Electronic Supplementary Material (ESI) for Chemical Communications

Electronic Supporting Information (ESI)

Hybrid nanocomposites of ZIF-8 with graphene oxide exhibiting tunable morphology, significant CO_2 uptake and other novel properties

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Experimental Section

Materials: All the reagents and solvents were commercially available and used as supplied without further purification. $Zn(NO_3)_2.6H_2O$, 2-methylimidazole were obtained from Aldrich Chemical Co.

Room temperature synthesis of nanoscale ZIF-8 crystals: Nanoscale ZIF-8 with hexagonal morphology was prepared according to the literature procedure reported by Wiebcke *et al*.[1] In a typical synthesis methanolic solution (25 ml) $Zn(NO_3)_2\cdot 6H_2O$ (16 mmol, 366 mg) was slowly added into a methanolic solution (25 ml) of 2-methylimidazole (8 mmol, 811 mg) with constant stirring. Stirring was stopped after combining the component solutions and a *gel*-like solid was recovered by centrifugation and washed with metahnol for three times and then dried under vacuum. Yield: 60%. Anal. Calcd. for $C_8H_{10}N_4Zn$: C, 42.18; H, 4.3; N, 24.6; Found: C, 41.54; H, 4.86; N, 24.39 %.

Synthesis of Graphite Oxide (GO): GO was prepared using a modified Hummers and Offeman method.[2] In typical synthesis, 1.5 g of $NaNO_3$ and 1.5 g graphite powder were slowly added to 75 ml conc. H_2SO_4 in ice bath and allowed to mix properly under constant stirring for 10 min. 10 g KMnO4 was added to this uniform mixture and then it was transferred into an oil bath (40 °C) under stirring condition for 0.5 h. Oxidation of graphite occurred and very viscous dark brown product formed after 30 min. To this mixture 75 ml deionized water was added and the temperature of oil bath was raised to 75 °C. The reactants were stirred at 75 °C for another 15 min. Then 15 ml H_2O_2 (30%) was mixed with 150 ml warm water (~70 °C) and added to the reaction mixture. Colour of dispersion was changed from brown to yellow. Then product was centrifuged and washed several times with water. Washed product was dispersed in water and dialysis was performed for 24 h. Dialysed product was centrifuged to remove excess water and solid product was transferred to petri dish. The obtained product was stored under vacuum for drying.

Preperation of GO@ZIF-8 hybrid nanocomposites*:* First bare X mg of GO was dispersed in methanol and sonicated for 5 hours. For the synthesis of GO@ZIF-8 composites, different wt% of GO solution added during preparation of ZIF-8 nano crystals in the strring condition. The resultant solution was centrifuged and washed several times with water-methanol mixture and dried at 60 ^{o}C. The resulting solid composites obtained by variation of GO content were denoted by ZG-X, X indicated wt% (X = 1, 2, 4, 10 and 20 wt %) of GO in comparison to Zn(II) metal. The obtained samples were designated as **ZG** (**ZG-0**, **ZG-1**, **ZG-2**, **ZG-4**, **ZG-10** and **ZG-20**) based on the different amount of GO loading.,

Preparation of GO@ZnS hybrid nanocomposites: For the *in situ* stablization of zinc sulphide (ZnS) nanoparticles on the graphene sheets, as-prepared **ZG-20** (20 wt% of GO) was added into a round bottom flask containing thioacetamide (0.5 M) in 50 ml methanol and 5 ml water at 60 °C. The mixture was refluxed for 6 h under vigorous stirring. The resultant product was collected by centrifugation, washed with anhydrous methanol and dried under vacuum.

Characterization*:* The assynthesized ZIF-8, GO@ZIF-8 hybrid nanocomposites and Go@ZnS composite were characterized through different techniques. Powder X-ray diffraction (PXRD) patterns were recorded on a Bruker D8 Discover instrument using Cu-Kα radiation. The morphology and porous nature of ZG-Xs' were characterized with

Transmission electron microscopy (TEM) (JEOL JEM-3010 with an accelerating voltage at 300 KV). The Raman spectrum of the sample recorded in backscattering arrangement, using 532 nm laser excitation using 6 mW laser power. Thermogravimetric analyses (TGA) were carried out under nitrogen (flow rate of 50 mL/min) with Metler Toledo TGA-850 TG analyzer in the temperature range between 25 - 600°C at a heating rate 3°C / min.

