

Supplementary Information for

Mesoporous ZnS nanospheres: a high activity heterogeneous catalyst for synthesis of 5-substituted 1*H*-tetrazoles from nitriles and sodium azide

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Experimental section

Materials

Poly(N-vinyl-2-pyrrolidone) (PVP, Mw=58000), zinc acetate, thiourea, zinc chloride, zinc bromide, sodium tungstate, sodium sulfide, *N, N*-dimethyl formamide (DMF) and ethylene glycol were obtained from Sinopharm Chemical Reagent Co., Ltd.. NaN₃ and all nitriles were purchased from Sigma-Aldrich Chemical Co., USA. All chemicals were of analytical grade and used without further purification.

Preparation of mesoporous ZnS nanospheres (MZNSS)

MZNSS were prepared according to the previous work with some modifications. In a typical experiment, PVP (5 g), zinc acetate (8 mmol) and thiourea (16 mmol) were dissolved in ethylene glycol (150 mL) under ultrasonic. Then the transparent solution was heated to 190 °C and maintained at this temperature for 2 h under stirring. The product was obtained with the milky white color, separated from the reaction mixture by centrifugation and washed with ethanol for several times. Then the product was treated with 0.1 M HNO₃ for 5 minutes and was dried in a vacuum oven for characterization.

*Typical procedure for preparation of 5-substituted 1*H*-tetrazole*

MZNSS treated with HNO₃ (0.1 g, 1.0 mmol) was added to a mixture of benzonitrile (0.257 g, 2.5 mmol) and sodium azide (0.350 g, 5.4 mmol) in DMF (5 mL) and the resulting composition was heated at 120 °C for 36 h under stirring. After the resulting

mixture was cooled to room temperature, the catalyst was separated from reaction mixture by centrifugation and washed with ethyl acetate (5 ml) for three times. The filtrate was treated with ethyl acetate (15 ml) and 6 M HCl (20 ml) under vigorously stirring for 5 min. The resultant organic phase was separated and the aqueous phase was again extracted with ethyl acetate (2×15 ml). The combined organic phase were washed with H₂O (2×20 ml) and concentrated to give the crude 5-phenyltetrazole; Pure products (0.349 g) were obtained after a flash chromatography using silica gel G60; yield: 95.6 %. ¹H NMR (300MHz, CDCl₃): δ = 8.00 (m, 2H), 7.59 (m, 3H), MS (70 eV): *m/z* (%) = 146.1 (M+, 6.87%), 118.1 (M-N₂, 100.0%), 103.1(M-HN₃, 10.3%), 91.1 (M-HCN₃, 30.35%), 77.1 (M-HCN₄, 14.93%), 63.0 (M-H₃C₂N₄, 9.72%), and 51.0 (M-H₃C₃N₄, 5.73%).

Characterization of MZNSS catalyst

The morphologies of the catalyst were characterized by transmission electron microscopy (TEM) (Japan JEOL JEM-200CX, transition electron microscope). High-Resolution TEM (HRTEM) images were obtained on a Philips TECNAI F-30 FEG instrument at an accelerating voltage of 300 kV. SEM images and the energy dispersive spectrum (EDS) were obtained by a JEOL S-4800 apparatus. The phase purity of the products were characterized by X-ray power diffraction (XRD), (Shimadzu XD-3A X-ray diffractometer with Cu K α radiation, λ = 0.15417 nm). The BET (Brunauer-Emmett-Teller) surface area was measured by ASAP2020 (Micromeritics, United States).

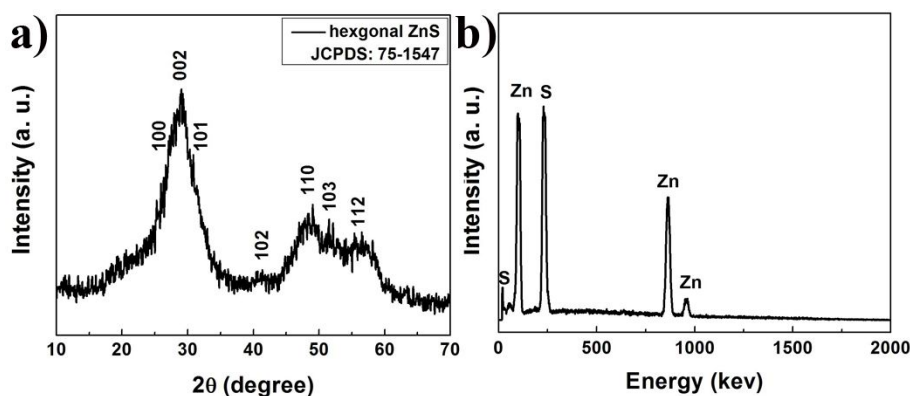


Fig. S1 (a) X-ray diffraction (XRD) pattern and (b) ED spectrum of MZNSS. The obvious broadened diffraction peaks of XRD indicate the small size of crystallites, of which porous ZnS nanospheres is composed.

