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Facet-Dependent NiS₂ polyhedrons on counter electrodes for dyesensitized solar cells

Jinlong Zheng, Wei Zhou *, Yiran Ma, Wei Cao, Chengbo Wang, and Lin Guo *

School of Chemistry and Environment, Beihang University, Beijing 100191, China

Preparation of NiS₂ Polyhedrons

The NiS₂ octahedrons and cubes were prepared by using a hydrothermal process. In a typical synthesis of the NiS₂ octahedrons, 0.1 mmol of NiCl₂· $6H_2O$, 0.25 mmol of Na₂S₂O₃· $6H_2O$ and 0.055 g of polyvinylpyrrolidone (PVP; average MW 58 000, Alfa Aesar) were dispersed in 38 mL of ultrapure water, then the solution was kept at room temperature for 30 min under magnetic stirring. Afterwards, the solution was transferred into 50-mL Teflon-lined autoclave. The autoclave was sealed and heated at 150 °C for 12 hrs in an oven, and then cooled down to room temperature. The product was collected by centrifugation and washed several times with deionized water and ethanol.

The synthesis of NiS₂ cubes was similar to that of NiS₂ octahedrons. 1.2 mmol of Ni(NO₃)₂· $6H_2O$, 0.4 g of CN₂H₄S, 0.3 g of PVP and 0.05 mmol of NaOH were dispersed in 20 mL of ultrapure water, then the solution was kept at room temperature for 30 min under magnetic stirring. The subsequent processes of preparation were the same as the preparation for NiS₂ octahedrons.

Characterizations

The morphologies of the samples were studied using a field-emission gun scanning electron microscope (Hitachi 7500, 5 KV). Transmission electron microscopy (TEM) investigations were carried out using a JEOL JEM-2100F microscope. The X-ray diffraction (XRD) spectra of the samples were recorded by a Rigaku Dmax 2200 X-ray diffraction with Cu-K_a radiation ($\lambda = 1.5416$ Å). Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were measured on the CHI660D electrochemical workstation (Shanghai Chenhua Co. Ltd., China). The electrical conductivity measurements of NiS₂ were realized by using a Four-probe resistivity tester (Guangzhou Kunde Technology Co. Ltd., China). CV was performed using a three-electrode system

in an ACN-based solution, containing 10.0 mM NaI, 1.0 mM I₂, and 0.1M LiClO₄. In the experiments, a Pt foil and an Ag⁺/Ag electrode were used as the counter and reference electrodes, while platinum, NiS₂ octahedron and NiS₂ cube were separately used as the working electrode. The photocurrent density (*J-V*) curves were measured under a solar-simulated light source (AM 1.5 G filtered, 100 mW cm⁻², 69911, Oriel) with a CHI-660D electrochemical workstation.

Cell Fabrication

Pt CE was prepared by dropping 50 μ L of H₂PtCl₆ in isopropanol (5 mM) on a 1.5 × 2 cm² FTO glass (F: SnO₂, 14 Ω square⁻¹, Nippon Sheet Glass Group, Japan) followed by heat treatment at 400 °C for 30 min. The loading amount of the Pt on the substrate was 16 μ g cm⁻². 1.5 mg of NiS₂ polyhedrons were dispersed in 10 mL of ethyl alcohol by sonication for 1 h. 100 μ L of the solution was dropped on the FTO-coated glass with an exposed area of 0.5 × 0.5 cm². The loading amount of the NiS₂ on the substrate was 60 μ g cm⁻². Then the films were dried at room temperature.

TiO₂ films with an exposed area of 0.5×0.5 cm² and a thickness of 15 µm were coated on FTO glass by a screen-printing technique. TiO₂ films were soaked overnight in an ethanol solution containing 3 mM of N719 (bis-tetrabutylammonium *cis*-bis (isothiocyanato) bis (2,2'-bipyridyl-4,4'-dicarb-oxylato) ruthenium(II), Suzhou Chemsolarism, China). The redox electrolyte (0.03 M I₂, 0.6 M 1,2-dimethyl-3-*n*-propylimidazolium iodide, 0.1 M guanidinium thiocyanate and 0.5 M 4-*tert*-butylpyridine using anhydrous acetonitrile as a solvent) was injected into the interspace between the TiO₂ photoanode and Pt CE. Other DSSCs were assembled using NiS₂ octahedron and cube CEs instead of Pt CE.

