Microwave-assisted synthesis of NiS$_2$ nanostructures for supercapacitors and cocatalytic enhancing photocatalytic H$_2$ production

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Uniform NiS$_2$ nanocubes are successfully synthesized with a microwave-assisted method. Interestingly, NiS$_2$ nanocubes, nanospheres and nanoparticles are obtained by controlling microwave reaction time. NiS$_2$ nanomaterials are primarily applied to supercapacitors and cocatalytic enhancing photocatalytic H$_2$ production. Different morphologies of NiS$_2$ nanostructures show different electrochemical and cocatalytic enhancing H$_2$ production activities. Benefited novel nanostructures, NiS$_2$ nanocube electrodes show a large specific capacitance (695 F g$^{-1}$ at 1.25 A g$^{-1}$) and excellent cycling performance (the retention 93.4% of initial specific capacitance after 3000 cycles). More importantly, NiS$_2$ nanospheres show highly cocatalytic enhancing photocatalytic for H$_2$ evolution, in which the photocatalytic H$_2$ production is up to 3400 μmol during 12 hours under irradiation of visible light (λ≥420 nm) with an average H$_2$ production rate of 283 μmol h$^{-1}$.

Electrochemical capacitors are known by different names, such as ultracapacitors or supercapacitors, and have attracted considerable attention over the past decades owing to their higher power density and longer cycle life than secondary batteries and conventional electrostatic and electrolytic capacitors. In particular, supercapacitors based on ruthenium oxides have shown ultrahigh pseudocapacitance and excellent reversibility. However, the high cost of ruthenium makes this material unsuitable for commercial applications. Hence, searching for alternative and inexpensive electrode materials with good capacitive properties becomes urgent$^{1-7}$.

Hydrogen production from photo-induced water splitting has received increasing attention because of its potential in simultaneously solving energy and environmental problems. In order to utilize the abundant solar energy, the development of visible-light active photocatalysts is of great importance. To date, many semiconductor photocatalyst systems have been reported to be active under visible light. Besides metal-oxide semiconductors, efficient photocatalyst systems for hydrogen evolution have been obtained with some sulfide photocatalysts$^{8-12}$.

Metal chalcogenide nanomaterials have attracted great attention due to their excellent properties and promising applications in electronic, optical and optoelectronic devices$^{13,14}$. Among the family of metal sulfides, nickel sulfides have attracted much interest not only because the nickel sulfide system contains a number of phases, but also because of their multiple applications as a possible transformation toughened. So, different phases and morphologies of nickel sulfides sometimes coexist. Thus to obtain a uniform morphology with a pure phase of nickel sulfides is still a challenge and has attracted a lot of attention$^{15-17}$.

NiS$_2$, a pyrite structure, has interesting electrical, optical and magnetic properties$^{18,19}$. However, it has been difficult to control the synthesis of uniform NiS$_2$ micro/nanoparticles due to their natural chemical properties. There are few literature sources on the morphology control synthesis of NiS$_2$ nanocrystallites$^{20,21}$. Microwave irradiation has been demonstrated for the synthesis of a variety of nanomaterials including metals, metal oxides, chalcogenides, bimetallic alloys and semiconductors with controlled size and shape but without the need for high temperature or high pressure$^{22-30}$.

Herein, we have synthesized uniform NiS$_2$ nanocubes with a microwave-assisted method, and its possible growth mechanism has been further explored. More importantly, NiS$_2$ nanocubes, nanospheres and
nanoparticles were successfully applied to electrode materials of supercapacitors and cocatalytic enhancing photocatalytic H\(_2\) production. As a result of their novel nanostructures, NiS\(_2\) nanocube electrodes show a large specific capacitance (695 F g\(^{-1}\)) and excellent cycling performance (maintaining 93.4% of initial specific capacitance after 3000 cycles). What's more, the performance of H\(_2\) production indicates the effectively cocatalytic enhancing photocatalytic activity of NiS\(_2\) nanospheres, in which the photocatalytic H\(_2\) production is up to 3400 \(\text{mol}\) during 12 hours under irradiation of visible light (\(\lambda > 420\) nm) with an average H\(_2\) production rate of 283 \(\text{mol m}\text{s}^{-1}\).

