Research Article

Synthesis of Submicron Hexagonal Plate-Type SnS_2 and Band Gap-Tuned $\text{Sn}_{1-x}\text{Ti}_x\text{S}_2$ Materials and Their Hydrogen Production Abilities on Methanol/Water Photosplitting

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SnS_2 and $\text{Sn}_{1-x}\text{Ti}_x\text{S}_2$ ($x = 0, 0.1, 0.3, 0.5$, and 0.7 mol) materials were designed using solvothermal method with the aim to enhance hydrogen production from water/methanol water photosplitting. Scanning electron microscopy revealed hexagonal plates with one side, $3.0\ \mu\text{m}$ in length, in the SnS_2 materials. Pure SnS_2 showed absorption band edges of above $660\ \text{nm}$, and the absorption was shifted to low wavelengths with the insertion of Ti ions. The evolution of H_2 from $\text{MeOH}/\text{H}_2\text{O}$ (1:1) photosplitting over SnS_2 hexagonal plates in the photocatalytic liquid system was $0.016\ \text{mL h}^{-1}\ \text{g}^{-1}$, and the evolutions were enhanced in $\text{Sn}_{1-x}\text{Ti}_x\text{S}_2$. In particular, $0.049\ \text{mL h}^{-1}\ \text{g}^{-1}$ of H_2 gas was produced in $\text{Sn}_{0.7}\text{Ti}_{0.3}\text{S}_2$ without electrolytes and it increased significantly to more than 90.6% ($0.47\ \text{mL h}^{-1}\ \text{g}^{-1}$ evolutions) at higher pH using 0.1 M of KOH. Based on the UV-visible absorption spectra, the high photocatalytic activity of $\text{Sn}_{1-x}\text{Ti}_x\text{S}_2$ was attributed to the existence of an appropriate band-gap state that retarded recombination between the electrons and holes.

1. Introduction

Many attempts have been shown to produce hydrogen as a renewable energy carrier to satisfy future demands because of its versatility and friendly properties. With this in mind, the photocatalytic formation of hydrogen and oxygen on semiconductors, such as pure TiO_2 (anatase) [1, 2] and metal loaded- TiO_2 [3–6] or non-metal loaded- TiO_2 [7–9], has been studied extensively because of their relatively low band gap and high corrosion resistance. On the other hand, these materials are activated only by UV because of their large energy band gap (e.g., 3.2 eV for anatase TiO_2). To improve the utilization of solar energy, considerable research effort has focused on shifting the photocatalytic hydrogen producing activity of TiO_2 into the visible wavelength above 450 nm, which accounts for ~42% of solar energy. Recently, studies of metal sulfide photocatalysts, particularly ZnS , Bi_2S_3 , and CdS -loaded TiO_2 , have covered topics ranging from synthesis to applications in new photocatalytic reaction mechanisms [10–15]. A narrow band gap makes it possible to absorb longer

wavelengths compared to the wide band gaps of conventional metal oxide semiconductor systems.

Some researchers have reported SnS_2 materials. In particular, nanostructures of SnS_2 often demonstrated shape and size-dependent physical and chemical properties that are of technological and scientific importance [16, 17]. Consequently, a great deal of effort has been focused on designing methods for the synthesis of SnS_2 with different characteristics [18, 19] to exploit their potential. SnS_2 has abundant optical, electrical, and photoelectric properties [20, 21] and has a band gap of 2.25 eV [22]. Owing to its photoconductivity, it is also considered a prospective candidate for solar cells and optoelectronic devices [20, 21]. Crystals of SnS_2 consist of planar triple layers (sandwiches, S–Sn–S with strong ion-covalent bonding) that are coupled weakly to one another by van der Waals forces. One of the most salient properties of layered SnS_2 is their ability to act as a host for atomic and molecular guest species, which are accommodated at the empty sites bounded by van der Waals forces between the adjacent close packed

SCHEME 1: Synthesis procedure of SnS₂ and Sn_{1-x}Ti_xS₂ by a solvothermal method.

chalcogen layers [23]. Owing to this property, lithium can be inserted into SnS₂, meaning that SnS₂ can become a promising candidate as a cathode material in the preparation of lithium batteries [24–26]. In addition, the absence of surface states associated with dangling bonds, which can act as recombination centers for photoinjected electrons, makes SnS₂ an ideal model system for dye sensitization studies and contributes to the high quantum yields [27]. Recently, the application of SnS₂ is shifting to its photocatalytic activity. Yang et al. [28] attributed the greatly enhanced photocatalytic activity of the SnS_x/TiO₂ composites to the matching band potentials and efficient charge transfer and separation at the tight-bonding interface between SnS_x and TiO₂. On the other hand, there are few reports of SnS₂ for photocatalytic hydrogen production, particularly the replacement of the SnS₂ framework with Ti ions (Sn_{1-x}Ti_xS₂).