Adsorption Measurements: Adsorption studies of N_2 (77 K) and CO_2 (195 K) on ZIF-8 and ZG composites were carried out using *QUANTACHROME AUTOSORB-1C* analyzer. Prior to the measurements, the samples were activated under high vacuum. In the sample chamber (~12 mL) maintained at T ± 0.03 K was placed the adsorbent sample (100-150 mg), which had been prepared at 433 K in 10^{-1} Pa for 24 hours prior to measurement of the isotherms. The adsorbate was charged into the sample tube, and then the change of the pressure was monitored and the degree of adsorption was determined by the decrease of the pressure on the equilibrium state. All operations were computer-controlled and automatic.

1. J. Cravillon, S. Münzer, S.-J. Lohmeier, A. Feldhoff, K. Huber, M. Wiebcke, *Chem. Mater.*, 2009, **21**, 1410.
2. W.Hummars and R. Offeman, *J. Am. Chem. Soc.*, 1995, **80**, 1339.

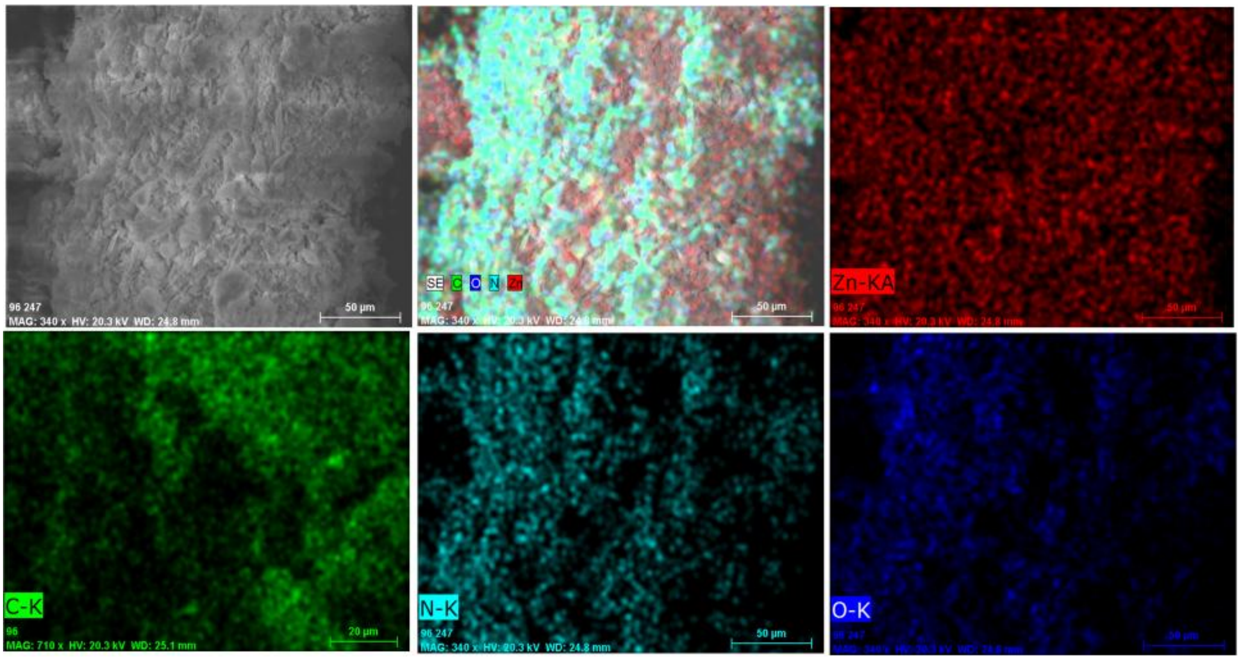


Fig. S1a Colour mapping of **ZG-10** sample showing phase purity with homogeneously distributed throughout the sample.