**Results**

A typical XRD pattern of the as-prepared product is displayed in Fig. 1a, showing that the sample has good crystallinity. All diffraction peaks can be clearly indexed to cubic pyrite NiS\(_2\), which is consistent with the reported data for NiS\(_2\) (JCPDS Card File No. 03-0734). A typical low-magnification scanning electron microscopy (SEM) image in Fig. 1b shows that the sample is composed of homogenous nanocubes. It has a diameter of \(\sim 200\) nm shown in Fig. 1c. The uniform nanocube morphology is further revealed by the transmission electron microscopy (TEM) image shown in Fig. 1d. More interestingly, these results demonstrate the highly crystalline nature of the product. The measured distances of the neighboring lattice fringes in Fig. 1e are 0.23 nm, corresponding well to the (211) lattice spacing.

NiS\(_2\) nanospheres were obtained after 2 hours microwave radiation (Fig. 2). The nanosphere is not uniform as the nanocube, whose size is in range from 50 to 150 nm from Fig. 2a, b and its size-distribution diagram in inset of Fig. 2b. The surface of NiS\(_2\) nanospheres is not smooth (Fig. 2c). These porous, rough surfaces do not only offer high surface areas, but provide small molecular and electrolyte accesses. The crystallization of a individual NiS\(_2\) nanosphere is polycrystalline in Fig. 2d, which is further proved by its corresponding SAED patterns.

To understand possible growth process during the shape evolution of the product, morphologies of the time-dependent products obtained at 150°C were carefully observed, as shown in Supplementary Information Fig. S1. From Fig. S1a, nanoparticles (size \(< 50\) nm) were obtained under microwave radiation for 30 minutes. After 2 hours microwave radiation, many nanospheres (50 < size < 150 nm) were observed in Fig. S1b. And after 3 hours microwave radiation, NiS\(_2\) nanocubes were successfully synthesized, which might have formed based on the NiS\(_2\) nanospheres (Fig. S1c). There are some formless nanocrystals dispersed among these NiS\(_2\) nanocubes. After microwave radiation for 4 hours, uniform NiS\(_2\) nanocubes were successfully obtained. TEM image of NiS\(_2\) nanoparticles was shown in Fig. S2. Clearly, the size of NiS\(_2\) nanospheres is \(< 50\) nm, which is in accordance with the result shown in Fig. S1. The shape changes of the NiS\(_2\) nanostructures and their morphological evolution is shown in Fig. 3, it is seen that shape changes of the NiS\(_2\) nanostructures have evaluated from formless nanoparticles to nanocubes.

To understand crystallographic evolutions, XRD patterns of samples obtained under different radiation times were measured seen in Fig. S3. Clearly, the NiS\(_2\) phase was successfully obtained after 30 min radiation, but all the peaks were wide and weak which means the crystallinity is not good. The crystallinity has been enhanced by the prolonged radiation time. When we prolonged the radiation time to 3 hours, all the peaks are strong and narrow, which is consistent with NiS\(_2\) (JCPDS Card File No. 03-0734). One notable observation from these XRD patterns is that with the formation of nanocubes from nanoparticles, the intensity of the (200) peak increases drastically compared to those of the other peaks. This exceptionally strong (200) peak for samples (3 hours, and 4 hours radiation time) suggests that the [100] facets of these NiS\(_2\) nanocubes are preferentially oriented parallel to the underlying substrate surface when a monolayer of nanocubes is deposited. Of course, the greater areas of the [100] facets relative to those of the other facets (that is, the [110] and
{111} facets) for the NiS\textsubscript{2} nanocubes may also contribute significantly to this interesting XRD effect.

To gain further insight into the specific surface area of NiS\textsubscript{2} nanostructures, Brunauer-Emmett-Teller (BET) measurements were performed. And the N\textsubscript{2} adsorption–desorption isotherms of NiS\textsubscript{2} nanomaterials were shown in Fig. S4. BET surface areas of NiS\textsubscript{2} nanocubes, nanospheres and nanoparticles are 12.0, 38.3 and 25.1 m\textsuperscript{2} g\textsuperscript{-1} respectively. Different BET surface areas of NiS\textsubscript{2} nanomaterials make different contacts of the electrolyte or water with many surface interfaces of these nanostructures.