In this study, the SnS₂ submicron hexagonal plate shaped particle was synthesized by a solvothermal method. Ti ions were incorporated into SnS₂ at various molar ratios (Sn_{1-x}Ti_xS₂) to regulate the potential energies of the valence and conduction bands for efficient hydrogen production from MeOH/H₂O photosplitting. The relationship between their spectroscopic properties and the photocatalytic performance on the production of H₂ is discussed and the characteristics of SnS₂ and Sn_{1-x}Ti_xS₂ were determined by X-ray diffraction (XRD), transmission electron microscopy (TEM), UV-visible absorption spectroscopy, and photoluminescence (PL) spectroscopy.

2. Experimental

SnS₂ and Sn_{1-x}Ti_xS₂ were prepared using a solvothermal method, as shown in the experimental flowchart in Scheme 1. To prepare the sol mixture, SnCl₄, sulfur powder, and TiCl₄ were used as the Sn, S, and Ti precursors, respectively. First, 1 - *x* moles (*x* is Ti concentration, *x* = 0, 0.1, 0.3, 0.5, and 0.7 mol) of SnCl₄ were dissolved in N, N-dimethylformamide as a solvent. 2 moles of S powders and 0, 0.1, 0.3, and 0.5 moles of TiCl₄ were added slowly to the solution with constant stirring and stirred to homogeneity for 2 h. Subsequently, the

final solution was transferred to an autoclave for the thermal treatment. Sn and Ti ions were sulfurized during thermal treatment at 200°C for 24 h in a nitrogen environment. The resulting precipitates were obtained, washed with acetone, and dried at 50°C for 24 h. Finally, four different materials, SnS₂, Sn_{0.9}Ti_{0.1}S₂, Sn_{0.7}Ti_{0.3}S₂, and Sn_{0.5}Ti_{0.5}S₂ were prepared.

The synthesized SnS₂ and Sn_{1-x}Ti_xS₂ particles were examined by XRD (X'Pert Pro MPD PANalytical 2-circle diffractometer at the Yeungnam University Instrumental Analysis Center) using nickel-filtered CuKα radiation (30 kV and 30 mA). The sizes and shapes of the SnS₂ and Sn_{1-x}Ti_xS₂ particles were examined by field emission scanning electron microscopy (FE-SEM, S-4100, Hitachi). The UV-visible absorption spectra of SnS₂ and Sn_{1-x}Ti_xS₂ particles were obtained using a Cary 500 spectrometer with a reflectance sphere. PL spectroscopy was also performed to determine the number of photoexcited electron hole pairs using a photoluminescence mapping system (LabRamHR, Sci-Tech Instruments).

Photosplitting in a MeOH/H₂O solution was carried out using a liquid photoreactor designed in our laboratory, as shown in Figure 1. For water photosplitting, 0.5 g of SnS₂ or Sn_{1-x}Ti_xS₂ particles were added to 1.0 L distilled water in a 2.0 L Pyrex reactor. UV-lamps (6 × 3 W cm⁻² = 18 W cm⁻², 30 cm length × 2.0 cm diameter; Shinan Com., Korea) emitting radiation of 365 nm were used. Methanol/water (MeOH/H₂O) photosplitting was carried out for 10 h with constant stirring, and hydrogen evolution was measured at an interval of 1 h. The concentration of each added electrolyte was 0.1 moles. The hydrogen gas (H₂) produced during water photosplitting was analyzed by TCD-type gas chromatography (GC, model DS 6200; Donam Instruments Inc., Korea). To determine the products and intermediates, the GC was connected directly to the water decomposition reactor. The following GC conditions were used: TCD detector; Carboxphere column (Alltech, Deerfield, IL, USA); 140°C injection temp.; 30°C initial temp.; 150°C final temp.; 300°C detector temp.

