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Chemically Exfoliated ReS$_2$ Nanosheets$^\dagger$

Takeshi Fujita$^a$, Yoshikazu Ito$^a$, Yongwen Tan$^a$, Hisato Yamaguchi$^b$, Daisuke Hojo$^a$, Akihiko Hirata$^a$, Damien Voiry$^c$, Manish Chhowalla$^a$, Mingwei Chen$^{a,d}$

The production of two-dimensional rhenium disulfide (ReS$_2$) nanosheets by exfoliation using lithium intercalation is demonstrated. The vibrational and photoluminescence properties of the exfoliated nanosheets are investigated, and the local atomic structure is studied by scanning transmission electron microscopy. The catalytic activity of the nanosheets in a hydrogen evolution reaction (HER) is also investigated. The electrochemical properties of the exfoliated ReS$_2$ nanosheets include low overpotentials of ~100 mV and low Tafel slopes of 75 mV dec$^{-1}$ for HER and are attributed to the atomic structure of the superlattice 1T$'$ phase. The presence of bandgap photoluminescence demonstrates that the nanosheets retain their semiconducting nature. ReS$_2$ nanosheets produced by this method provide unique photocatalytic properties that are superior to those of other two-dimensional systems.

The transition-metal dichalcogenide (TMD) family is composed of compounds with the formula MX$_2$, where “M” is a transition metal from groups 4–10 and “X” is a chalcogen. Thanks to recent developments in graphene technology, layered TMDs have received much attention for their versatile chemistry and applications in a variety of fields, including catalysis, energy storage, sensing, and electronic devices. $^{1,13}$ Chemical exfoliation from bulk materials is an effective TMD production method, and lithium intercalation provides scalable production of thin films and composites. $^{1,14,15}$ Lithium intercalation of bulk materials is a well-known and effective exfoliation technique, $^{16,17}$ and in group-6 TMDs a transformation from the semiconductor phase (2H: hexagonal structure) to the metallic phase (1T: octahedral structure) is induced during lithium intercalation. $^{18,19}$ In addition, the 2H $\rightarrow$ 1T phase transformation is accompanied by an improvement in catalytic activity. Recent studies showed that metallic exfoliated MoS$_2$ and WS$_2$ nanosheets exhibit excellent catalytic performance in hydrogen evolution reactions (HERs). $^{20-24}$ However, the practical availability of other systems is very limited, and to the best of our knowledge chemical exfoliation of ReS$_2$ has not been demonstrated previously.

In this study, we produced chemically exfoliated ReS$_2$ nanosheets from bulk powders using a solvent-free method involving Li. The local atomic structure of the nanosheets was investigated using transmission electron microscopy (TEM), atomic force microscopy (AFM), and X-ray photoelectron spectroscopy (XPS); in addition, we studied their vibrational properties, photoluminescence (PL), and catalytic activity in HERs. The production of ReS$_2$ nanosheets by liquid or chemical exfoliation has not been reported previously in literature, $^{1,14,25}$ and the ability of Li intercalation to produce ReS$_2$ nanosheets is largely unknown. We found that a solvent-free method $^{25}$ involving the reaction of ReS$_2$ powder with lithium borohydride (LiBH$_4$) is effective for intercalating Li, and this method could replace the conventional protocol involving a butyl lithium solution. $^{16}$ The common butyl lithium reagent did not work well for the exfoliation in this study. The results suggest that the butyl lithium reagent may not be efficient enough to intercalate between the ReS$_2$ layers to obtain sufficient yield of exfoliation via the chemical route. The surface morphology of the as-received ReS$_2$ powders was investigated using scanning electron microscopy (SEM), and the SEM images are shown in Figure 1a. The grain size varied from 100–500 nm, and some grains showed layered filaments. X-ray diffraction data from as-received ReS$_2$ and MoS$_2$ in powder form were collected and are shown in Figure S4 in the Electronic Supporting Information (ESI†). The crystal structure change was confirmed, but no significant change in interlayer spacing was observed. These trends were different from those present in MoS$_2$ and Li,MoS$_2$; therefore the intercalation mechanism of Li in ReS$_2$ requires further investigation. Figure 1b shows as-exfoliated ReS$_2$ nanosheets whose size, 50–100 nm, was much smaller than the initial grain size. (Figure S1 in the ESI† shows additional low-magnification scanning TEM (STEM) images indicating their morphology and quality.) Figure 1c is a photograph of a typical dark-brown suspension of chemically exfoliated ReS$_2$ in water. The AFM results indicated that the average thickness of an exfoliated nanosheet was $\approx$2.3 nm; this thickness corresponds to that of a bilayer because the expected monolayer thickness is $\approx$1 nm, $^{26}$ as shown in Figure S3 in the ESI†. Some of nanosheets were exfoliated down to monolayers, a fact confirmed by high-angle annular dark-field STEM (HAADF STEM). Images from monolayer regions (Figures 1d and e)
showed the characteristic superlattice of the 1T’ phase, which we previously observed in MoS₂ and WS₂ monolayers produced by lithium intercalation, as well as a maze-like pattern of chained clusters.20,21 The original crystal structure of ReS₂ is a distorted 1T structure with chains of Re clusters.27-29 The particularly large gain in the d³ electron count of Re coincides with the fact that the distortion is energetically favorable.30 However, a salient difference from the original structure is that the Re₄ clusters31 tend to be more clearly separated from each other; greater Jahn–Teller distortion is therefore expected in ReS₂ nanosheets. The XPS measurements also confirm the structural changes after the exfoliation (see Figure S5 in the ESI†). Moreover, the zeta potentials of the ReS₂ nanosheets are 10 mV lower than that of their bulk counterpart (see Table S2 in the ESI†). After annealing the exfoliated ReS₂ nanosheets at 500 °C for 1 h, the original crystal structure recovered; the 1T structure with chains of Re clusters was confirmed by HAADF STEM imaging, as shown in Figure S2 in the ESI†.

