Selective Ion Exchange and Photocatalysis by Zeolite-Like Semiconducting Chalcogenide

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Abstract: The development of novel photocatalysts usually centers on features such as band structures, various nano-, micro-, or macro-forms, and composites in efforts to tune their light absorption and charge separation efficiency. In comparison, the selectivity of photocatalysts with respect to features of reactants such as size and charge has received much less attention, in part due to the difficulty in designing semiconducting photocatalysts with uniform pore size. Here, we use crystalline porous chalcogenides as a platform to probe reactant selectivity in photocatalytic processes. The 3-in-1 integration of high surface area, uniform porosity, and favorable band structures in such chalcogenides makes them excellent candidates for efficient and selective photocatalytic processes. We show that their photocatalytic activity and selectivity are closely related to their differing affinity and selectivity for different guest species. In particular, unlike common solid-state photocatalysts with neutral framework, the anionic nature of the porous chalcogenide framework used here endows them with a high degree of selectivity for cationic species in both guest exchange and closely coupled photocatalytic transformation of such guests. Another interesting discovery is the observation of an unusual ion exchange process involving a transient state of over-saturation of exchanged ions, which can be explained by a transition from an initially kinetically controlled process to a subsequent thermodynamically controlled one. This work is part of ongoing efforts to contribute to the development of a new generation of crystalline porous photocatalysts with custom-designed selectivity for various reactants or products.

Introduction

Selectivity to pre-defined characteristics of reaction species is one of the most important considerations in the design of advanced catalysts. Great progress has been made in the design of conventional heterogeneous catalysts with high selectivity.[3] For example, zeolites, which are a family of highly useful solid acid catalysts, can exhibit high selectivity with respect to the size and shape of reactants, intermediates, and products, due to their uniform pore size.[2] In comparison, similarly selective photocatalysts are few, because heterogeneous photocatalysts are predominantly non-porous materials such as TiO$_2$ and CdS.[3] So far, research on photocatalysts has been mostly centered on features such as band structures, morphologies, and co-catalysts.[4–6] The selectivity of photocatalysts has received much less attention, likely due to the difficulty in designing semiconducting photocatalysts with structural and topological properties similar to those of zeolites.[7,8]

In the past two decades, we and others have made dramatic progress in the synthesis of open-framework metal chalcogenides,[9–14] which is one series of crystalline porous materials[13,14] with semiconducting properties, uniform porosity, and high surface area. A common basic structural building unit is the supertetrahedral cluster, denoted as T$n$ cluster, where $n$ is the number of metal sites along each edge of the cluster. These supertetrahedral clusters can replace tetrahedrally coordinated Si$^4+$/Al$^{13+}$ sites in zeolites to form 3D open-framework materials, thus mimicking zeolite connectivity. The highly porous character has endowed them with unique properties and applications, such as gas sorption, ion exchange, ionic conductivity, and photocatalytic production of H$_2$.[17,18]

Most traditional photocatalysts are based on non-porous materials,[19,20] The photo-generated electron-hole pairs in such dense solids may have to travel a relatively long distance in order to reach target reactants on the surface. This can not only be detrimental to the reaction kinetics, but also contributes to a greater degree of electron-hole recombination. With crystalline porous semiconductors,[21] redox chemistry can occur within the internal pore space, which can contribute to reduced probability for electron-hole recombination and high...
photocatalytic efficiency. It may also be possible to permit or block the access of reactants to the internal pores based on their size or charge, leading to differing photocatalytic rates of different species and high selectivity.

In this work, we select a zeolite-like semiconducting chalcogenide, CPM-120-ZnGaGeS-AEM (denoted as 1-AEM here, CPM = Crystalline Porous Material and AEM = 4-(2-aminoethyl)morpholine), as the platform for the study of selective photocatalysis. The bulky protonated AEM cations here can be exchanged with Cs⁺, which gives the structural analogue, named as 1-Cs here. In the following, we show the dramatic effect of porosity, charge of the framework, and ion-exchange properties of 1-Cs and 1-AEM on the selective adsorption and photocatalytic reactions of dye molecules.

