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Letter

Hydrothermal synthesis of transition-metal sulfide dendrites or microspheres with functional imidazolium salt

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ABSTRACT

A series of transition-metal sulfide (PbS, CdS, ZnS, CoS, Cu_2S) compounds were successfully synthesized through a facile hydrothermal method using 1-butyl-3-methlyimidazole thiocyanate ([BMIM][SCN]) as both sulfur source and capping ligand. The resultant products were characterized by X-ray powder diffraction (XRD) measurements in order to determine the crystalline phase of the products. The structural and morphological features of the samples were investigated by scanning electron microscopy (SEM), which showed that the morphologies of PbS and CdS were novel hierarchical dendrites, but rough exterior microspheres of ZnS, CoS and Cu_2S. A possible reaction process was simply discussed in the end.

1. Introduction

In recent years, the synthesis and properties characterization of nanometersized transition-metal semiconductors with novel controlled shape and structure have been attracting an increasing interest owing to their excellent physical and chemical properties [1–3] and their potential applications on photo-electronic transition devices [4–9]. However, considerable efforts have been devoted to the preparation of transition-metal sulfide semiconductors [10–12]. Many methods have been exploited to prepare these metal sulfide semiconductors, such as microwave irradiation [13], pyrolysis [14], vesicles [15], organic–metallic precursor [16,17], hydrothermal synthesis [18], solid reaction [19] and so on.

Room temperature ionic liquids (ILs) have been widely investigated as a new kind of reaction media owing to their unique properties such as low volatility, nonflammability, high chemical and thermal stabilities, designable structures, high ionic conductivity, broad electrochemical windows, etc [19]. Recently efforts have been focused on the fabrication of inorganic materials with novel and improved properties using ILs as templates or cosolvent systems [20]. For instance, Zhou and Antonietti [21] reported a novel preparation of highly ordered monolithic super-microporous lamellar silica with a series of ionic liquids (ILs), 1-alkyl-3-methylimidazolium chloride, as templates via a nanocasting technique. Yang et al. [22] reported a facile synthesis of ZnS spherical nanocrystals modified with 3-Ferrocenyl-2-crotonic acid from Zn(II) coordination polymer in an IL ([BMIM]BF_4) solution system. Taubert [23] introduced a novel protocol for the controlled synthesis of CuCl nanoplatelets with a well-developed crystal habit and a tunable particle size and connectivity from the Cu-containing ionic liquid crystal and 6-O-palmitoyl ascorbic acid. Also we have been working on the applications of ionic liquids in controlling synthesis of inorganic metal oxides and sulfides for some time [24–27]. Hererin, we firstly reported the synthesis of novel hierarchical CdS and PbS dendrites, ZnS, CoS and Cu_2S microspheres with matte surface by a facile hydrothermal method using 1-butyl-3-methlyimidazole thiocyanate ([BMIM][SCN]) as both sulfur source and capping ligand in aqueous solution.

2. Experimental

All chemicals used in our experiment were analytical-grade and without further purification. The 1-butyl-3-methlyimidazole thiocyanate ([BMIM][SCN]) was prepared according to the literature [28].

The preparation of transition-metal sulfide dendrites or microspheres involves the precipitation of M^{2+} (M = Cd, Pb, Zn, Co, Cu) and SCN^- at a consequent hydrothermal treatment at 200 °C for 24 h. A typical procedure of transition-metal sulfide is as follows: 1 mmol corresponding MCl_2 (M = Cd, Co, Cu) or $M(CH_3COO)_2$ (M = Pb, Zn) and 2 mmol [BMIM][SCN] were dissolved in distilled water (10 ml), respectively, to form clear solutions. Then, they were mixed together with vigorous magnetic stirring at room temperature to form a homogeneous solution and transferred into a 50 ml Teflon-lined stainless-steel autoclave, which contained 20 ml of distilled water. The tank was heated to and maintained at 200 °C for 24 h, and allowed to

