h. The precipitates were filtered, washed sequentially with water to remove ions possibly remnant in the final products, and dried at 60°C. The resulting powders were respectively labeled as S_1, S_2, S_3 and S_4. The optimized sample S_3 was treated as pristine WO_3 sample for ruthenium loading. The as-synthesised pristine WO_3 powder was dispersed into an aqueous solution of ruthenium chloride hydrate ($RuCl_3 \cdot xH_2O$ s. d. fine chem ltd.) with Ru concentration of 0.25, 0.5 and 1 wt % of WO_3 and mildly heated on a hot plate at 60°C until the mixture was dried into powder. Dried powders were ground and subsequently annealed in air at 400°C for 2 h. Powder had a gray-green color. The pristine WO_3 powder was sample S_3 and 0.25, 0.5 and 1 wt % were labeled as R_1, R_2 and R_3 respectively.

Sensor fabrication and test method

For device fabrication, a proper amount of sintered WO_3 powder was ground with few drops of butyl carbitol acetate in an agate mortar to form slurry. The slurry was then coated onto an alumina substrate by screen printing technique. The coating was dried for 30 minutes at room temperature. The sensor element was heated for 2 h at 400°C to remove added binders of the paste. Silver contacts were provided for the electrical measurements.

A glass assembly having a ceramic sample holder with two probes, on which the sensor was placed coaxially inside a temperature control furnace. The gas sensing properties were evaluated by measuring the change in resistance of the sensors before and after introduction of the test gas. During the calculation, the gas sensitivity (response) is defined as the ratio Ra/Rg

$$(S = Ra/Rg) \qquad \ldots\ldots(1)$$

Where Ra and Rg are the resistances measured in air and in the test gas atmosphere, respectively. The response time and recovery time are defined as the time required for the variations in the resistance of the gas sensor to reach 90% of the total variation in resistance during the process of target gas adsorption and desorption, respectively. To make the evaluation process reliable and

clear, the parameters on sensing performance were mainly presented by response (Ra/Rg) value. For the selectivity, the sensors were investigated toward s acetone, ammonia, ethanol, trimethylamine, xylene, propanol, diethanolamine and hydrogen sulphide gas.

Photocatalytic activity test:

The photocatalytic activity of Ru loaded WO_3 catalysts were evaluated by the degradation of Rhodamine B. The reaction suspension was prepared by adding 0.3 g photocatalyst powder into 100 ml of Rhodamine B aqueous solution (5 mg L^{-1}) at room temperature. Before light was turned on, the suspension was continuously stirred for 60 min in dark to attain an adsorption–desorption equilibrium and subsequently, the solution was placed in a beaker with magnetic stirring and irradiated under natural sunlight. The period of the experiment was between 11:00 and 14:30 during the months of October. The average intensity of natural sunlight was measured using a digital lux meter and it was found to be 8.95 x 104 lux. Sample aliquots were withdrawn from the reaction mixture at a regular time interval, centrifuged and then dye concentration of residual solution during the degradation was determined by using a Cary UV-60 Spectrophotometer, Agilent Technologies. Changes in the concentration of Rhodamine B were observed from its characteristic absorption band maximum at 553 nm. The decolorization efficiencies of the dyes were estimated by the equation:

$$\eta(\%) = \frac{(C_i - C_f)}{C_i} \times 100 \qquad (2)$$

Where C_i and C_f represents the concentration of dye in solution before & after irradiation respectively. Effect of various parameters such as irradiation time, initial concentration of Rhodamine B, decolourization efficiency were also investigated.

Analysis method:

The crystal structures of the as prepared products were characterized by powder X-ray diffraction(XRD) on D/max 2550 V X-ray diffractometer (Rigaku, Tokyo, Japan) with monochromatized Cu Kα radiation (λ = 1.54056 Å; scanning rate = 0.01° s−1 in the range of 10−80°) incident radiation. Morphologies and sizes of all products were analyzed with Field Emission Scanning Electron Microscopy (FESEM, Bruker XFlash 6130) and Transmission Electron Microscopy (TEM, FEI Techni, G2 operated at 300 kV). High-resolution transmission

electron microscope images (HRTEM) and selective area electron diffraction pattern (SAED) were characterized using JEM-2100 microscope. In the preparation of samples for TEM observation, the materials were first dispersed in ethanol using an ultrasonic bath and then dropped onto a copper grid, which was dried in air at room temperature and kept in vacuum for 20 min before TEM observation. The specific surface area was measured using a ST-2000 surface area and pore size analyzer (Quantachrome Instruments). The pore size distribution was determined using the BJH method applied to the desorption branch of adsorption-desorption isotherms.