FIGURE 1: Liquid photoreactor designed in our laboratory for photosplitting in a MeOH/H₂O solution.

FIGURE 2: XRD patterns of the as-synthesized SnS₂ and Sn_{1-x}Ti_xS₂ particles.

3. Results and Discussions

Figure 2 shows XRD patterns of the SnS₂ and Sn_{1-x}Ti_xS₂ particles. The XRD peaks in the SnS₂ materials corresponded to pure hexagonal phase SnS₂ (Berndtite-2T, P-3ml, JCPDS card number 23-677), whereas those of Sn_{1-x}Ti_xS₂ revealed the formation of SnS₂ and anatase TiO₂ (tetragonal phase, JCPDS card number 65-5714) mixtures. The XRD patterns

in hexagonal phase SnS₂ showed the main peaks at 15.0, 28.3, 32.2, 42.2, 50.1, 52.6, 55.3, 60.9, 67.3, 70.5, 82.4, and 88.4° 2 θ , which were assigned to the (001), (100), (101), (102), (110), (111), (103), (201), (202), (113), (211), and (212) planes, respectively. In the case of Sn_{0.9}Ti_{0.1}S₂, although there was very little reduction in intensity, the peak positions for the SnS₂ structure were not changed and no peaks assigned to TiO₂ were observed despite the addition of Ti ions to the framework because of the very small amount. The peaks for TiO₂ at 25.38, 38.08, 48.28, 54.8, and 63.8° were assigned to the (101), (004), (200), (105), and (204) crystal planes in Sn_{0.7}Ti_{0.3}S₂ [29]. The peaks for Sn_{0.5}Ti_{0.5}S₂ were very weak, which might be caused by structural damage to the SnS₂ hexagonal phases depending on the level of substitution of Ti ions. This result can be predicted as follows more specifically. The sample nonadded Ti ingredient (SnS₂) exhibits a complete hexagonal crystal structure. However, the SnS₂ framework turns into a new crystal structure (orthorhombic SnS) with an increase of Ti concentration. Sn_{0.9}Ti_{0.1}S₂ including Ti 0.1 mol presented to the same framework of SnS₂; however two crystal structures (SnS₂ and SnS) coexisted in Sn_{0.7}Ti_{0.3}S₂ with Ti concentration increasing to be 0.3 mol. Here the crystal growth directions in two structures are different, and thus the two crystals are competitively grown, and eventually the peak intensities in XRD patterns are decreased. At this time, the anatase TiO₂ crystals rapidly formed between Ti components which not fully inserted into SnS₂ framework are shown in Sn_{0.5}Ti_{0.5}S₂ and Sn_{0.7}Ti_{0.3}S₂ samples. It is maybe attributed to too slow crystal growth of SnS₂ and SnS. The result was also similar in Sn_{0.5}Ti_{0.5}S₂. Otherwise, the Sn_{0.3}Ti_{0.7}S₂ expressed an orthorhombic SnS crystal structure; thus the crystal growth rate increased and finally the strong peak intensities in XRD patterns were

shown in $\text{Sn}_{0.3}\text{Ti}_{0.7}\text{S}_2$. On the other hand, the full width at half maximum (FWHM) of the 25.38 2θ peak for $\text{Sn}_{0.7}\text{Ti}_{0.3}\text{S}_2$ and $\text{Sn}_{0.5}\text{Ti}_{0.5}\text{S}_2$ was estimated. The Scherrer's equation was used to estimate the crystallite size [30]. The calculated crystallite sizes of the $\text{Sn}_{0.7}\text{Ti}_{0.3}\text{S}_2$ and $\text{Sn}_{0.5}\text{Ti}_{0.5}\text{S}_2$ were 13.7 and 10.0 nm, respectively. Surprisingly, the diffraction peaks of the $\text{Sn}_{0.3}\text{Ti}_{0.7}\text{S}_2$ were rather similar to the orthorhombic SnS (JCPDS card, number 01-0984, Pmcn, $a = 3.99$ Å, $b = 4.34$ Å, $c = 11.2$ Å) structure. This suggests that the hexagonal SnS_2 structure can be transferred to an orthorhombic SnS structure when many Ti ions are inserted.