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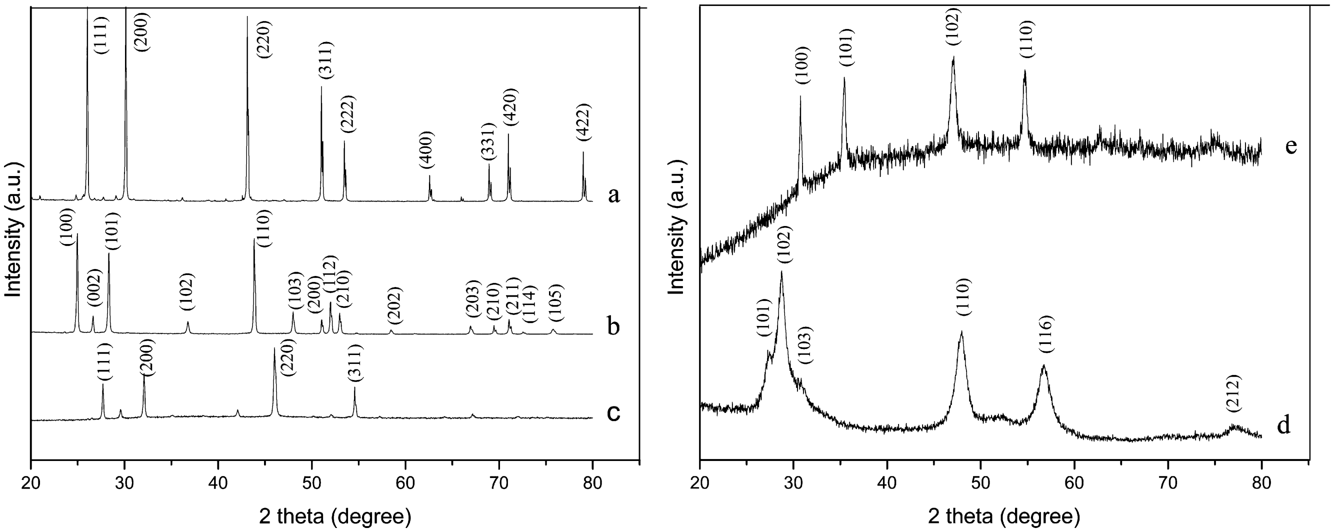

Fig. 1. XRD patterns of: (a) PbS, (b) CdS, (c) Cu_2S, (d) ZnS and (e) CoS.

cool to room temperature naturally. The insoluble products were collected by filtration, washed several times with distilled water and ethanol, and then dried in a vacuum at 60 °C for 10 h. The preparation of Cu_2S hierarchical microspheres use the same procedure described above except for the addition of 5 ml ethanol.

The X-ray powder diffraction (XRD) patterns were recorded by a Holland Philips X'Pert (PW3040/60) using Cu (Kα) radiation (λ = 0.15418 nm) operating at 40 kV and 40 mA with 2θ ranging from 10° to 80°. The scanning electron microscope (SEM) images were taken with Japan Hitachi S-4800 field-emission scanning electron microscope to observe the morphologies and microstructures. The particle composition was determined using energy dispersive X-ray spectroscopy (EDX) unit attached to scanning electron microscope with the samples deposited on conductive tape without gold coating when the accelerating voltage is 15.0 kV.

3. Results and discussion

The powder XRD patterns of the as-prepared products are shown in Fig. 1. Fig. 1a shows all the peaks match well with cubic PbS phase (JCPDS Card No. 05-0592). In Fig. 1b, the pattern can be easily indexed to the hexagonal CdS phase (JCPDS Card No. 75-1545); that of Fig. 1c, to the cubic phase of Cu_2S (JCPDS Card No. 84-1770); that of Fig. 1d, to the wurtzite ZnS phase (JCPDS Card No. 89-2739); that of Fig. 1e, to the hexagonal phase of CoS (JCPDS Card No. 75-0605). No other impure diffraction peaks were detected, indicating that the as-synthesized products are high pure. The crystalline size is calculated from the full-width at half-maximum (FWHM) of the most intense diffraction peaks using Debye–Scherrer formula [35] and listed in Table 1. It is possible to realize that the microspheres of ZnS, CoS and Cu_2S originate from an arrangements of nanoparticles. As the non-spherical morphology, the particles size of CdS and PbS are not presented here.