Results and Discussion

Structural description and ion-exchange property

1-AEM is isostructural to CPM-120-ZnGeS-AEM reported previously. 1-AEM has a super-sodalite-type structure made of T2 clusters (Figure 1 and Figure S21 in Supporting Information) and it has high thermal and hydrothermal stability. The chemical composition of the T2 cluster is \([\text{Zn}_{0.76}\text{Ga}_{0.70}\text{Ge}_{2.54}\text{S}_{8}]^{2+}\), according to energy dispersive X-ray spectroscopy (Figure S14). These T2 clusters are joined by corner-sharing sulfur atoms to form a 3D structure. The sodalite cage contains 4- and 6-membered rings and the aperture size of the 6-membered ring is 7.66 Å. The framework is negatively charged, leading to the interaction between the negatively charged sulfur atoms of the host framework and the positively charged extra-framework species. In the as-synthesized form of 1-AEM, protonated AEM cations occupy the void space in the framework and serve as the charge-balancing species. These AEM cations can be completely ion-exchanged by smaller Cs⁺ (the Cs⁺-exchanged form is denoted as 1-Cs). While 1-AEM displays no porosity, 1-Cs is highly porous. The BET surface areas of 1-Cs and 1-AEM, determined by nitrogen adsorption, are quite different, as shown in Figures S2 and S3. The BET surface area of 1-Cs is 467.19 m² g⁻¹ while 1-AEM possesses a BET surface area of only 7.28 m² g⁻¹. This is because the bulky protonated AEM cations block the accessible pores in 1-AEM, and the ion-exchange with much smaller Cs⁺ cations gives rise to porous 1-Cs. In addition to the difference in porosity, the ion exchange rates of 1-Cs and 1-AEM with dye cations such as RhB⁺ are also different (Figure S9c) and the exchange rate of RhB⁺ with 1-Cs is much faster than that with 1-AEM. This indicates that the cation exchange with bulky protonated AEM cations is much slower than that with smaller Cs⁺ cations. Here it is worth noting that unlike most photocatalysts that have neutral frameworks, 1-AEM and 1-Cs have negatively charged frameworks.

Charge selectivity by open-framework chalcogenide

For ease of detection, dye molecules are selected as model compounds to study selective properties of our photocatalysts. To study the selectivity with respect to the charge of the dye molecules, a cationic dye molecule (methylene blue, MLB⁺, 15.1×6.51 Å) and an anionic dye molecule (methyl orange, MO⁻, 14.92×6.28 Å) were selected. These two molecules have similar molecular mass and dimensions but opposite charges, which makes them ideal to study the effect of the charge. Here, we firstly demonstrate the charge-dependent selective adsorption using single-component dye solutions. To do this, the same amounts of 1-Cs were immersed in two colored aqueous solutions (blue MLB⁺ and orange MO⁻) for 3 days. Both solutions possess the same volume and concentration of MLB⁺ and MO⁻. Following the addition of 1-Cs, the concentrations of two dye molecules in solutions were monitored by UV/Vis spectroscopy. This shows that 97% of MLB⁺ disappeared from solution and was encapsulated in the pores (through ion-exchange with Cs⁺ within the pore). In comparison, for MO⁻, almost all remained in the solution (Figure 2a and b) even after 3 days, due to the rejection of MO⁻ by the negative chalcogenide framework. (All relative concentrations are expressed as \(C/C_0\) where \(C\) is the concentration at a given time and \(C_0\) is the original concentration).

We then demonstrate the charge-dependent selective adsorption using mixed dye solutions. To do this, a mixture solution of MLB⁺ and MO⁻ with the same concentration is prepared. Then 1-Cs crystals with the same amount as that in the first set of experiment were immersed in the mixture. The concentration of MLB⁺ underwent a dramatic decrease with time while the concentration of similarly sized MO⁻ decreased only slightly (Figure 2c). The above observation demonstrates that...
MLB\(^+\) can be selectively encapsulated into the pores of the chalcogenide framework whereas the access by MO\(^-\) is denied. The selectivity for cationic organic molecules by this chalcogenide open framework shows that the ion-exchange properties of porous frameworks can be employed to selectively respond to guest species with different charge properties.