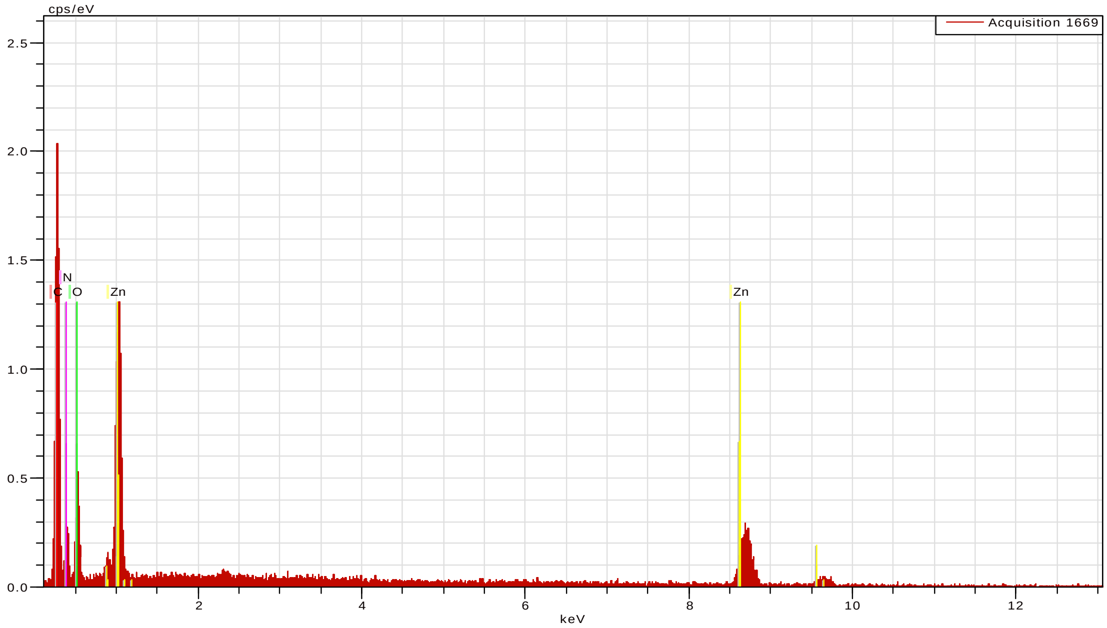


Fig. S1b Energy dispersive X-ray spectroscopy (EDAX) analysis of **ZG-10** sample showing presence of C, N, O and Zn elements.

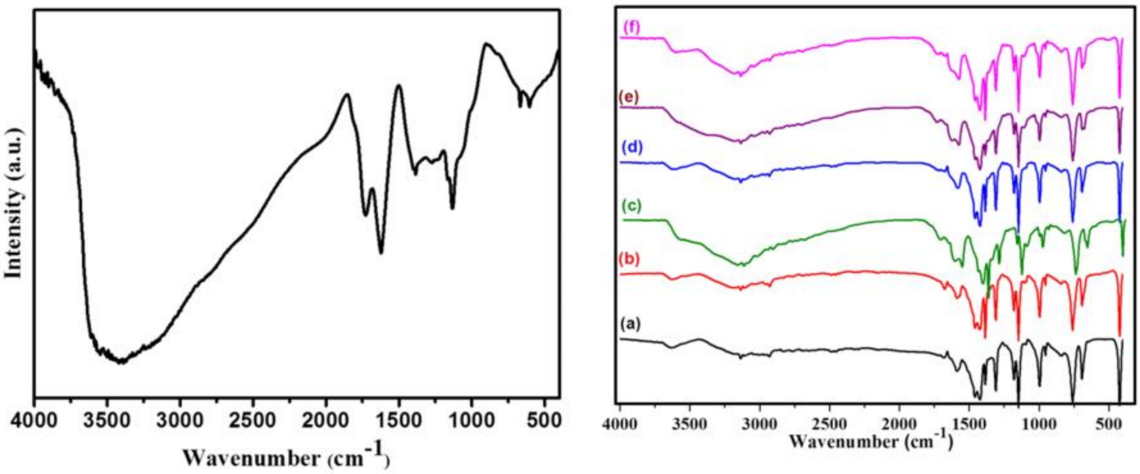


Fig. S2 (Left) FT-IR spectra of GO; (Right) (a) ZG-0 (ZIF-8) (b) ZG-1 (c) ZG-2 (d) ZG-4 (e) ZG-10 and (f) ZG- 20.