The size and morphology of the sulfides were examined by SEM. Figs. 2 and 3 show the typical SEM images of MS (M = Cd, Pb, Zn, Co) products. Fig. 2 shows that the CdS (Fig. 2a) and PbS (Fig. 2c) process a novel dendritic structure. The orientation of the dendrites is very unique. A higher magnification SEM image clearly reveals well-defined dendritic fractal structure with a pronounced trunk and highly ordered branches, as demonstrated in Fig. 2b. As shown in Fig. 2d, it is obvious that some regular shaped nanostructure are on the pronounced trunk of the PbS fractal dendrite as well as highly ordered branches. It can be seen from Fig. 3(a and c) that the as-prepared products (ZnS and CoS) show spherical morphologies with diameters of approximate 1–2 μm. Higher magnification SEM images are shown in Fig. 3(b and d), which offer a clearer view of the exterior morphology. Fig. 3b reveals that some small nanocrystals are on the sphere surface and composed of the microsphere compound. Close observation (Fig. 3d) shows the surface of the CoS spherical structure is not smooth and constructed by interleaving rice-like rods.

It is interesting to find that the as-prepared Cu_2S are flower-like microspheres with diameters ranging from 2 to 5 μm (Fig. 4a and b). A magnified SEM image in Fig. 4c indicates that the walls of the elegant spherical structure is build up by tens to hundreds of nanosheets with average thicknesses of 40 nm. These nanosheets interconnect with each other to form an entangled network-like architecture with irregular shaped pore in the Cu_2S microspheres.

The chemical composition and stoichiometry of the transition-metal sulfides were revealed by the EDX spectrum (Fig. 5). In Fig. 5a, it shows only the peaks for Cd and S. Elemental analysis reveals that the molar ratio of Cd/S is 53:47, in good agreement with the stoichiometric CdS within experimental error. Similar observations are noticed from the EDX spectrum recorded for PbS sample, which is showed in Fig. 5b. Elemental analysis reveals the atomic percentages of Pb and S to be 52 and 48, respectively, which is consistent with the stoichiometric PbS within the experimental error. The purity and composition of the rest products were displayed in Fig. 5(c–e). The curve reveals the presence of M (Metal) and S peaks and the average atomic percentage ratios of M:S are 52:48, 52:48 and 67:33 for the particles of CoS, ZnS, Cu_2S, respectively. Two relatively weak carbon and oxygen peaks in the spectrum probably originates from unavoidable surface-adsorption of oxygen or carbon dioxide on to the spheres from exposure to air during sample processing.

Table 1
Valus of FWHM and particles size of various transition-metal sulfides.

Sample	Morphology	Bragg angle θ (°)	Peak ($h\,l\,k$)	FWHM (°)	Particle size (nm)
CdS	Dendrites	24.85	(1 0 0)	0.15	–
PbS	Dendrites	26.15	(1 1 1)	0.14	–
Cu_2S	Microspheres	27.67	(1 1 1)	0.21	38.5
CoS	Microspheres	30.76	(1 0 0)	0.29	28.1
ZnS	Microspheres	28.71	(1 0 2)	1.74	4.7