Size selectivity by open-framework chalcogenide

Having demonstrated the selectivity towards the charge of dye species, we next probed the selectivity towards dyes with different sizes, but the same charge. Five cationic molecules with different dimensions were chosen: rhodamine B (RhB\(^+\)) > crystal violet (CV\(^+\)) > basic fuchsin (BF\(^+\)) > phenosafranine (Phf\(^+\)) > MLB\(^+\). The molecular structures and dimensions are shown in Figure S6. Note that all of them have a charge of +1. These five dyes, with the same amount of moles, were dissolved into five aqueous solutions with the same volume and then the same amount of 1-Cs was immersed into each solution. The ion-exchange process was monitored by UV/Vis spectroscopy periodically. As shown in Figure 3, there is a general trend that both ion exchange rate and the extent of exchange are correlated with the size of dye molecules. The smallest MLB\(^+\) shows the fastest exchange rate and the highest degree of exchange, whereas the bulkiest RhB\(^+\) exhibits the slowest exchange rate and the lowest exchange capacity.

The ion exchange behavior of BF\(^+\) is of particular interest because it deviates from all others. During the first 4 hours, although possessing relatively large size, the exchange rate of BF\(^+\) is even larger than that of MLB\(^+\). However, during the next 8 hours, some of the adsorbed BF\(^+\) molecules are slowly released back to the aqueous solution, leading to an increase in the concentration of BF\(^+\) in the solution. Then, the normal trend resumes as the framework continues to undergo ion exchange with BF\(^+\) molecules, leading to a gradual decrease in the concentration of BF\(^+\) in the solution.

Here we propose a possible mechanism for the above observed ion exchange behavior of BF\(^+\). For all other dyes except BF\(^+\), the ion exchange process is slow enough so that there is an adequate amount of time to establish the thermodynamic equilibrium, leading to a thermodynamics-controlled ion-exchange process. On the other hand, the ion exchange process of BF\(^+\) is so fast initially that it shows kinetics-controlled behavior at the beginning. As the pore was being filled up, the ion exchange process slowed sufficiently, which then provides ample time to establish the thermodynamic equilibrium between cationic dyes and Cs\(^+\) cations. In short, the ion exchange process of BF\(^+\) was initially dominated by the kinetics-controlled process, which then gradually changed into the thermodynamics-controlled process.

The unique behavior of BF\(^+\) is related to its different structural features. In all other dyes studied here, the positive nitrogen center is bonded to three alkyl groups, in distinct contrast with BF\(^+\) in which the positive nitrogen site is bonded to only one alkyl group and two hydrogen atoms. This means that BF\(^+\) has a charged, more hydrophilic site that is also capable of forming hydrogen bonds. Since the surface of the chalcogenide framework is highly negative and hydrophilic, it is expected to have much stronger interactions with BF\(^+\), as compared with other cationic dyes. Such stronger interaction is likely responsible for the very fast ion exchange behavior of BF\(^+\) with the chalcogenide framework, contributing to its unusual ion exchange behavior with a transient state of over-saturation in the concentration of exchanged BF\(^+\).

**Figure 2.** a) Relative MO\(^-\) content in the presence of 1-Cs with time. b) Relative MLB\(^+\) content in the presence of 1-Cs with time. c) UV/Vis spectra of equimolar mixture solution of MO\(^-\) and MLB\(^+\) in the presence of 1-Cs with time.

**Figure 3.** Relative content of 5 different sized cationic dyes in aqueous solutions in the presence of 1-Cs with time.
It is worth noting that in their most common conformations, some dimensions of dye molecules chosen here may be larger than the aperture size of super-sodalite cage in 1-Cs. The successful ion-exchange process with Cs\(^+\), as determined by UV/Vis spectra, can be ascribed to the dynamic molecular shapes, as well as possible association and dissociation equilibria of metal-chalcogen bonds in the chalcogenide framework. To further confirm that dye cations are ion-exchanged into the internal pore, instead of being adsorbed onto the external particle surface, microscopic images were taken on the intact and crosscut single crystals after ion exchange. Here RhB\(^+\) loaded 1-Cs crystals were chosen as an example because RhB\(^+\) is the bulkiest among the dye molecules studied. As confirmed by the uniform dyeing throughout the entire crystal, it is clear that RhB\(^+\) stayed inside the crystal after cation exchange (Figure S7). To further prove RhB\(^+\) are located inside the cages of the framework as charge balancing species after ion exchange, a reversible ion-exchange experiment was performed here. 1-Cs was firstly immersed in the RhB\(^+\) aqueous solution. The result shows that after 77 days, there are almost no RhB\(^+\) cations left in the solution. Then the crystals were filtered and transferred to 1 m CsCl aqueous solution with the same volume. The UV/Vis spectroscopy shows that after 11 days, 52% of RhB\(^+\) was exchanged back to the aqueous solution (Figure S12). This process demonstrated that after the first cation exchange, RhB\(^+\) cations were introduced into the cages of the framework. Then the RhB\(^+\) cations in the pores could be exchanged out by Cs\(^+\) cations. The exchanged-out RhB\(^+\) cations exhibit the same characteristic absorbance peak at 554 nm, indicating the intactness of RhB\(^+\) during the whole process.