Figure 3 shows low-magnification SEM images of SnS_2 and $\text{Sn}_{1-x}\text{Ti}_x\text{S}_2$ particles. SEM revealed hexagonal plates of one side $3.0\text{ }\mu\text{m}$ in the SnS_2 materials. In contrast, the morphologies of the $\text{Sn}_{1-x}\text{Ti}_x\text{S}_2$ materials varied according to the level of Ti ions insertion: broken sheets, coexisting forms with TiO_2 nanoparticles, and peanut-shaped have been appeared in $\text{Sn}_{0.9}\text{Ti}_{0.1}\text{S}_2$, $\text{Sn}_{0.7}\text{Ti}_{0.3}\text{S}_2$, and $\text{Sn}_{0.5}\text{Ti}_{0.5}\text{S}_2$, respectively. Otherwise, microrods with a similar morphology to SnS were observed in $\text{Sn}_{0.3}\text{Ti}_{0.7}\text{S}_2$. On the other hand, the specific surface areas of SnS_2 , $\text{Sn}_{0.9}\text{Ti}_{0.1}\text{S}_2$, $\text{Sn}_{0.7}\text{Ti}_{0.3}\text{S}_2$, $\text{Sn}_{0.5}\text{Ti}_{0.5}\text{S}_2$, and $\text{Sn}_{0.3}\text{Ti}_{0.7}\text{S}_2$ exhibited 38.72, 44.24, 54.20, 68.52, and $48.30\text{ cm}^2/\text{g}$, respectively. Typically, it is well known that the surface area differs on the particle shape and size. However, the specific surface area values in this study seem to be related to the bulk pores formed by the contacts between the particles rather than the particle size and shape. Especially the larger surface area in the case of $\text{Sn}_{0.5}\text{Ti}_{0.5}\text{S}_2$ sample can be considered by bulk pores much formed between the smaller and round-shaped particles. Generally, the larger surface area has, the catalytic performance increases. However, the surface area in our study was not directly related to the catalytic activity. The surface area in $\text{Sn}_{0.7}\text{Ti}_{0.3}\text{S}_2$ was greater than $\text{Sn}_{0.5}\text{Ti}_{0.5}\text{S}_2$; however, the photocatalytic activity (hydrogen production) was more excellent in $\text{Sn}_{0.5}\text{Ti}_{0.5}\text{S}_2$. It can be concluded in this study that the proper band gap and light absorption ability of samples were more advantageously affected to the catalytic activity.

Figure 4 shows the UV-visible diffuse reflectance spectra of the as-synthesized SnS_2 and $\text{Sn}_{1-x}\text{Ti}_x\text{S}_2$ powders. All products displayed optical absorption capabilities over the entire visible light spectrum (400–700 nm). The broad spectrum response suggests that the as-synthesized SnS_2 hexagonal plates should be an excellent visible light responsive photocatalyst for MeOH/ H_2O splitting. With Ti ion insertion, the curves were shifted to shorter wavelengths. The optical band-gaps were determined based on the theory of optical absorption for direct band gap semiconductors [31]: $\alpha h\nu = B(h\nu - E_g)^{1/2}$. The curves of $(\alpha h\nu)^2$ versus $(h\nu)$ for the as-synthesized SnS_2 hexagonal plates were plotted. By extrapolating the straight line portion of the plots of $(\alpha h\nu)^2$ versus $(h\nu)$ to $\alpha = 0$, the E_g values of the as-synthesized SnS_2 , $\text{Sn}_{0.9}\text{Ti}_{0.1}\text{S}_2$, $\text{Sn}_{0.7}\text{Ti}_{0.3}\text{S}_2$, and $\text{Sn}_{0.5}\text{Ti}_{0.5}\text{S}_2$ were estimated to be 1.87 (670 nm), 1.88 (660 nm), 1.90 (650 nm), and 2.25 (550 nm) eV, respectively. Generally the band gaps of SnS_2 and SnS are 2.2 and 1.08 eV [32]. However, the absorption in the visible region was attributed to the transition from the ground state to a few defect related deep states. This

excitation character of the absorption spectra indicated the excellent crystal quality of the semiconductor. A red-shift is observed in the optical absorption spectra of the SnS_2 hexagonal columns, which indicates that the SnS_2 particles were too large to show quantum confinement related effects. This absorption in the visible region was attributed to the transition from the ground state to a few defect related deep states. Consequently, the band gap can be varied according to the particle size or crystal defects.