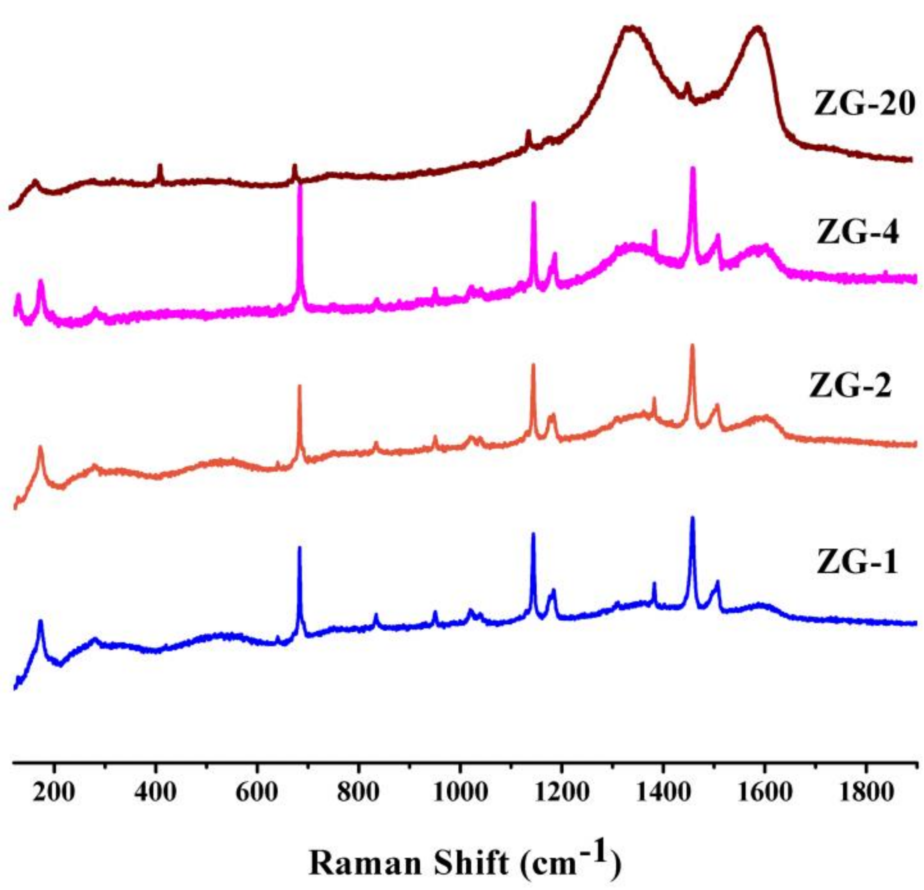


Fig. S3 Raman spectra of ZG composites with different GO content.

