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Controlling Na Diffusion by Rational Design of Si-Based Layered Architectures

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By means of density functional theory, we systematically investigate the insertion and diffusion of Na and Li in layered Si materials (polysilane and H-passivated silicene), in comparison with Si bulk. It is found that Na binding and mobility can be significantly facilitated in layered Si structures. In contrast to Si bulk, where Na insertion is energetically unfavorable, Na storage can be achieved in polysilane and silicene. The energy barrier for Na diffusion is reduced from 1.06 eV in the Si bulk to 0.41 eV in polysilane. The improvements in storage energetics and in the activation energy for Na diffusion are attributed to the large surface area and available free volume for the large Na cation. Based on these results, we suggest that polysilane may be a promising anode material for Na-ion and Li-ion batteries with high charge/discharge rates.

I. Introduction

Advanced energy storage is essential for the realization of many emerging technologies, such as hybrid electric vehicles (HEVs) and grid harvesting from renewable sources (e.g. solar and wind).1 Li-ion batteries are currently the most popular electrochemical energy storage devices, but their future long-term and large-scale application faces some serious concerns, such as limited lithium resources and its increasing price.2 It is, therefore, desirable to develop rechargeable batteries based on abundant and cheaper alternatives. In this respect, sodium-ion (Na-ion) batteries represent an attractive solution for the applications in smart electric grids that store clean renewable energy. The production of Na is relatively simple and clean, which makes Na-ion batteries considerably more environment-friendly. Based on the above motivation and a growing market for electricity storage, Na-ion batteries receive growing scientific attention.3,9 However, despite the significant advances in the cathode research with many suitable cathode compounds identified,10-12 the knowledge on prospective anode materials is still limited. Interestingly, the reactivity of sodium and lithium with anode materials is quite different despite their close chemical properties. For instance, silicon has been a particularly attractive and actively-studied anode material for Li-ion batteries due to its ultra-high specific capacity (~4.200 mAh·g⁻¹, about ten times larger than that of the conventional graphite anode) and large abundance. Remarkable performance has been achieved with Si nanoparticles,13 nanowires,14, 15 nanosheets,16, 17 and composite materials.18-20 However, recent studies showed that crystalline Si is not attractive as an anode material for Na-ion batteries.21-23 Theoretical studies show that although the formation of the NaSi compound is thermodynamically favorable, Na insertion into crystalline Si is limited. These observations indicate that the limited Na insertion arises from the slow diffusion at low Na concentrations.23-25 The main challenges are associated with the larger size of Na as compared to Li (ionic radii of 0.98 Å and 0.68 Å, respectively),4 resulting in both slow bulk diffusion and prohibitive insertion. Since Na ion is about 44% larger than Li ion, Si and some other host materials with good potential for Li storage do not have sufficiently big interstitial space to accommodate Na ions. This suggests that, the usual diamond bulk structure of silicon may not be suitable for Na-ion batteries.22, 23 Much effort has been made to explore new anode materials for Na-ion batteries, such as tin, antimony, phosphorus, or oxides.26-30 Identification of suitable anode materials and further understanding of Na diffusion mechanisms have become critical challenges for further development of Na-ion batteries.

Here, we suggest that the challenges of poor Na kinetics can be efficiently tackled by an alternative approach – rational design of Si-based anode morphology. It is known that fast kinetics and high capacity can be achieved in battery materials by introducing porosity and large void spaces, as demonstrated in nanotubes and porous/yolk-shell structures.31-33 Besides, improvements in charge/discharge rates can be achieved in layered materials and ultra-thin nanosheets, where lithium storage mainly takes place on the surfaces (in a pseudo-capacitive manner), maintaining rapid Li surface diffusion and electron transport.34 Polysilane and silicene are novel materials belonging to a broad family of layered 2D nanomaterials.35, 36 Polysilane (Si₆H₆) has a layered structure, composed of corrugated H-terminated Si(111) planes with a hexagonal atomic arrangement.37-39 Moreover, the polysilane precursor can be further exfoliated into single-layer Si nanosheets by a solution method as demonstrated by Nakano et al.39-42 Pristine or passivated single-layer Si (silicene) has become
the subject of active research, both theoretical and experimental, since it exhibits a graphene-like band structure with the charge carriers behaving as massless Dirac fermions, quantum spin Hall effect (QSHE) and other attractive properties.\(^5\) \(^3\) \(^4\) \(^5\) \(^6\) \(^7\) Note that a layered structure of Ge (i.e. germanane) has been synthesized for the first time in 2013,\(^8\)\(^9\) promising a bright future for this class of materials.\(^10\) Importantly, polysilane has been successfully tested as an anode material in Li-ion batteries, demonstrating a first charge capacity of 1677 mAh/g and good capacity retention after 10 cycles.\(^11\) \(^12\) \(^13\) \(^14\) \(^15\)\(^16\) The diffusion coefficients of Li during the first charge in the layered polysilane and Si powder electrodes were estimated to be 2.3\(\times\)10\(^{-9}\) and 4.9\(\times\)10\(^{-10}\) cm\(^2\)/s, respectively.\(^17\) Moreover, the specific capacity and reversibility of a polysilane anode can be improved by further modification, such as carbon coating.\(^18\) \(^19\) However, there have been no studies on layered Si materials for sodium-ion batteries so far.