Photoluminescence (PL) spectroscopy measures the spectrum emitted by the recombination of photogenerated minority carriers and is a direct way of measuring the band gap. On the other hand, the large quantity of impurities induces a large free carrier density in the bands. Consequently, different carrier interactions cause remarkable modifications of the line shape and spectral energy of the PL features. Figure 5 shows the PL spectra of SnS_2 and $\text{Sn}_{1-x}\text{Ti}_x\text{S}_2$ taken at room temperature. The spectra exhibited a strong emission peak at 549.9 nm corresponding to green emission. The strong PL peaks might be related to crystalline defects induced during growth. SnS_2 exhibits a luminescence peak for near band emission at 549.78 nm (2.25 eV). The intensities of PL curves of samples were smaller with an increase of Ti insertion, and those were decreased in the following order: $\text{SnS}_2 < \text{Sn}_{0.9}\text{Ti}_{0.1}\text{S}_2 < \text{Sn}_{0.5}\text{Ti}_{0.5}\text{S}_2 < \text{Sn}_{0.7}\text{Ti}_{0.3}\text{S}_2$. Otherwise, the emission bands of TiO_2 (at 420 nm) were not observed because SnS_2 is a real light sensitizer. Typically, a smaller PL intensity indicates better photoactivity [33].

Figure 6 summarizes the evolution of H_2 from MeOH/ H_2O photosplitting over the SnS_2 , $\text{Sn}_{0.9}\text{Ti}_{0.1}\text{S}_2$, $\text{Sn}_{0.7}\text{Ti}_{0.3}\text{S}_2$, and $\text{Sn}_{0.5}\text{Ti}_{0.5}\text{S}_2$ photocatalysts in a batch-type liquid photosystem. The catalytic activity of $\text{Sn}_{1-x}\text{Ti}_x\text{S}_2$ was enhanced considerably compared to that of pure SnS_2 . 0.08 mL of H_2 gas was collected over 0.5 g SnS_2 photocatalyst after MeOH/ H_2O photosplitting for 10 h. SnS_2 easily absorbed longer wavelengths in UV-visible absorption but the recombination between the excited electrons and holes also rapidly generated rapid catalytic deactivation. In contrast a significant amount of H_2 gas was collected over the $\text{Sn}_{1-x}\text{Ti}_x\text{S}_2$, and the amount of H_2 produced reached 0.245 mL ($0.049\text{ mL h}^{-1}\text{ g}^{-1}$) over 0.5 g $\text{Sn}_{0.7}\text{Ti}_{0.3}\text{S}_2$. $\text{Sn}_{1-x}\text{Ti}_x\text{S}_2$ will show stronger oxidation-reduction ability than pure SnS_2 with decreased electron-hole recombination due to the wider band gap, which increases the photocatalytic performance. This can be related to the PL result. The PL intensity of $\text{Sn}_{0.9}\text{Ti}_{0.1}\text{S}_2$ sample was larger, and this fact means that the recombination between holes and electrons in $\text{Sn}_{0.9}\text{Ti}_{0.1}\text{S}_2$ sample is larger than those in $\text{Sn}_{0.5}\text{Ti}_{0.5}\text{S}_2$. The holes and electrons generated from $\text{Sn}_{0.9}\text{Ti}_{0.1}\text{S}_2$ eventually did not play well in catalytic reaction. Consequently, the recombination time between electrons and holes for sample with mixed structure is expected to be longer rather than a sample having a perfect crystal structure like as SnS or SnS_2 . In particular, the catalytic performance for MeOH/ H_2O decomposition over $\text{Sn}_{0.7}\text{Ti}_{0.3}\text{S}_2$ was enhanced further in the alkali solution electrolytes (B). Hydrogen production was increased dramatically in the alkali solution (NaOH and KOH) due to the generation of more OH radicals from

FIGURE 3: Low-magnification SEM images of the as-synthesized SnS_2 and $\text{Sn}_{1-x}\text{Ti}_x\text{S}_2$ particles.