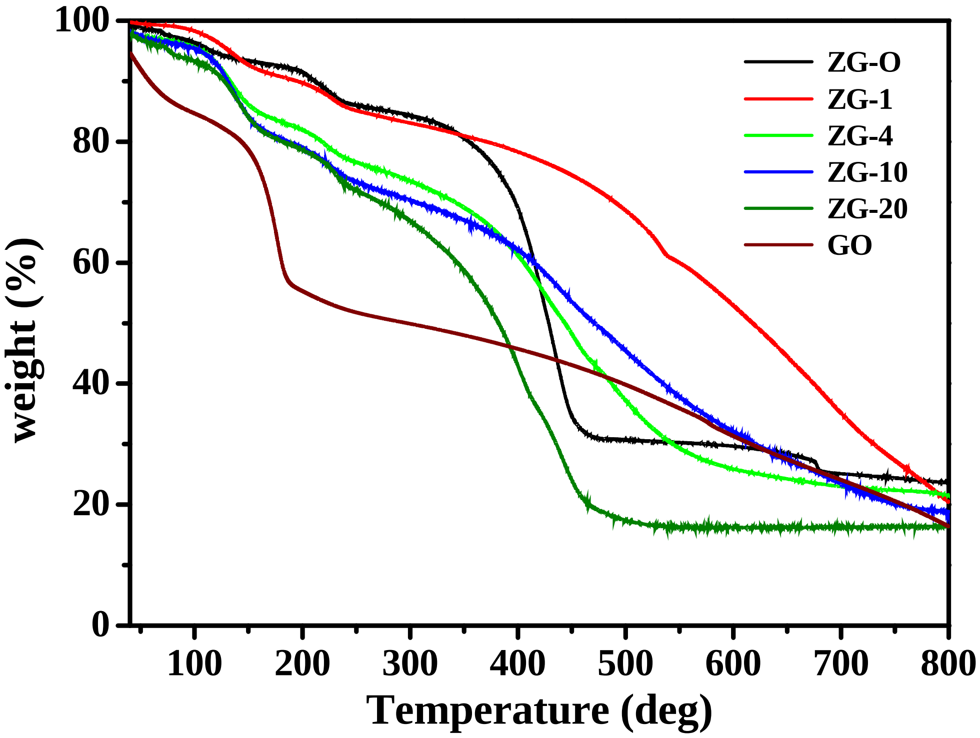


Fig. S4 TGA of as-synthesized ZIF-8, GO and ZG composites.