Surface Energy Calculations

All the calculations were carried out based on the DFT+U approach,¹ to model the ion-electron interaction as implemented in the Vienna Ab-initio Simulation Package (VASP) code.² For the calculations, we used the generalized-gradient approximation of Perdew-Burke-Ernzerhof (PBE) for the exchange-correlation interactions, plane wave basis set with a kinetic energy cutoff of 500 eV, and the projector-augmented wave (PAW) method for electron-ion interactions.³ The $2 \times 2 \times 1$ K-points was chose. In the calculations, the Hamiltonian formulation introduced by Liechtenstein and

Dudarev was adopted, in which the strong on-site Coulomb repulsion parameter U and the screened exchange interaction parameter J were used to describe the localized Ni 3d orbitals. $U_{eff} = 6.39 \text{ eV}$ was adopted according to the previous study.⁴



Fig. S1 XRD patterns of the NiS₂ octahedrons (a) and NiS₂ cubes (b) with peaks in agreement with the standard card (JCPDS No. 11-0099), showing the component of NiS₂.



Fig. S2 SAED patterns of NiS₂ octahedron (a) and NiS₂ cube (b) with electron beam along the [111] and [001] directions, respectively. The single crystalline nature of the octahedron and cube can be confirmed by the SAED. The patterns present well-defined spots in Fig. S2a could be well indexed to the (2 - 2 0), (2 - 1 - 1), (2 0 - 2), (1 1 - 2) and (0 2 - 2) planes of NiS₂ (JCPDS No. 11-0099). The (1 - 1 0), (1 0 - 1) and (0 1 - 1) planes marked by red circles came from secondary diffraction of crystals.⁵ The (010) plane marked in Fig. S2b also came from secondary diffraction. FeS₂ has the same space group and spot patterns as NiS₂. The similar spot patterns of FeS₂ had been reported by other researchers.^{6, 7}

Resistivity of NiS₂ Polyhedrons

The electrical conductivity (κ) measurements on NiS₂ octahedrons and cubes were realized by using a four-probe resistivity tester. The powder is prepared as a square sheet with 1 cm in length and 100 μ m in thickness by a tablet machine for measurement.

 κ (S/cm) can be obtained by the following equation (1):

$$\kappa = 1/\rho \tag{1}$$

 ρ ($\Omega \cdot$ cm) is the resistivity and can be calculated by equation (2):

$$\rho = \mathbf{R}_{\Box} \mathbf{W} \tag{2}$$

 R_{\Box} (Ω) is the square resistance and W (cm) is the thickness of the sample. The R_{\Box} values are calculated by equation (3):

$$R_{\Box} = (V/I) * F(S/D) * F(W/S) * (F_{sp}/F_t)$$
(3)

V (mV) is the voltage, I (mA) is the current, S (cm) is the distance between probes, D (cm) is the the length of square sample, W (cm) is the thickness of sample, F(S/D) is the correction factor of the thickness, F(W/S) is the correction factor of the length, F_{sp} is the correction factor of the distance between probes and Ft is the correction factor of the temperature. The results of the measurements are summarized in Table S1.

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	$\mathrm{R}_{\Box}\left(\Omega ight)$	$\rho \left(\Omega \cdot cm \right)$	κ (S/cm)
NiS ₂ cube	34.57	0.35	2.89
NiS ₂ octahedron	30.52	0.31	3.23

NiS₂ octahedron has lower R_{\Box} , ρ and higher κ than cube indicating that NiS₂ octahedron exhibits better electrical conductivity which is in accord with the results of EIS analysis.

J₀ Values Calculated from Equation and Tafel Polarization Curves

The J_0 values can be calculated by the following equation, $J_0 = \text{RT/nFR}_{ct}$, where R is the gas constant (8.314 J·mol⁻¹·K⁻¹), T is the temperature (298 K), n is the number of electrons involved in the reduction, F is the Faraday's constant (96500 C·mol⁻¹) and R_{ct} is the charge-transfer resistance extracted from the EIS spectra. The J_0 values are obtained by the equation with the R_{ct} of different CEs. The values are summarized in Table S2.