Supporting information SI-2

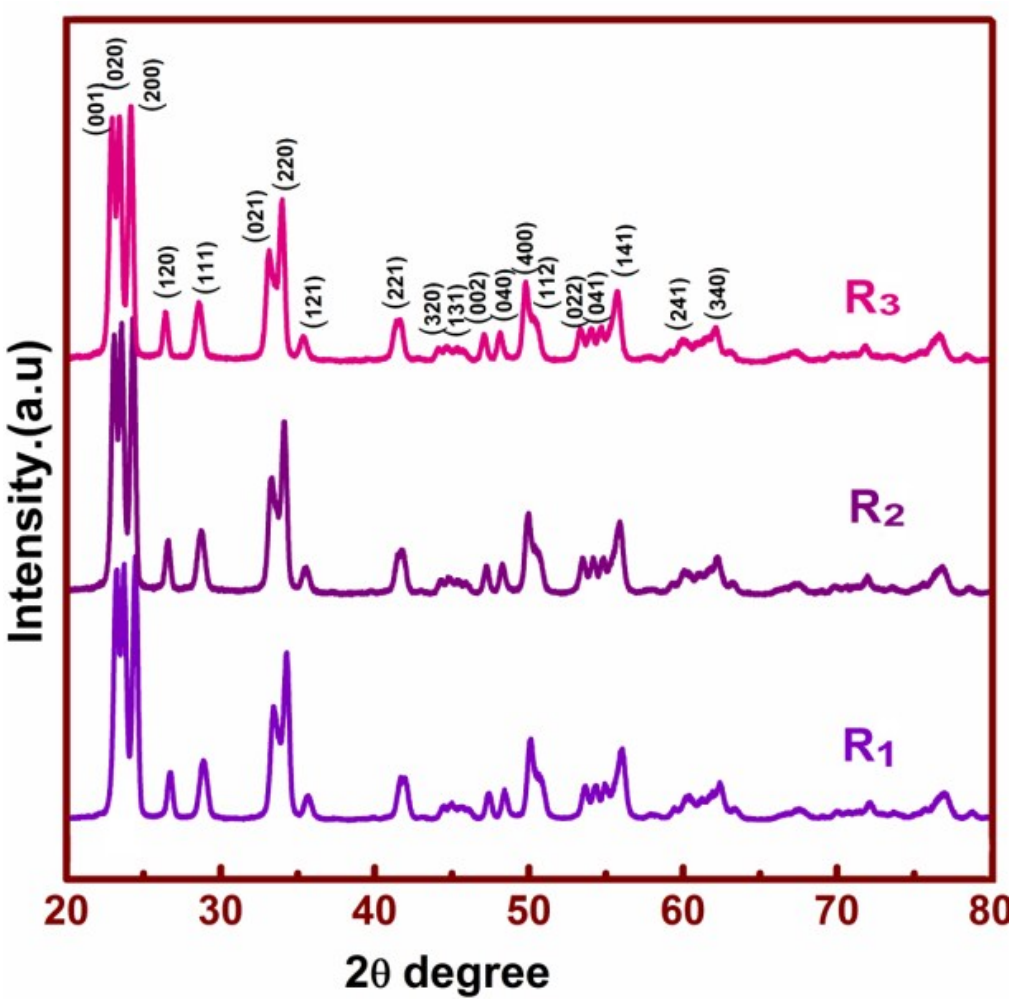


Fig S1. XRD profiles of sample R_1, R_2, R_3.

Table S1: Crystallite size and lattice parameters for different Ru/WO_3 samples.

Sample id	**Crystallite size(nm)**	**Lattice parameters (Å)**
R_1	11.93	a=3.85, b=7.53, c=7.31
R_2	11.95	a=3.85, b=7.53, c=7.31
R_3	11.98	a=3.85, b=7.53, c=7.31