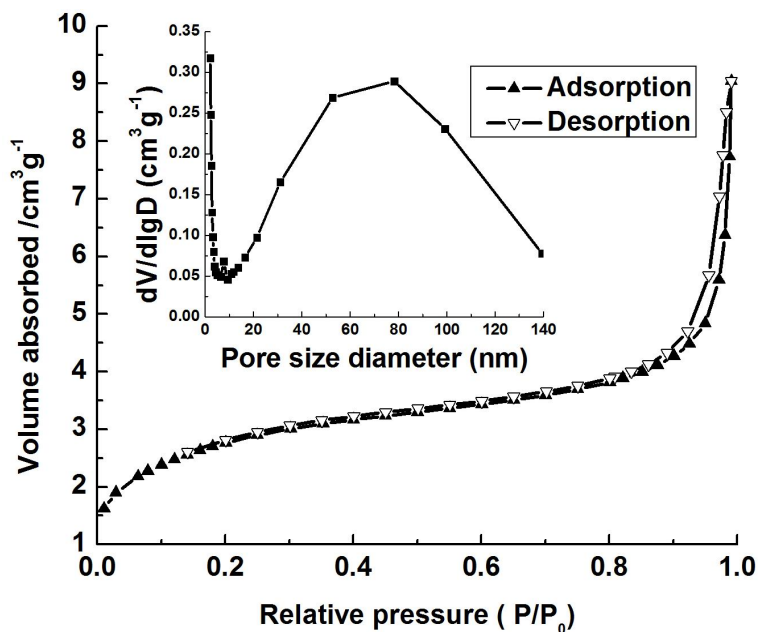


Fig. S2 The N_2 adsorption-desorption isotherm and Barrett-Joyner-Halenda (BJH) pore size distribution plot (inset) of MZNSS. The MZNSS have two kinds of pore size distribution, which can be seen from the inset of Fig. S2. Mesopores less than 10 nm diameter is attributed to the gaps among the nanoparticles forming ZnS nanosphere, while the large pores (> 80 nm) belongs to the spaces among ZnS nanospheres.