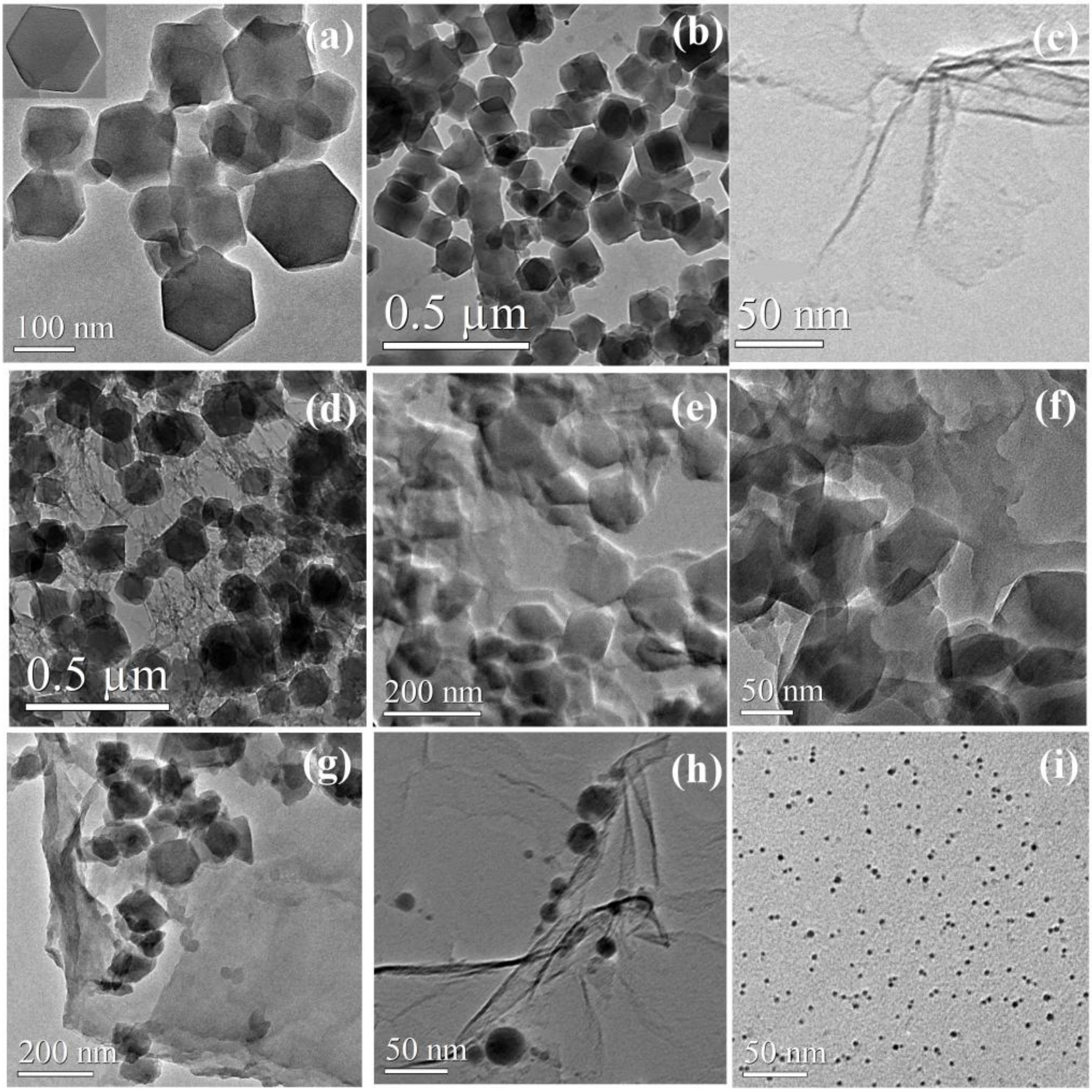
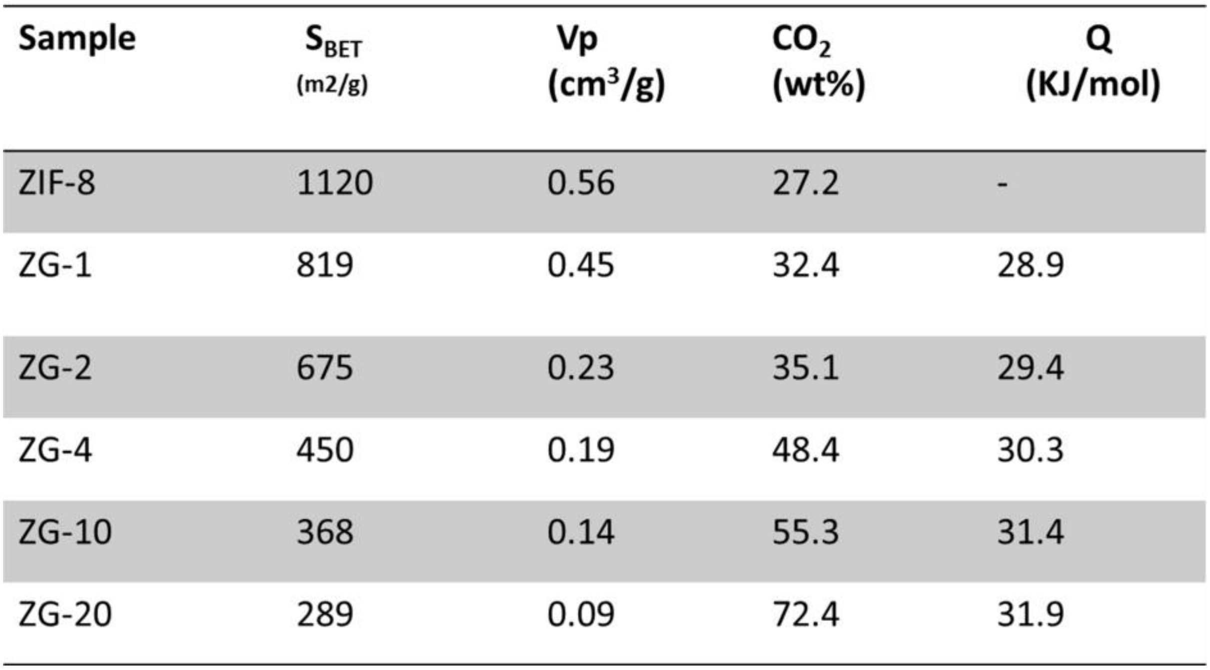


Fig.S5 TEM images of ZG samples (a-b) ZG-0; (c) GO ; (d) ZG-1; (e) ZG-2; (f-g) ZG-4 (h) ZG-10 (i) ZG-20.

Table S1. Textural parameters and CO_2 storage capacities for as-synthesized nanocrystals of ZIF-8 and ZG composites.