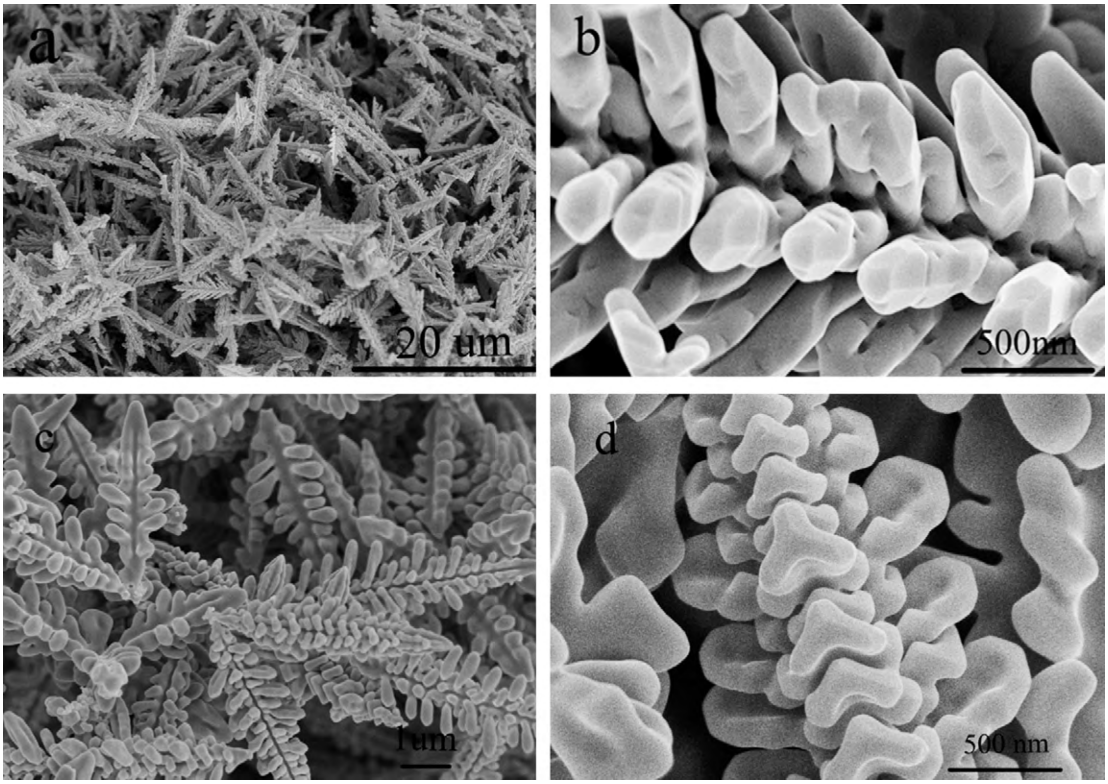

Fig. 2. The SEM images of: (a and b) CdS dendrites; (c and d) PbS dendrites.

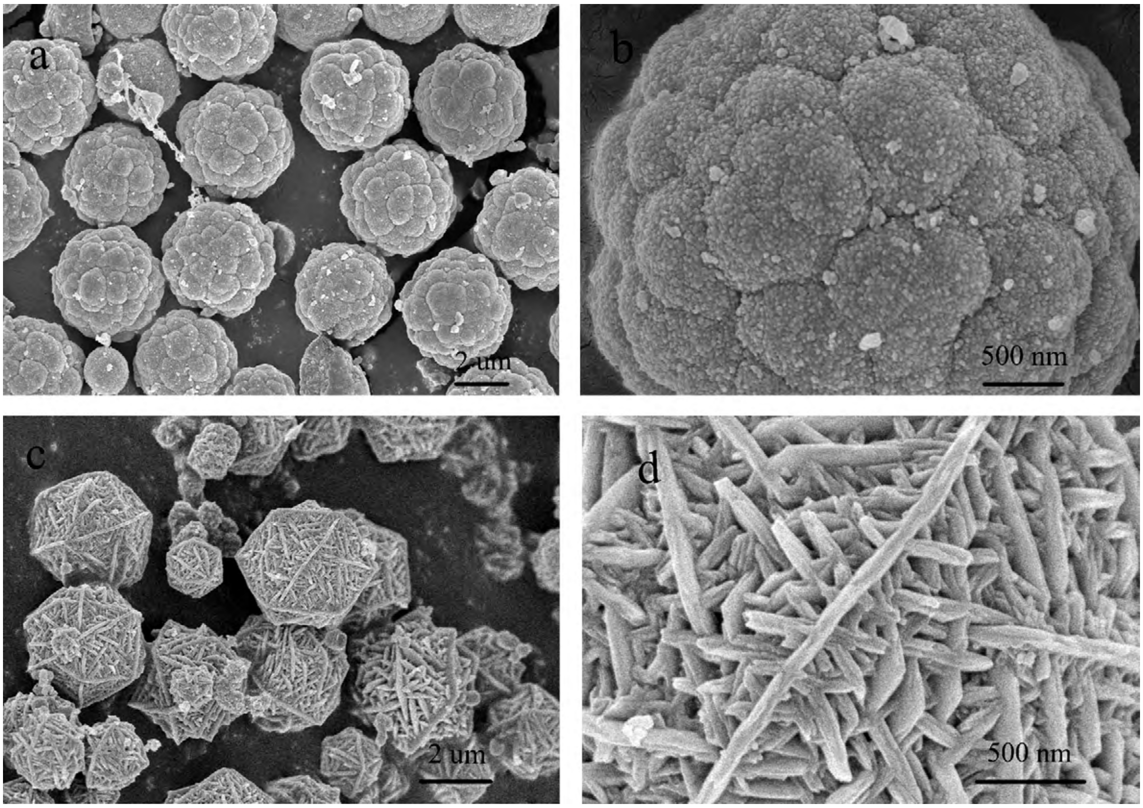

Fig. 3. The SEM images of: (a and b) ZnS microspheres; (c and d) CoS microshperes.