Photocatalytic activity and selectivity by open-framework chalcogenide

Having demonstrated the charge and size selective adsorption behaviors of dye molecules in the porous semiconducting 1-Cs, we next seek to study how such selective adsorption affects the photocatalytic activity and selectivity of these metal chalcogenides. In order to probe the effect of porosity on the photocatalytic properties, both porous 1-Cs and non-porous 1-AEM were used as possible catalysts in the photocatalytic experiment involving RhB\(^+\) and MO\(^-\). Here 1-AEM is deemed non-porous because the direct ion exchange between protonated AEM within the cavities of the framework and organic dye cations in the solution was negligible (Figure S9c in Supporting Information). The RhB\(^+\) aqueous solution with 1-AEM was stirred in the dark for 1 hour. Then after 6 hours of visible light irradiation, nearly 80% of RhB\(^+\) was decomposed, as monitored by measuring the characteristic absorption peak of RhB\(^+\) at 554 nm (Figure S10b). For anionic MO\(^-\), after 6 hours of UV/Vis light irradiation, the concentration of MO\(^-\) monitored by UV/Vis spectroscopy at 464 nm was decreased by 88% (Figure S11b).

A dramatic change in the photocatalytic activity was observed when the porous phase 1-Cs was used instead of 1-AEM. The RhB\(^+\) aqueous solution containing 1-Cs was also stirred in the dark for one hour. Then after 1.5 hours of visible light irradiation, almost all of the RhB\(^+\) were degraded, which was much faster and more complete than that in the presence of 1-AEM (Figure 4). The photocatalyst remained stable after the photocatalytic reaction as demonstrated by the PXRD patterns (Figure S4 and S5). In comparison, the photocatalytic conversion rate of MO\(^-\) with 1-Cs was almost the same as that in 1-AEM (Figure 5). The control experiment showed that only 2% of RhB\(^+\) disappeared after 3 hours under visible light irradiation without any catalysts. The reaction rates of RhB\(^+\) over those two photocatalysts can be fitted to the pseudo first order reaction kinetics equation (Figure S10c). The determined rate constant for RhB\(^+\) with 1-Cs is 2.39 h\(^{-1}\), nine times larger than that in 1-AEM (0.27 h\(^{-1}\)). In comparison, the reaction rates of MO\(^-\) over those two catalysts are nearly the same.

For comparison, under similar conditions, TiO\(_2\) with self-doped Ti\(^{3+}\) was used for photocatalytic decomposition of RhB\(^+\). It is reported that self-doped Ti\(^{3+}\) can help enhance the visible light photocatalytic activity. After three hours, only 10%

![Figure 4. Photocatalytic activity of RhB\(^+\) in different conditions with time. When the catalyst (1-Cs or 1-AEM) was added to photocatalytic reaction, the solution was stirred in the dark for 1 hour to reach the adsorption equilibrium (from −1.0 to 0.0 hour period). Vis: Visible light irradiation.](image)

![Figure 5. Photocatalytic activity of MO\(^-\) under different conditions with time. When the catalyst (1-Cs or 1-AEM) was added to photocatalytic reaction, the solution was stirred in the dark for 1 hour to reach the adsorption equilibrium (from −1.0 to 0.0 hour period). UV/Vis: UV-visible light irradiation.](image)
of RhB\(^{-}\) was decomposed. Even with 400 nm cutoff filter instead of 420 nm, only 21\% of RhB\(^{-}\) was decomposed after 3 hours (Figure S19). Those data serve to illustrate that the porous 1-Cs is a highly efficient photocatalyst. Moreover, the recycling ability of the photocatalytic materials has also been tested. The decomposition amount of RhB\(^{-}\) on 1-Cs remained higher than 95\% during 4 cycles, showing the good recycling ability and stability of the material (Figure S20).