Sample	S_{BET} (m2/g)	Vp (cm^3/g)	CO_2 (wt%)	Q (KJ/mol)
ZIF-8	1120	0.56	27.2	-
ZG-1	819	0.45	32.4	28.9
ZG-2	675	0.23	35.1	29.4
ZG-4	450	0.19	48.4	30.3
ZG-10	368	0.14	55.3	31.4
ZG-20	289	0.09	72.4	31.9

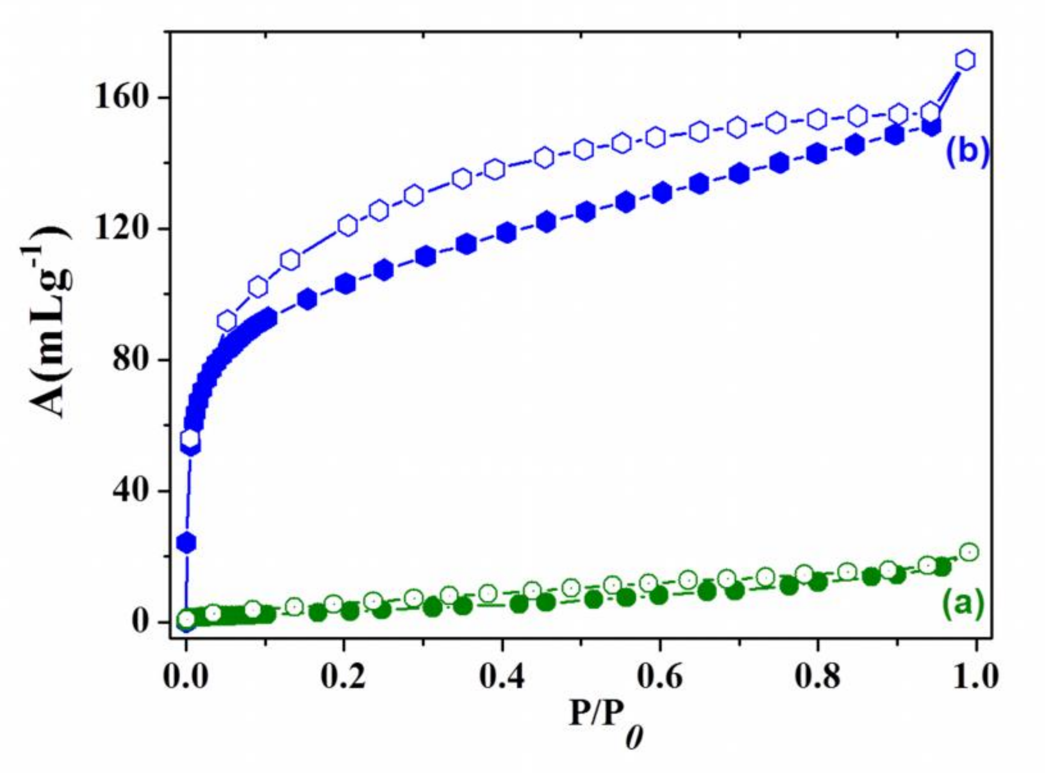


Fig. S6 (a) N_2 and (b) CO_2 adsorption isotherm for GO at 77 K and 195 K respectively.