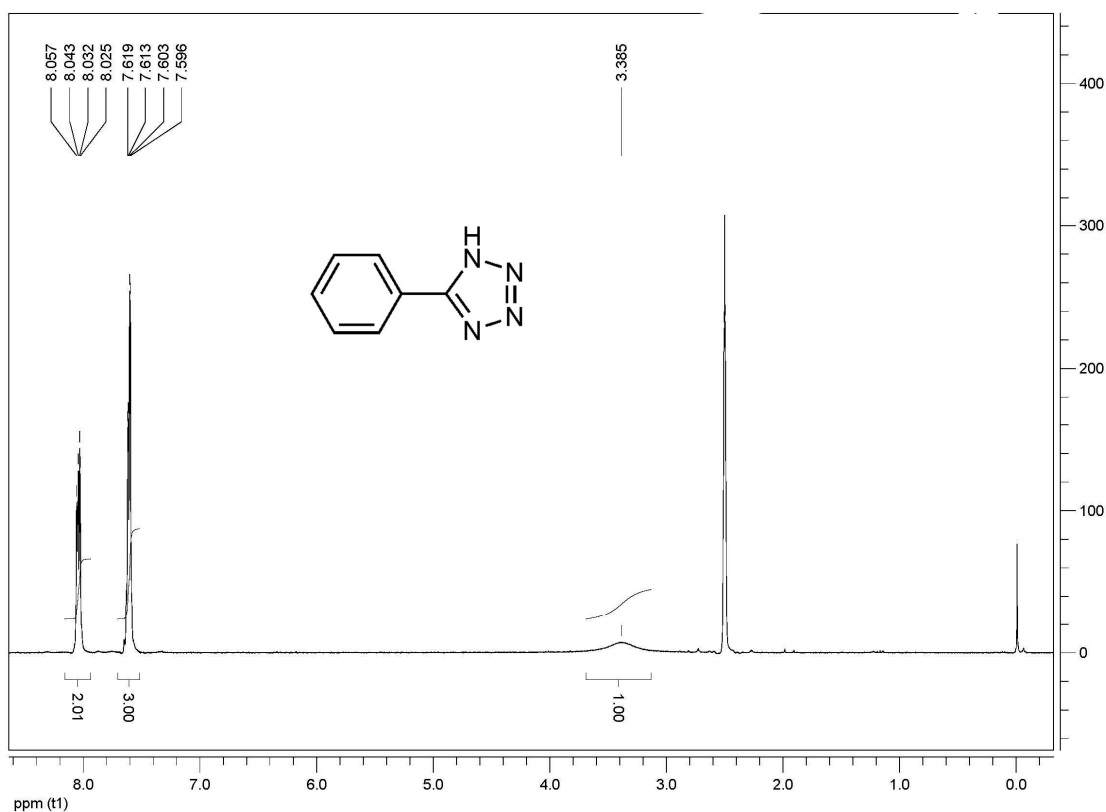


Fig. S3 ^1H NMR spectrum of 5-substituted 1*H*-tetrazole synthesized from benzonitrile and sodium azide. ^1H NMR (300MHz, CDCl_3): δ = 8.02-8.06 (m, 2H), 7.59-7.62 (m, 3H), 3.39 (m, 1H), MS (70 eV): m/z (%) = 146.1 (M+, 6.87%), 118.1 (M-N₂, 100.0%), 103.1 (M-HN₃, 10.3%), 91.1 (M-HCN₃, 30.35%), 77.1 (M-HCN₄, 14.93%), 63.0 (M-H₃C₂N₄, 9.72%), and 51.0 (M-H₃C₃N₄, 5.73%).

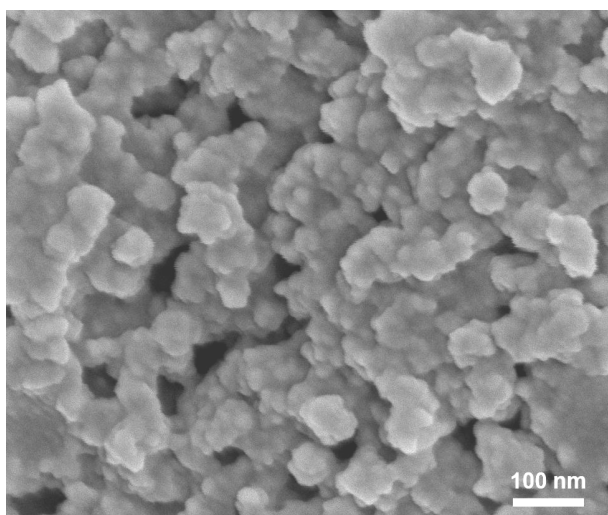


Fig. S4 SEM image of MZNSS after reaction.

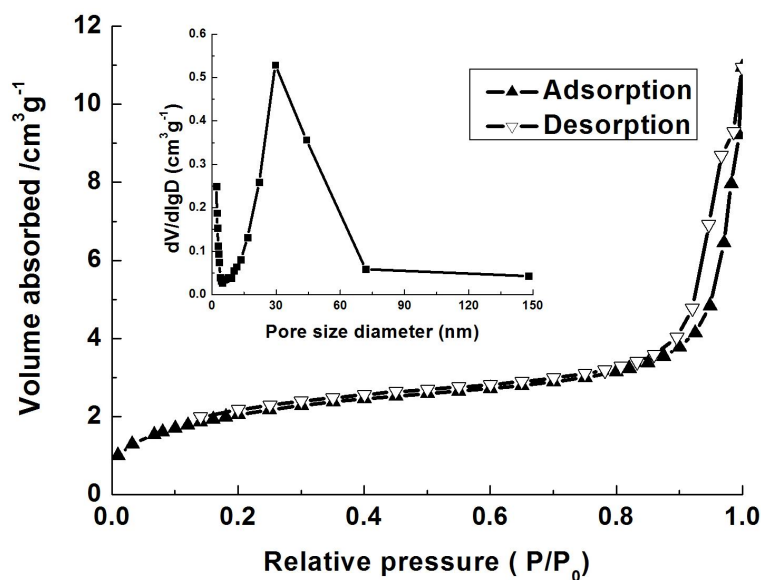
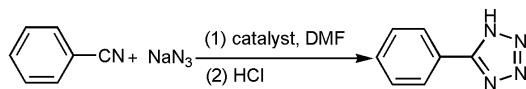


Fig. S5 The N₂ adsorption-desorption isotherm and Barrett-Joyner-Halenda (BJH) pore size distribution plot (inset) of MZNSS after reaction. The BET (Brunauer-Emmett-Teller) surface area and single point total pore volume are 170.2 m² g⁻¹ and 0.22 cm³ g⁻¹, respectively, which remain the mesoporous characterization.

Table S1 Preparation of 5-substituted 1H-tetrazoles with various catalysts^a



Entry	catalyst ^b	Yield [%] ^c	TON ^d
1	ZnS ^e	65	1.58
2	ZnWO ₄ ^f	83	2.01
3	CdS ^g	45	1.09
4	CdS ^h	41	0.99
5	ZnSe ⁱ	77	1.87
6	CdSe ⁱ	36	0.87

^a Reaction conditions: benzonitrile (2.5 mmol), NaN₃ (5.4 mmol), DMF (5 ml), reaction time 36 h, 120 °C. ^b Amount of Zn²⁺ catalyst used is equivalent to that of 0.1 g MZNSS. ^c Isolated yields. ^d The moles of tetrazoles formed per mol catalyst. ^e ZnS treated by 0.1 M HNO₃. ^f MZNSS treated with 0.005 M HNO₃. ^{g, i} prepared by precipitation method. ^h treated by 0.1 M HNO₃.