It is quite interesting to emphasize that the positively charged molecule RhB\(^{-}\) shows quite different photocatalytic activities with 1-AEM and 1-Cs, respectively. There is a nine-fold increase of photocatalytic rate of degradation of RhB\(^{-}\) in 1-Cs when compared with 1-AEM. Although negatively charged molecule MO\(^{-}\) has much smaller dimension than that of RhB\(^{-}\), it shows almost the same photocatalytic behavior in the presence of non-porous 1-AEM or porous 1-Cs. To better understand the observed photocatalytic properties, we compared the optical and physical properties of these two materials (1-AEM and 1-Cs).

The dramatic difference in photocatalytic activities of 1-Cs and 1-AEM with respect to cationic dye molecules is primarily due to the effect of their different porosity, instead of other factors such as stability, the nature of counter cations, or difference in band structures. PXRD patterns of 1-AEM and 1-Cs show that before and after ion-exchange all peaks match well with the simulated one (Figure S4 and S5). A control experiment was carried out to evaluate the impact of Cs\(^{+}\) on the photocatalytic reaction of RhB\(^{-}\). The result also illustrates that Cs\(^{+}\) plays no role in the photocatalytic degradation of RhB\(^{-}\) (Figure 4). From the adsorption edges, 1-AEM possesses a band gap of 2.13 eV while 1-Cs has a band gap of 2.18 eV, determined using Kubelka–Munk methods (Figure S13). The transition is likely the result of charge transfer from the S\(^{2-}\) dominated valence band to the metal cation dominated conduction band. It is apparent that the extra-framework cations (protonated AEM or Cs\(^{+}\)) have little influence on the band gap. The morphologies and particle size of two photocatalytic materials are almost the same before and after the ion exchange, as shown from scanning electron microscopy (SEM) images (Figure S16, S17, and S18).

During the photocatalytic process of RhB\(^{-}\) in the presence of 1-Cs, the position of the maximum absorbance peak of RhB\(^{-}\) solution shifts from 554 to 504 nm after 1.5 hours of visible light irradiation (Figure S10a). Such a dramatic hypsochromic shift of RhB\(^{-}\) is attributed to a step-by-step diethylation of -N(Et)\(_{2}\) on RhB\(^{-}\). In open-framework chalcogenide, the anionic sulfur is balanced by the positively charged nitrogen of -N(Et)\(_{2}\) group from RhB\(^{-}\) after ion-exchange. In addition, S 3p orbitals make a great contribution to the valance band, which accumulates the photogenerated holes and induces the diethylation.

The dramatically different photocatalytic activity of RhB\(^{-}\) and MO\(^{-}\) over 1-AEM and 1-Cs can be ascribed to the structural properties of the framework. As the framework is negatively charged, RhB\(^{-}\) can diffuse into the pores through cation exchange with Cs\(^{+}\) in 1-Cs and utilize the active sites inside the pore. In 1-AEM, due to the bulky protonated AEM cations, the cation exchange between RhB\(^{-}\) and AEM\(^{-}\) is slow. Thus, less active sites are utilized and the photocatalytic rate is much slower than that over 1-Cs. While for negatively charged MO\(^{-}\), it cannot diffuse into the pores of framework due to electrostatic repulsion. As a result, only the active sites on the external surface of chalcogenide crystals can be used for photocatalytic reaction of anionic MO\(^{-}\), resulting in the low photocatalytic rates in both 1-AEM and 1-Cs.

Conclusion

In summary, this work demonstrates that open-framework chalcogenides can be used as efficient and selective porous photocatalytic materials for the decomposition of organic species in aqueous solutions. The porous chalcogenides, uniquely combining uniform porosity and semiconductivity, exhibit both size and charge selectivity in ion-exchange processes. By comparing photocatalytic activities of porous 1-Cs and non-porous 1-AEM, we show that the porosity contributes dramatically to the photocatalytic properties. This study demonstrates a promising platform for the development of charge and size selective photocatalytic materials.