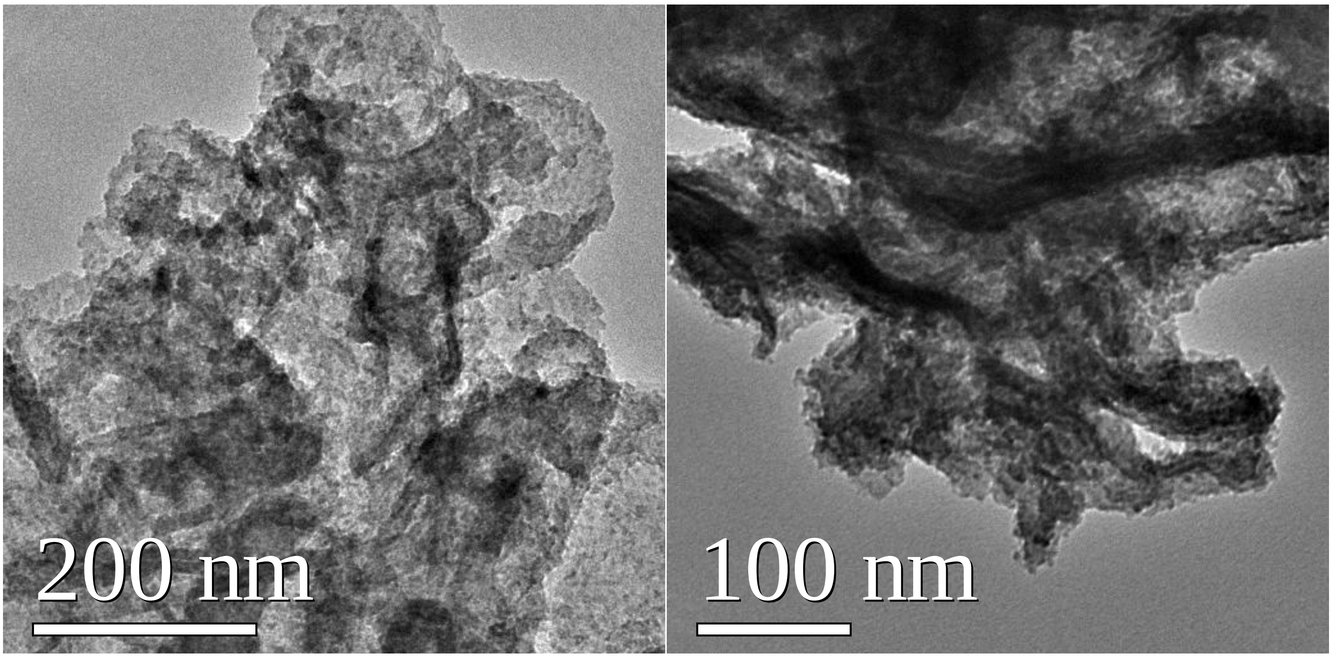


Fig. S7 Stabilization of ZnS nanoparticles on the GO sheets.

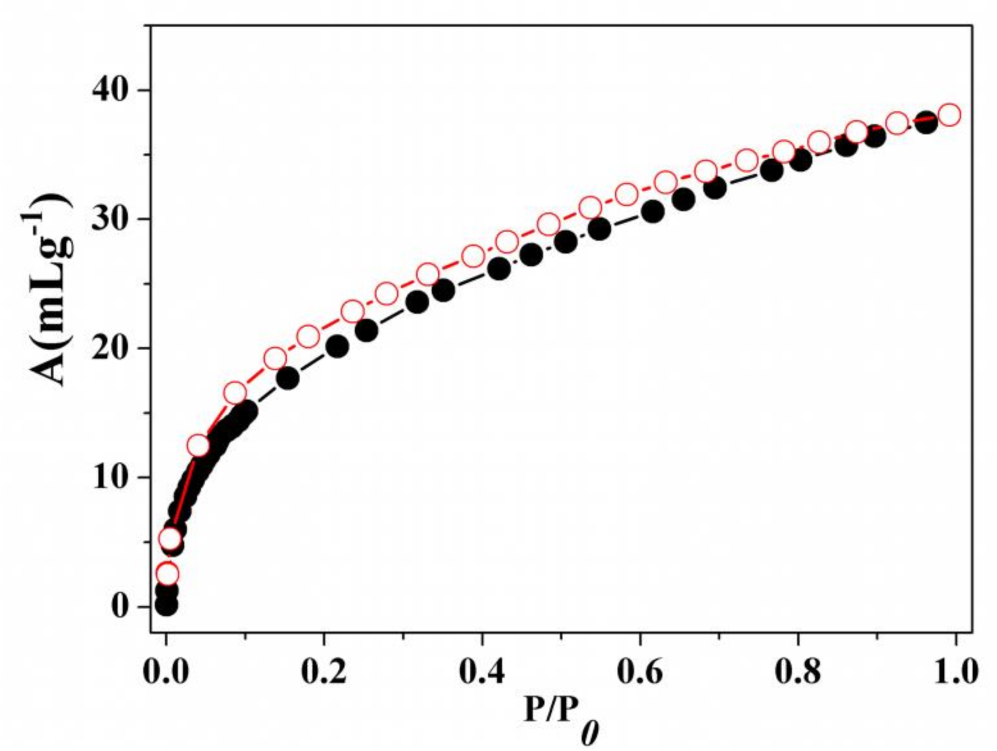


Fig. S8 CO_2 adsorption profile of GO@ZnS nanocomposite at 195 K.