Supporting information SI-3

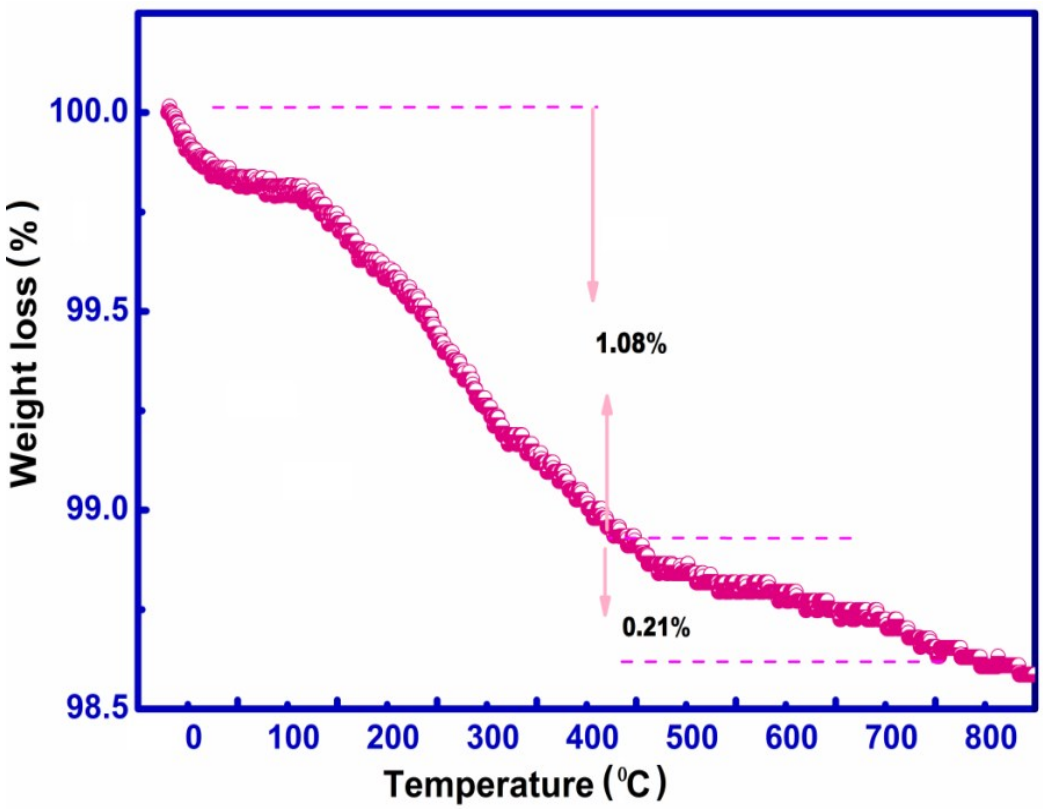


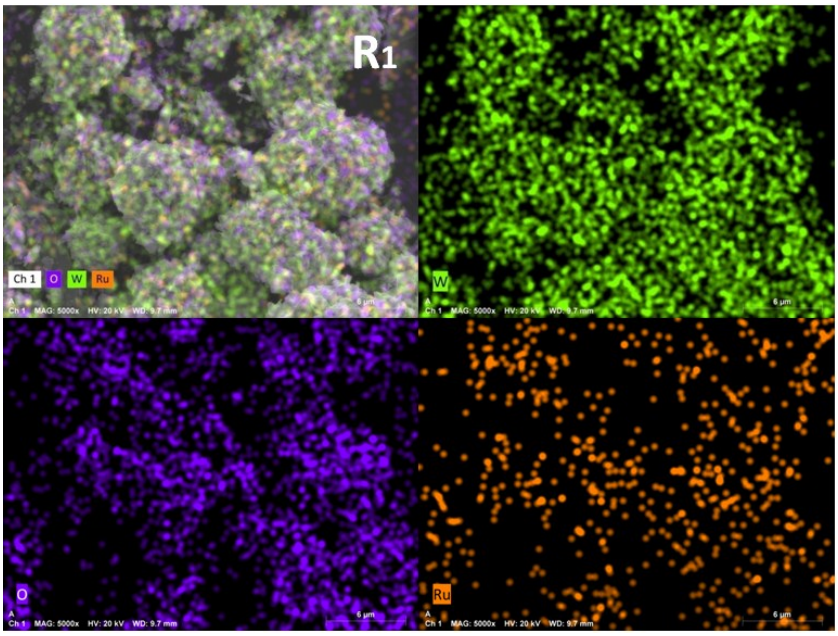
Fig S2. TG- plot of dried precipitate of sample S_3

Supporting information SI-4

Table S2: Variation of response/recovery time and sensitivity of H_2S with Ru concentration, operating temperature (200°C), and H_2S concentration

Ru conc. (wt %)	Response time (s)	Recovery time (s)	Sensitivity (Ra/Rg)
0 (10 ppm)	58	363	1.11
0.25 (10 ppm)	55	243	1.91
0.5 (1 ppm)	48	197	82
1.00 (10 ppm)	56	253	13.05