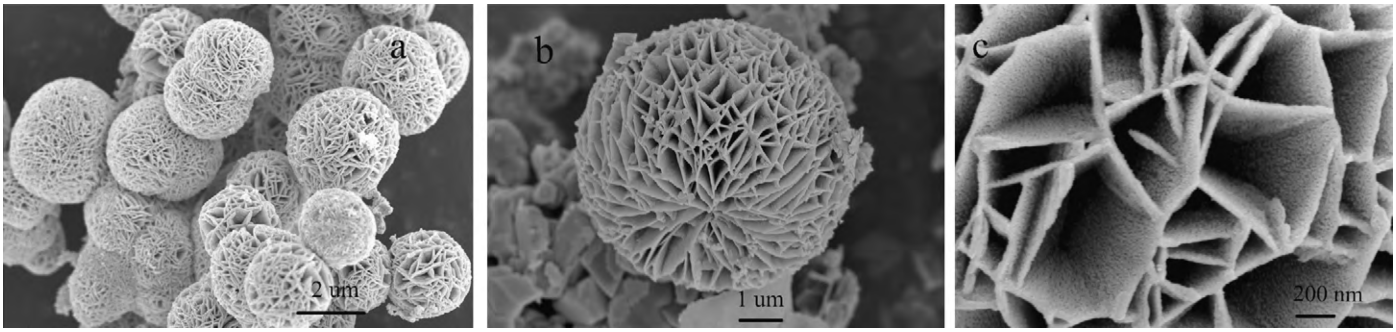

Fig. 4. (a and b) The typical SEM images of Cu_2S porous microspheres. (c) The high magnification SEM image of Cu_2S porous microspheres.

Kusumoto co-workers [29] have reported the mineralizer-assisted shape-controlled synthesis of CdS microcrystals. The $Cd(NO_3)_2$ was used as start material as well as potassium thiocyanate, then the processor $Cd(SCN)_2$ were taken thermal decomposition under open atmospheric conditions at 300 and 400 °C to form hexagonal microtowers and octahedral geometries. Xue and co-workers [30] have fabricated dendritic metal sulfides (PbS and CdS) with template-free and surfactant-free hydrothermal method. The potassium thiocyanate was used as initial material to release sulfur ions when the temperature increased to 240 °C. In our experiment, functional ionic liquid ([BMIM][SCN]) was for the first time introduced as sulfur source to synthesize transition-metal sulfides. As a good capping ligand, SCN anion has been extensively studied in the region of coordination chemistry and supramolecular chemistry [31,32]. When metal salts were added into aqueous solution containing [BMIM][SCN], the homogeneous solution gradually turned into white flocculent precipitate for Cd^{2+} and Pb^{2+}, colored solutions for Zn^{2+} and Co^{2+}, and black sticky matter for Cu^{2+} [33] at room temperature. It is suggested that metal cations may coordinate with the anions from functional ILS to form metal-ionic liquid complexes according to the phenomenon distinguished from directly mixture of metal cation and thiocyanate anion solutions. Here the white flocculent precipitation for cadmium might be a novel N-alkylimidazolium cadmium thiocyanate complexes