alkali compounds, and it is reaching up to $0.47 \text{ mL h}^{-1} \text{ g}^{-1}$ evolution in a KOH solution. In acidic solutions as like H_2SO_4 and CH_3COOH , the hydrogen production decreased because the unstable S ions in the $\text{Sn}_{0.7}\text{Ti}_{0.3}\text{S}_2$ catalyst which dissolved in acidic solution oxidized with O ions in water

and resulted in forming SO_4^{2-} ions. The ions combined with the hydrogen ions generated during the $\text{MeOH}/\text{H}_2\text{O}$ photosplitting process to form H_2SO_4 , and thus the hydrogen production was decreased. Otherwise, when neutral Na_2SO_4 compounds are added into the reaction solution, there is

FIGURE 4: UV-visible diffuse reflectance spectra of the as-synthesized SnS_2 and $\text{Sn}_{1-x}\text{Ti}_x\text{S}_2$ powders.

FIGURE 5: PL spectra of the as-synthesized SnS_2 and $\text{Sn}_{1-x}\text{Ti}_x\text{S}_2$ at room temperature.

already the excess amount of SO_4^{2-} ions, and thus SO_4^{2-} ions formations are suppressed by the principle of Le Chatelier. Consequently, the catalytic activity in Na_2SO_4 solution relatively increased compared to it in the solution with nonadditives.

The UV-visible absorption and PL spectra indicated two photocatalysis models, as shown in Scheme 2. In model (a), combination between TiO_2 and SnS_2 was perfectly formed as in the $\text{Sn}_{0.9}\text{Ti}_{0.1}\text{S}_2$ composite, despite the initial photoreaction being slower because of the larger band gap but the recombination of electrons and holes was slower, resulting in an increase in catalytic performance. In model (b), if TiO_2 particles are physically loaded on the surface of SnS_2

particles, the first electronic transition would occur in the SnS_2 semiconductors from the 365 nm radiation source, and the electrons at a higher conduction band in SnS_2 move to the TiO_2 conduction band, whereas the holes in TiO_2 move to the valence band of SnS_2 , which is formed by the current recycle. Therefore, the recombination of excited electrons and holes will be suppressed during photocatalysis. These phenomena increase the evolution of OH radicals formed from the electrons and holes that will eventually enhance the photocatalytic performance of MeOH and H_2O degradation. Therefore, the $\text{Sn}_{1-x}\text{Ti}_x\text{S}_2$ composites exhibited better catalytic performance than the TiO_2 and SnS_2 monocatalysts.

FIGURE 6: Evolution of H₂ gases from MeOH/H₂O photosplitting over the as-synthesized SnS₂, Sn_{0.9}Ti_{0.1}S₂, Sn_{0.7}Ti_{0.3}S₂, and Sn_{0.5}Ti_{0.5}S₂ photocatalysts. (a) On the photocatalysts without electrolytes and (b) on Sn_{0.7}Ti_{0.3}S₂ with various electrolytes.

SCHEME 2: Two photocatalysis models suggested in this study. (a) Ti ions are inserted into SnS₂ framework, and (b) TiO₂ particles are loaded on the surface of the SnS₂ particles.

4. Conclusions

This reported the development of new photocatalysts using a metal sulfide framework for hydrogen production from MeOH/H₂O splitting. SnS₂ and Sn_{1-x}Ti_xS₂ exhibiting activity in the visible radiation were synthesized using a solvothermal method. UV-visible absorption spectroscopy revealed estimated band gaps of 1.87, 1.88, 1.90, and 2.25 eV for

the as-synthesized SnS₂, Sn_{0.9}Ti_{0.1}S₂, Sn_{0.7}Ti_{0.3}S₂, and Sn_{0.5}Ti_{0.5}S₂, respectively. The PL intensity of SnS₂ and Sn_{1-x}Ti_xS₂ decreased with the addition of Ti and was smallest in Sn_{0.7}Ti_{0.3}S₂. A significant amount of H₂ gas was collected over the Sn_{0.7}Ti_{0.3}S₂ photocatalyst, and the amount reached 0.049 mL h⁻¹ g⁻¹ without an electrolyte with a maximum yield of 1.88 mL after 8 h in a KOH solution. This is due most likely to the slower recombination of electrons

and holes, which enables higher catalytic performance for $\text{Sn}_{0.7}\text{Ti}_{0.3}\text{S}_2$.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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