Discussion

Cyclic voltammogram (CV) studies were employed to characterize the capacitive performances of the NiS\textsubscript{2} nanocubes. Fig. 4a shows the CVs of the NiS\textsubscript{2} nanocubes electrodes (a mass loading of 5 mg) in 3.0 M KOH electrolyte at different scan rates in the range 5–50 mV s\textsuperscript{-1}.

As seen in Fig. 4a, the CVs are almost symmetric, indicating good reversibility of the oxidation and reduction processes. The CVs show a broad redox peak due to faradic reactions of NiS\textsubscript{2} nanocubes, and it indicates that the Faradaic pseudocapacitive property of NiS\textsubscript{2} is based on the surface redox mechanism of Ni\textsuperscript{2+} to Ni\textsuperscript{3+} at the surface. Fig. 5 shows a simple possible route for diffusion of ions and electrons during the electrochemical process. The single nanocrystal, NiS\textsubscript{2} nanocube, shows different diffusion rates of electrons along different crystal planes. And due to the fewer inner crystal interfaces of NiS\textsubscript{2} nanocubes, the diffusion rate of electrons in NiS\textsubscript{2} nanocubes is much quicker than that of polycrystal NiS\textsubscript{2} nanospheres. Moreover, a great number of inner crystal interfaces of NiS\textsubscript{2} nanospheres may cause large inner resistance and contact resistance, which stops electrons from diffusing quickly.

Chronopotentiometry (CP) curves at different current densities are shown in Fig. 4b and Fig. S5. The symmetrical characteristic of
charging/discharging curves is good, which means that the NiS₂ nanocube electrodes with excellent electrochemical capability and redox process are reversible. The relationships between the specific capacitances calculated by CP curves and current densities are given in Fig. 4c. Based on the CP curves, NiS₂ nanocube electrodes have the large specific capacitance and reach up to 695 F g⁻¹ at a current density of 1.25 A g⁻¹ and remain 158 F g⁻¹ even 12.5 A g⁻¹, while that of NiS₂ nanoparticle electrodes is 34 F g⁻¹ at 12.5 A g⁻¹. The specific capacitance of NiS₂ nanocube is significantly better than some nickel based nanomaterials, such as NiO nanowires (0.5 A g⁻¹, 180 F g⁻¹)³ⁱ, NiO nanotubes (0.28 A g⁻¹, 47 F g⁻¹)³², Mesoporous NiO (165 F g⁻¹), NiO with ordered mesoporous structure (120 F g⁻¹)³³, but lower than NiO flowers (1 A g⁻¹, 710 F g⁻¹)³⁴ and other supercapacitor materials³⁵,³⁶.

Specific energy and specific power are the two key factors for evaluating the power applications of electrochemical supercapacitors. A good electrochemical supercapacitor is expected to provide both high energy density and specific capacitance. Fig. 4d shows the
Ragone plot for NiS$_2$ nanostructured electrodes in 3.0 M KOH aqueous solution. For NiS$_2$ nanocubes electrodes, it also has well specific energy and specific power. The specific energy of NiS$_2$ nanocube electrodes decreases from 15.7 to 3.6 Wh kg$^{-1}$, while the specific power increases from 254 to 2537 W kg$^{-1}$ as the galvanostatic charge/discharge current density increases from 1.25 to 12.5 A g$^{-1}$. As a comparison, NiS$_2$ nanoparticle electrodes have very small specific energy (changing from 4.3 to 0.8 Wh kg$^{-1}$).

It is important for electrode materials to have good specific capacitance retention. Supercapacitors should work steadily and safely, which requires the specific capacitance of electrode materials to change as little as possible. Relationships of the specific capacitance against the cycling number of NiS$_2$ nanostructured materials are shown in Fig. 4e. It shows its excellent specific capacitance retention under 1.25 A g$^{-1}$. After 200 continuous charge–discharge cycles, NiS$_2$ nanocubes electrodes almost retain the same specific capacitance as its initial value. More importantly, NiS$_2$ nanocubes electrodes still retain more than 93.4% of its specific capacitance after 3000 continuous charge–discharge cycles, while the specific capacitance of NiS$_2$ nanoparticles has decreased nearly to zero.