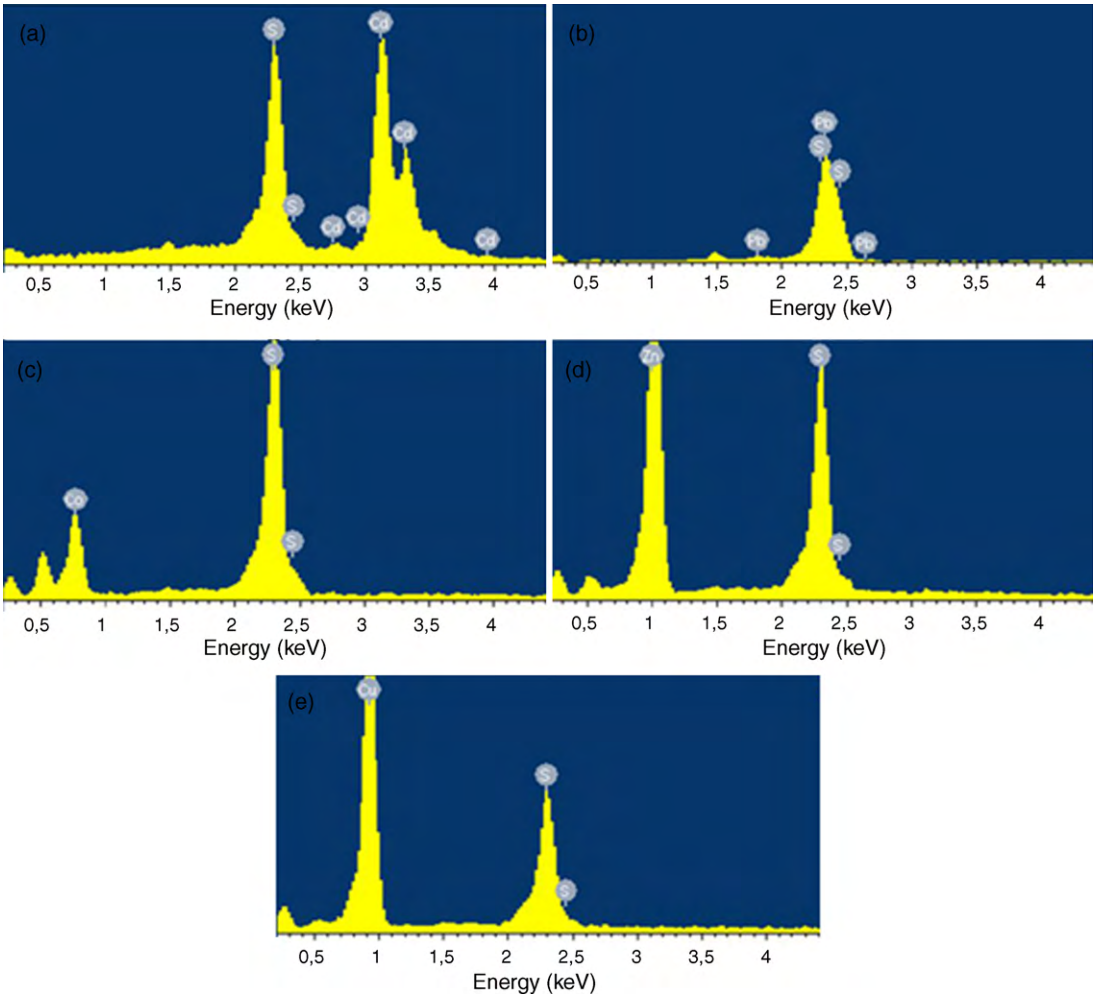

Fig. 5. Representative EDX spectrums of the samples: (a) CdS, (b) PbS, (c) CoS, (d) ZnS and (e) Cu_2S.

[BMIM][Cd(SCN)$_3$] [34]. Hence we deduced that the remaining metal ions combined with ionic liquid and formed novel complexes. At a certain temperature and pressure, the preformed complexes decomposed to release dissociative metal ions, and at the same time the S–C bond was broken to produce S^{2-} anions slowly and reacts with M^{2+} to generate MS nuclei. With the nucleation and its following-up growth, various MS trend to favor the growth direction. However, the functional groups within the ionic liquid can selectively adhere to the particular facet of the newly formed nanoparticles and provide a possible steric barrier to enhance the anisotropic characters in the growth process, which resulting in the variety of morphologies of transition-metal sulfides. More in-depth studies are still needed to explore the exact formation mechanism.

4. Conclusions

In summary, based on facile hydrothermal method, dendritic nanostructures of PbS and CdS, as well as ZnS, CoS and Cu$_2$S microspheres, have been prepared via a simple convenient approach using 1-butyl-3-methlyimidazole thiocyanate ([BMIM][SCN]) as both sulfur source and capping ligand. The XRD measurement has determined the crystalline phase of the products without other impurities. A possible formation of various morphologies of transition-metal sulfides was simply proposed. The prepared MS dendrites and porous microspheres may have potential applications related to their special shape and size.

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