Experimental Section

Chemicals

Germanium dioxide (GeO\(_{2}\), 99.999\%), gallium nitrate hydrate (Ga(NO\(_{3}\))\(_{3}\)·xH\(_{2}\)O, 99.9998\%) and zinc nitrate hexahydrate (Zn(NO\(_{3}\))\(_{2}\)·6H\(_{2}\)O, 98\%) were purchased from Acros. N-(2-aminoethyl)-morpholine (AEM, 98\%+) and sulfur powder (5, 100mesh, 99.5\%) were purchased from Alfa Aesar. All chemicals were used as purchased without further purification. TiO\(_{2}\) with self-doped Ti\(^{3+}\) was synthesized according to the literature.\(^{[32]}\)

Preparation of CPM-120-ZnGaGeS-AEM

125 mg GeO\(_{2}\), 117 mg Ga(NO\(_{3}\))\(_{3}\)·xH\(_{2}\)O, 90 mg Zn(NO\(_{3}\))\(_{2}\)·6H\(_{2}\)O, 260 mg S, and 3.0 mL AEM were mixed thoroughly in a 23 mL Teflon-lined stainless autoclave and stirred for 1 hour. After heating the sealed reaction mixture at 190 °C for 12 days, around 150 mg of small pale yellow rhombic-dodecahedral crystals were obtained. The powder impurities can be washed away using methanol. The pure crystals were obtained by filtering and washing with extra methanol. The phase purity was supported by Powder X-ray diffraction (PXRD). The presence and ratio of Zn/Ga/Ge/S were confirmed by energy dispersive spectroscopy (EDS).

General characterization

Powder X-ray Diffraction (PXRD) data were performed a Bruker D8 Advance powder diffraction meter with CuK\(_{α}\) radiation (40 kV, 40 mA, λ = 1.5418 Å). The simulated powder pattern was calculated using single-crystal X-ray diffraction data of CPM-120-ZnGeS and processed by the Mercury 2.3 program provided by the Cambridge Crystallographic Data Centre. Thermogravimetric analysis (TGA) was performed on a TA Instruments TGA Q500 in the temperature range of 30 to 1000 °C, under nitrogen flow, with a heating rate of 5 °C/min\(^{-1}\). Scanning electron microscopy (SEM) images and energy dispersive spectroscopy (EDS) data were carried out on Philips FEI XL30 field emission scanning electron microscope (FESEM) equipped with PGT-IMIX PTS EDS detector, or on Nova Nano-
Ion-exchange experiment with Cs+

CPM-120-ZnGaGeS-AEM was immersed in 20 mL 1 mM CsCl aqueous solution in a glass vial. The vial was then transferred in an 80 °C oven. During the exchange, the CsCl solution was refreshed every 12 hours. After 2 days, the crystals were filtered and washed with water to remove any residual Cs$^+$ cations on the surface.

Ion-exchange experiment with organic ions

Typically, the experiments were carried out by immersing the CPM-120 materials in the aqueous solutions containing ionic organic species. The solution was kept still during the entire ion-exchange process. 12 mg samples were immersed in 10 mL 2.5 x 10^{-3} M organic aqueous solution. The upper clear solution was taken out for measurement.

Photocatalytic activity test

The photocatalytic activities of CPM-120-ZnGaGeS-AEM and CPM-120-ZnGaGeS-Cs were evaluated by their capability to decompose substrates, including RhB$^+$ and MO$^-$, under visible or UV/Vis light irradiation. To carry out photocatalysis tests for the decomposition of RhB$^+$ and MO$^-$, 50 mg samples were immersed in 100 mL 10 ppm RhB$^+$ or MO$^-$ aqueous solution. Before irradiation, the solution was stirred in the dark for 60 min to reach the adsorption-desorption equilibrium. Then, the solution was irradiated using a 300 W xenon lamp with or without a 420 nm cutoff filter. The extent of degradation at different irradiation times was determined by the UV/Vis absorption measurement of 2 mL of the solution, after the removal of the catalyst by centrifugation at 6000 rpm for 10 min. The extent of photocatalytic activity is expressed as $A/A_0$, where $A$ is the absorption at each irradiated time interval of the maximum peak of the absorption spectrum and $A_0$ is the absorption when adsorption-desorption equilibrium was achieved after 1 hour stirring in the dark.

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Conflict of interest

The authors declare no conflict of interest.

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References