To identify the exact electrical conductivity of electrodes, we measured EIS spectrum of NiS$_2$ nanostructure electrodes at room temperature in the frequency range from 0.01 to $10^5$ Hz under open-circuit conditions, which is shown in Fig. 6a. An equivalent circuit used to fit the impedance curve is given in Fig. 6b, which is similar to the circuit employed for the working electrode of supercapacitors. The EIS data can be fitted by a bulk solution resistance $R_s$, a charge-transfer resistance $R_{ct}$, and a CPE to account for the double-layer capacitance. The charge-transfer resistance $R_{ct}$ of all the samples was calculated by ZSimpWin software. And from the calculated results, we found that NiS$_2$ nanocube electrodes have a lowest value 2.7 $\Omega$. And the detailed $R_s$, values of nanosphere and nanoparticle electrodes are 5.9 $\Omega$ and 17.2 $\Omega$ respectively. This clearly demonstrates the reduced charge-transfer resistance of the NiS$_2$ nanocube electrodes. In addition, the charge-transfer resistance $R_{ct}$, also called Faraday resistance, is a limiting factor for the specific power of the supercapacitor. It is the low Faraday resistance that results in the high specific power of NiS$_2$ nanocube electrodes. This cubic structure surface-interface character might also decrease the polarization of the electrode, and thus might increase the capacity.

The as-prepared NiS$_2$ nanomaterials (nanocubes, nanospheres and nanoparticles) are thus evaluated as a cocatalytic enhancing photocatalyst for H$_2$ production. Fig. 7 illustrates a possible mechanism of H$_2$ production on the as-prepared NiS$_2$ nanomaterials. Photons are captured by the ErY for activation of the electrons from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO). The activated electron is subsequently adopted by the NiS$_2$ catalyst with suitable Ni 3d and S 3p hybrid orbital. Nickel with a reduced valence state facilitates the proton reduction for the formation of H$_2$ gas. At the same time, the oxidized ErY is reduced to its ground state by TEOA as the electron donor. Fig. 8 shows the time course of H$_2$ evolution for different NiS$_2$ nanomaterials. In our system, in the first 8 hours, 3210 $\mu$mol of H$_2$ gas is generated under the irradiation of visible light ($\lambda > 420$ nm) for the NiS$_2$ nanospheres, while that of nanocubes and nanoparticles is 1980 and 2220 $\mu$mol. More importantly, after 12 hours, the total H$_2$ gas of NiS$_2$ nanospheres is up to 3400 $\mu$mol with an average H$_2$ production rate of 283 $\mu$mol h$^{-1}$. A high H$_2$ production rate of 5.66 mmol h$^{-1}$ g$^{-1}$ and such H$_2$ production performance is superior to those reported previously.$^{[12,39]}$. What is more, an apparent quantum efficiency of 13.6% at 420 nm is measured for NiS$_2$ nanospheres, while that of NiS$_2$ nanocubes and nanoparticles is 10.8% and 9.6%. On the contrary, only 1980 $\mu$mol (NiS$_2$ nanocubes) and 2220 $\mu$mol (NiS$_2$ nanoparticles) of H$_2$ gas is collected in 12 hours with an average H$_2$ production rate of 3.30 (NiS$_2$ nanocubes) and 3.70 mmol h$^{-1}$ g$^{-1}$ (NiS$_2$ nanoparticles). This clearly indicates the significantly improved photocatalytic activity of the NiS$_2$ nanospheres in photocatalytic enhancing hydrogen production. The cocatalytic enhancing photocatalytic performance may be related to the active surface of the defect of NiS$_2$ crystals. Some perfect NiS$_2$ crystals can improve the transformation of electrons, and the protons are reduced to generate H$_2$ on some defect NiS$_2$ crystals which enhances photocatalytic activities.