We measured the Raman spectra of the as-exfoliated ReS₂ nanosheets and as-received powders, and the results are shown in Figure 2. Because of the small size of the nanosheets, a comprehensive study on the dependence of the optical properties on the stack thickness could not be pursued. Raman spectra were acquired from the re-stacked nanosheets because the individual nanosheets are small and invisible under an optical microscope. The spectra were acquired several times from thick and thin re-aggregated areas, and there was no significant peak shift in the spectra between the ReS₂ nanosheets and the bulk material. The phonon dispersion of the ReS₂ nanosheets is nearly identical to that of the bulk material. A recent theoretical study showed that bulk ReS₂ behaves as electronically and vibrationally decoupled monolayers stacked together; Jahn–Teller distortion of the 1T structure prevents ordered stacking and minimizes the interlayer overlap of wavefunctions.28 This vibrational decoupling seems to be present not only in mechanically exfoliated nanosheets but also in chemically exfoliated ones. The peak near 150 cm⁻¹ assigned to the E₉ mode was different from that found in ref. 28. The difference may come from the differences of excitation laser wavelengths of 488 nm in ref. 28 and 512 nm in this study. Also, the in-plane motion in ReS₂ may be sensitive to the crystallinity; the starting powders in this study were commercially supplied and the material in ref. 28 was synthesized by a chemical vapor transport technique, resulting in a large single crystal.

In order to evaluate whether ReS₂ remains semiconducting or becomes metallic after chemical exfoliation, we investigated the PL properties of as-exfoliated samples. Figure 3 shows PL spectra from the re-stacked nanosheets on a Si substrate. In sharp contrast to the cases of MoS₂ and WS₂,21,26 as-synthesized ReS₂ nanosheets exhibit significant PL. In the thin and well-dispersed area shown in Figure S6 in the ESI†, a weak PL spectrum was obtained, and the 1T’ phase of ReS₂ retained its semiconducting nature. Distortion of the Re atom arrangement from perfect hexagonal symmetry creates a distortion of the S atom arrangement both perpendicular and parallel to the basal plane. This distortion opens an energy band gap due to mutual repulsion of the orbitals around the Fermi level.30

Moreover, we could not find any intense PL signals, unlike the case with MoS₂.32-34 The ReS₂ nanosheets did not show hot
luminescence from indirect-to-direct bandgap transitions or any dependence of PL on the number of layers. Although it was difficult to control the thickness of the ReS$_2$ nanosheets on the substrate in order to investigate the influence of layer thicknesses on PL, intense peaks were obtained only from the aggregated areas in Figures 3 and S6 in the ESI†, both of which were at 810 nm (1.53 eV). The stronger peaks are closely related to the increased volume/area of the probed regions. A blue shift is observed after exfoliation in comparison with the peak from bulk ReS$_2$ (as-received powders) at 850 nm (1.45 eV). The physical origin of this shift is unclear, but these trends in PL are in good agreement with previous results with mechanically exfoliated samples$^{28}$ and other TMDs.$^{35}$ Quantum size effects may also contribute to the blue shift.