Supporting information SI-5



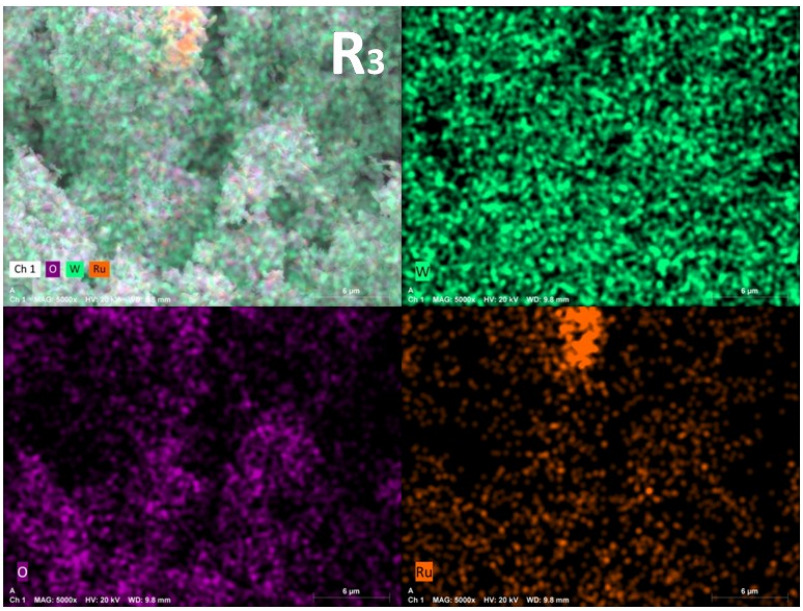


Fig S3: Elemental distribution of sample R_1 and R_3

Supporting information SI-6

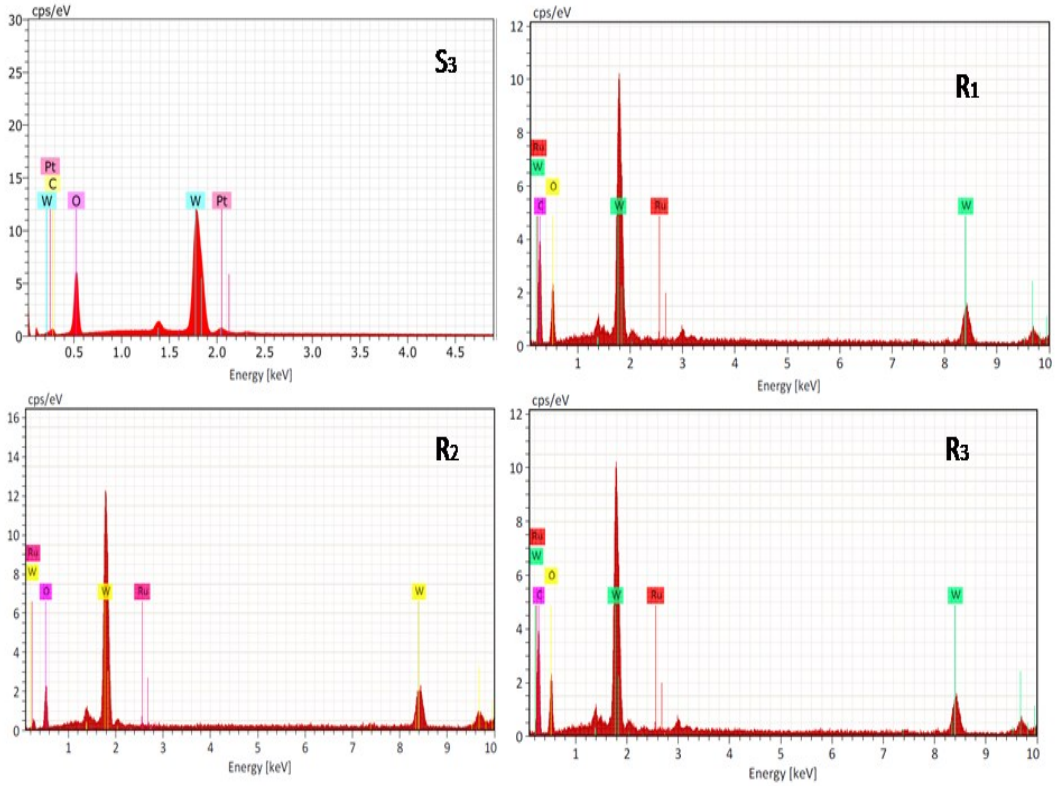


Fig S4. EDAS spectrum of sample S_3, R_1, R_2 and R_3.

Supporting information SI-7

Table S3: The textural properties of mesostructured WO_3 samples

Sample code	Element	Weight%	Atomic%
S_3	W	71.14	20.94
	O	23.38	79.06
R_1	W	71.81	16.26
	O	16.06	41.78
	Ru	0.21	0.13
R_2	W	57.87	10.68
	O	42.13	89.32
	Ru	0.44	0.28
R_3	W	81.83	29.13
	O	17.19	70.26
	Ru	0.93	0.6