However, the activity decreases as the irradiation is prolonged, which may be caused by the degradation of the ErY and triethanolamine (TEOA) for this activity loss.$^{[30,31]}$. More importantly, the variation of the reaction mixture solution (ErY in aqueous
The inorganic solid catalyst hybrid H₂ production system lies in the recycle ability of the solid catalyst. After the test for 12 h, the NiS₂ nanostructures was collected via a simple centrifugation, and re-dispersed in the same fresh TEOA solution with ErY dye for the second round of testing. As shown in Fig. S7, 2500 μmol of H₂ gas for NiS₂ nanospheres was collected in 12 h, which is over 73.5% of the amount obtained in their first round. That the activity deceased is possibly due to the damage of NiS₂ nanospheres, and the damage of their active surface under long time irradiation. Therefore, SEM images of the 2th circle run as indicated in Figure S7 are shown in Figure S8. NiS₂ nanostructures are still nanocubes, nanospheres and nanoparticles. However, NiS₂ nanocubes are not uniform as the before, the surface of NiS₂ nanospheres becomes smooth and NiS₂ nanoparticles form some aggregations after prolonged light irradiation. The dropping of activity may be also caused due to the change of NiS₂ morphologies.

This excellent H₂ production performance of the NiS₂ nanospheres may be caused by many factors. NiS₂ nanospheres have rough surfaces with high surface area, which largely facilitates the efficient transfer of photogenerated electrons to improve the photocatalytic efficiency. Ion diffusion and electron transport both play an important role in the performance of supercapacitors and enhancing-cocatalytic photocatalysis. Usually, photocatalytic reaction generally occurs on the surface of nanomaterials. Under such a condition, the electron does not need to diffuse into the inner of these materials. These materials with rough surfaces have large surface area structures, and always show better in cocatalytic enhancing photocatalysis due to effective surface photocatalytic reaction. This might be the reason for the highest cocatalytic enhancing photocatalytic activities of NiS₂ nanospheres with highest surface area, while the cocatalytic enhancing photocatalytic activities of nanoparticles are better than those of nanocubes.

But the resistance, arising from the inherent low electronic conductivity of active materials and the boundary interfaces among active material particles, would much limit the high power performance of supercapacitors. Moreover, the surface reaction of electrode materials largely limits its electrochemical activities. The electronic transport in a nanosized material electrode is shown schematically in Fig. 9, where some carbon additive is employed to improve the conductivity of total electrode. In some cases, small sized nanocrystal materials cannot effectively shorten the path length for electronic transport. Nanoparticles with a very high specific surface area and high surface energy (such as the as-prepared NiS₂ nanoparticles, NiS₂ nanospheres) are difficult to disperse and mix with a carbon additive. Accordingly, the electronic transport length is still very long because only a small number of nanoparticles can directly contact the carbon additive and obtain electrons (such as NiS₂ nanoparticle, nanosphere). Furthermore, the large interface resistance of NiS₂ nanoparticles, and nanospheres still exists, especially when the unit size of the particle is within a typical nano-scale, which is the reason that NiS₂ nanoparticle electrodes and NiS₂ nanosphere electrodes have large $R_{ct}$ and low specific capacitance.

However, different supercapacabilities of NiS₂ nanostructured electrodes should be attributed to many different reasons. The most important reason must be associated with easier paths for ions, electrons and electrolytes. The as-prepared single crystal NiS₂ nanocubic structure may have novel surface-interface characters and good electrical conductivity for electrochemical charge-discharge process. These novel chemical-physical characters bring the novel surface-interface and diffusion paths, leading to high electrochemical activities.