From Fig. 2d, the intersection of the cathodic branch and the equilibrium potential line (black solid line) could be considered as the exchange current density (J_0). The limiting diffusion current density (J_{lim}) of different electrodes corresponds to intersection of the cathodic branch with the *y*-axis. The J_0 values are calculated using extrapolation method from Tafel polarization curves, and the results are also summarized in Table S2.

CE	$R_{ct} \left(\Omega \ cm^2\right)$	$\log J_0$ (log mA cm ⁻²) calculated from the R _{ct}	$\log J_{\theta}$ (log mA cm ⁻²) calculated from Tafel polarization curves
Pt	6.25	0.91	0.90
NiS ₂ -cube	13.17	0.59	0.54
NiS ₂ - octahedron	9.86	0.71	0.73

Table S2 J_0 values calculated from R_{ct} and Tafel polarization curves of different CEs

From Table S2, the $\log J_0$ values of different CEs calculated from $J_0 = \text{RT/nFR}_{ct}$ are nearly the same as that calculated values from Tafel polarization curves. Although the $\log J_0$ values of NiS₂ octahedron and cube are a little different obtained by different methods, the $\log J_0$ increases in the order of NiS₂ cube < NiS₂ octahedron < Pt. The differences of the values may come from the deviations of different methods in the investigation of NiS₂ cube and NiS₂ octahedron.



Fig. S3 Crystal structure of a NiS_2 cell. NiS_2 has a cubic structure and Ni atoms occupying the sites in the face-centered cubic sublattices while the sulfur dimers centering about the anion positions.



Fig. S4 Crystal structures of the $\{111\}$ of NiS₂ from side view (a) and top view (b). The marked atoms by the red arrows show the exposed Ni atoms in NiS₂. Fig. S4b shows exposed Ni atoms on the top layer of the $\{111\}$ facet marked by red arrows.



Fig. S5 Crystal structures of the $\{100\}$ of NiS₂ from side view (a) and top view (b). The marked atoms by the red arrows in Fig. S5b are Ni atoms on the top layer of $\{100\}$ facet. Comparing Fig. S4b and S5b, there were more exposed Ni atoms on the top layer of $\{111\}$ facet than that of $\{100\}$ facet in the models.



Fig. S6 Perspective views of the crystal structures for NiS_2 along the [111] and [100] axes as the red arrows marked. The Ni-I bond distances, d(Ni-I), are 2.56 Å away from the (111) plane and 2.52 Å away from the (100) plane.

Adsorption energy of the I atom (E_{ad}^{I}) on the electrocatalyst surface was calculated. All the spin-polarized calculations were performed with PBE+U ($U_{eff} = 6.39 \text{ eV}$) functional using the VASP code.⁴ The project augmented wave (PAW) method was used to represent the core-valence electron interaction. The valence electronic states were expanded in plane wave basis sets with

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energy cutoff at 500 eV. The ionic degrees of freedom were relaxed using the Broyden-Fletcher-Goldfarb-Shanno (BFGS) minimization scheme until the Hellman-Feynman forces on each ion were less than 0.05 eV/Å.⁸ The vacuum between slabs is ~15 Å, and a corresponding $2 \times 4 \times 1$ k-points mesh was used during optimisations. The adsorption energy of E_{ad}^{I} was defined as:

 $E_{ad}^{I} = E(interface) - E(I/interface) + 1/2E(I_2)^{9,10}$

where E (interface), E (I/interface) and E (I₂) were the energies of the liquid/electrode interface, I adsorbed on the liquid/electrode interface and I₂ in the gas phase, respectively. For triiodide reduction reaction, E_{ad} ^I on the electrocatalyst surface played an essential role. Too high adsorption energy of I limited the overall activity due to the difficulty in I removal, while weak adsorption hindered I₂ molecular dissociation.⁸ The adsorption energy of E_{ad}^I at the CH₃CN/electrode interface range from around 0.33 to 1.20 eV, served as a good descriptor for the iodine reduction activity.^{9, 10} The adsorption energies for the {111} and {100} facets were estimated to be 0.98 eV and 1.49 eV, respectively.

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