We also investigated the HER catalyst performance of the chemically exfoliated 1T′ phase of ReS$_2$. Figure 4a compares the HER polarization curves for as-exfoliated and annealed (500 °C) ReS$_2$ nanosheets, as-received ReS$_2$ powders, and conventional Pt nanoparticles as a reference (all data not iR corrected). HER activity was dramatically enhanced in the as-exfoliated 1T′ nanosheets as compared to their annealed 1T counterpart and the bulk material. Tafel plots derived from these data are shown in Figure 4b; the linear portions of the data in Figure 4b were fitted to the Tafel equation to determine the slopes (dashed lines), and these were used to determine the overpotential of the electrochemical reaction. The Tafel plots reveal slopes of 75 mV dec$^{-1}$ for the as-exfoliated ReS$_2$ nanosheets, 88 mV dec$^{-1}$ for the annealed ReS$_2$ nanosheets, 211 mV dec$^{-1}$ for the as-received powders, and 37 mV dec$^{-1}$ for the Pt nanoparticles, indicating reduced overpotential in the nanosheets. The Tafel plot of the as-exfoliated ReS$_2$ nanosheets is comparable with the results of our previous study on as-exfoliated WS$_2$ nanosheets$^{20}$ and it exhibits slightly higher values than other nanostructured MoS$_2$ materials such as MoS$_2$ nanoparticles on highly conductive reduced graphene oxide$^{26}$ and exfoliated 1T MoS$_2$ nanosheets.$^{31,32}$

In our previous study of chemically exfoliated WS$_2$ and MoS$_2$, we found that regions of the metallic phase induced by local strains acts as active sites for enhanced HER. Experimental results suggest that a similar scenario can be applied to the as-exfoliated ReS$_2$ nanosheets as the 1T′ superlattice phase, shown in Figures 1d and e, can be considered as a “strained” 1T phase. This explanation for enhanced HER in as-exfoliated ReS$_2$, resulting from improved electrical conductivity from local strains, is consistent with it possessing the lowest overpotential of ~100 mV (Figure 4b) and the lowest Tafel slope among the ReS$_2$ materials investigated in this study. After annealing at 500 °C, the metastable 1T′ phase relaxes to the ground-state 1T phase (Figure S2, ESI†), losing its improved electrical conductivity; it has fewer active sites, a higher overpotential of ~200 mV, and a higher Tafel slope. These results suggest the origin of the high catalytic activity of metastable-phase TMDs such as the 1T′ phase of WS$_2$ and MoS$_2$. The high catalytic performance of as-exfoliated ReS$_2$ combined with the unique intrinsic band gap that is evident in the PL data (chemically exfoliated MoS$_2$ and WS$_2$ are metallic thus do not exhibit PL) indicate materials properties that are promising for realizing highly active TMD photocatalysts without the need for photocatalytic materials such as TiO$_2$, which are currently essential.$^{37}$

Electrochemical stability is important to the viability of a HER catalyst. In order to investigate the stability of these materials under electrocatalytic operation, we have measured the HER characteristics of the metastable 1T′ electrodes by subjecting them to over 1,100 cycles and monitoring the current density at ~0.3 V, as shown in Figure 5. The current density shows slight degradation to 70% of its original value after 1,000 cycles, which might be caused by the consumption of H$^+$ or strain relaxation in the 1T′ phase. The cycling stability of the metastable 1T′ electrodes is expected to be further improved by modifying the electrode with an effective current collector.$^{21}$

**Fig. 4.** HER electrocatalytic properties of exfoliated ReS$_2$ nanosheets: (a) polarization curves of ReS$_2$ nanosheets—as-exfoliated and after annealing at 500 °C—and Pt nanoparticles and as-received ReS$_2$ powders for comparison, (b) corresponding Tafel plots obtained from the polarization curves, showing slopes of 75 and 88 mV dec$^{-1}$ for the as-exfoliated and annealed ReS$_2$ nanosheets, respectively. There is significant reduction in the Tafel slope for exfoliated samples as compared to as-received powder samples. The dashed lines represent the slope for each sample.

**Fig. 5.** Cycling stability of the metastable 1T′ electrodes at a constant overpotential of 300 mV.

**Conclusions**

In summary, we have established a synthesis route for chemically exfoliated ReS$_2$ nanosheets starting from powders. These nanosheets show high HER activity originating from the
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Notes and references

1 T’ superlattice phase, and they also maintain their semiconductor properties, as demonstrated by PL results. ReS$_2$ nanosheets may therefore fulfill roles in photocatalysis that other 2D systems cannot play. The ReS$_2$ nanosheets may also be useful for other catalysis applications, such as sulfur-tolerant hydrogenation and hydrodesulfurization.$^{38,39}$