In summary, uniform NiS₂ nanocubes have been successfully synthesized through a microwave-assisted method. Different nanostructured NiS₂ samples show different surface-interface conditions, which plays key roles to ion intercalation/extraction and electrolyte accesses. The measurement of electrochemical and catalytic enhancing photocatalytic activities of nanostructured NiS₂ materials is important work, which illustrates NiS₂ nanomaterials can be applied as an electroactive material for supercapacitors and the high performance of cocatalytic enhancing photocatalytic H₂ production. Interestingly, the electron transport of NiS₂ nanostructures may determine the electrochemical capacitor performance. It means...
Cocatalytic enhancing photocatalytic H₂ production. The method is the same as that in reference 12. Visible light-driven photocatalytic water splitting reaction was conducted in a top window Pyrex cell connected to a closed gas circulation and evacuation system (the intensity of the light employed was 125.8 mW cm⁻²). In a typical round, 50 mg of catalyst and 200 mg of Erythrosin Yellowish (ErY) were dispersed in 100 mL of triethanolamine aqueous solution (15% v/v of TEOA, pH 8.5) under vigorous stir. A 300 W Xenon lamp equipped with a cut-off filter (λ > 420 nm) was used to provide incident visible light. The temperature of the photoreaction cell was kept between 19 and 20°C by circulating the cooling water. Before the reaction, the system was evacuated and refilled with argon gas for several times to remove the air and finally filled with argon gas to approximately 30 torr. The produced hydrogen gas is analyzed by an online gas chromatograph (Agilent 6890N, TCD detector, argon as carrier gas, 5 Å molecular sieve column). The apparent quantum efficiency (QE) is measured under the same reaction conditions and the lamp is equipped with a band pass filter (Newport, center wavelength 420 nm, bandwidth 10 nm). The reaction solutions are irradiated under 420–480 nm for 4 h before switching to band pass filters during the quantum efficiency measurement. The amount of hydrogen produced in the subsequent 4 h was used to calculate the quantum efficiency using the equation below. The number of photons from the radiation source was measured using a silicon photodiode. QE = [(Σ the number of evolved H₂ molecules)/the number of incident photons] × 100%. 

**Methods**

All the samples were prepared in a microwave system (2.45 GHz, 150 W, Discover SP, CEM), which is equipped with in situ magnetic stirring. The exposure time and temperature were programmed. The automatic temperature-control system allowed continuous monitor and control (1 °C) of the internal temperature of reaction systems. The preset profile (desired time and temperature) was followed automatically by continuously adjusting the applied microwave power.

**Characterizations.** The morphology of as-prepared samples was observed by a JEOL JSM-6701F field-emission scanning electron microscope (FE-SEM) at an acceleration voltage of 5.0 kV. The phase analyses of the samples were performed by X-ray diffraction (XRD) on a Rigaku-Ultima III with Cu Kα radiation (λ = 1.5418 Å). Nitrogen adsorption-desorption measurements were performed on a Gemini VII 2390 Analyzer at 77 K with the volumetric method. The specific surface area was obtained from the adsorption isotherms using the absolute ethanol, and dried in the air.

**Electrochemical measurement.** Electrochemical study on NiS₂ nanostructured electrodes was carried out on a CHI 660D electrochemical working station (Shanghai Chenhua Instrument, Inc.). All electrochemical performances were carried out in a conventional three-electrode system equipped with platinum electrode and a saturated calomel electrode (SCE) as counter and reference electrodes, respectively. Before taking the electrochemical measurement, we have purged out O₂ from the solution by the inert gas Ar. The working electrode was made by mixing active materials (NiS₂ nanoparticles), acetylene black, and PTFE (polytetrafluoroethylene) with a weight ratio of 80:15:5, coated on a piece of foamed nickel foam of about 1 cm², and pressed to be a thin foil at the pressure of 5.0 MPa. The electrolyte was a 3.0 M KOH solution. Cyclic voltammetry and galvanostatic charge–discharge methods were used to investigate capacitice properties of NiS₂ nanostructured electrodes. And electrochemical impedance spectroscopy measurements of all the samples were conducted at open circuit voltage in the frequency range of 100 kHz to 0.01 Hz with AC voltage amplitude of 5 mV by using PARSTAT2273.
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Author contributions
H.P., J.S.Z., J.C., S.J.L. and C.Z.W conceived and designed the experiments. H.P., X.X.L., G.C.L. and Y.H.M. analyzed the measurements. H.P., J.S.Z., J.C., S.J.L. and C.Z.W. wrote the manuscript in collaboration with all the authors.

Additional information
Expect another supplementary information accompanies this paper at http://www.nature.com/scientificreports

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