In this work, we use first-principles calculations with van der Waals corrections to study energetics, electronic properties, and diffusion of Na atoms in layered Si nanomaterials. To gain a better understanding of interactions of alkali atoms with the Si host, we compare Na and Li insertion properties in silicene/polysilane with those in bulk Si.\(^20\)\(^21\) We find that, in contrast to Si bulk where Na insertion is energetically unfavorable, Na storage can be achieved in polysilane and silicene. The energy barrier for Na diffusion is reduced from 1.06 eV in the Si bulk to 0.41 eV in polysilane. The improvements are attributed to an unusual layered structure of polysilane which provides large interstitial sites and channels for Na atoms. Although our study does not fully describe the possible evolution of the layered structures (for instance, the amorphization of the layered polysilane by insertion of Li (and possibly Na) to 0 V),\(^22\) but the obtained results can be useful to explain the initial stage of Na/Li diffusion which was identified as important rate-limiting step for the Na-ion/Li-ion batteries.\(^23\) \(^24\) \(^25\) \(^26\) \(^27\) Based on our study, we suggest that polysilane may be promising anode material for the Na-ion batteries.

II. Computational Methods

Our calculations are performed within the density-functional theory (DFT) framework, as implemented in the Quantum Espresso package.\(^28\) The exchange-correlation functional is approximated by the generalized gradient approximation (GGA),\(^29\) using the Perdew-Burke-Ernzerhof (PBE) functional.\(^30\) Ultrasoft pseudopotentials of Rappe-Rabe-Kaxiras-Joannopoulos type are used for the description of electron-ion interactions.\(^31\) The kinetic-energy cutoffs for valence electron wavefunctions and charge density are set to 37 Ry and 370 Ry, respectively. The Brillouin zone is sampled by 5\(\times\)5\(\times\)5, 5\(\times\)5\(\times\)5, and 5\(\times\)5\(\times\)1 Monkhorst-Pack \(k\)-points grid for Si bulk, polysilane, and silicene, respectively. All structures are treated with periodic boundary conditions. A 64-atoms cubic cell is used to model bulk Si. We use 11.52\(\times\)11.52\(\times\)10.9 Å and 11.52\(\times\)11.52\(\times\)20 Å supercells to model polysilane and silicene, respectively. In the latter case, a vacuum layer of greater than 15 Å is added to the supercell to prevent the interaction of single-layer silicene with its periodic images. These supercell sizes have been shown to produce reliable binding energies and migration barriers in the previous studies on Si bulk,\(^24\) \(^25\) \(^26\) \(^27\) \(^28\) and surfaces.\(^31\) \(^32\) \(^33\) \(^34\) \(^35\) The optimized structures are obtained by relaxing all atomic positions using the Broyden-Fletcher-Goldfarb-Shanno quasi-Newton algorithm until all forces are smaller than 0.01 eV/Å.

The Na/Li binding energy per Na/Li atom \((E_b)\) is defined as follows:

\[
E_b(Na/Li) = \frac{E(Na/Li) - E(Si) - nE(Na/Li))}{n}
\]

where \(E(Na/Li - Si)\), \(E(Si)\), and \(E(Na/Li)\) are the total energies of the Si host with \(n\) inserted Na/Li atoms, pure Si host, and a single Na/Li atom (in a large vacuum box), respectively. According to this equation, \(E_b\)\(\times\)0 represents a favorable interaction between Li/Na and Si, while \(E_b\)\(\times\)0 indicates the Li/Na insertion is not energetically favorable.

Activation barriers for Li diffusion are calculated using the climbing-image nudged elastic band (CI-NEB) method.\(^36\) In this method, a set of images (i.e. geometric configurations of the system) is constructed to describe a diffusion pathway. The initial guess of the diffusion trajectory is generated by linear interpolations between the initial and final points of the pathway. The NEB method has been used successfully in the previous studies to determine Li diffusion rates in silicon structures.\(^23\) \(^24\) \(^25\) \(^37\) as well as various electrode materials.\(^38\) \(^39\) \(^40\) \(^41\) \(^42\) \(^43\)

III. Results and Discussion

Crystal structures of bulk Si, layered polysilane and single-layer silicene

The calculated lattice parameters and structural properties of bulk silicon, layered polysilane and single-layer silicene are reported in Table 1. For each case, the lattice vectors and internal atomic coordinates were fully optimized. The optimized lattice parameter of bulk Si is 5.46 Å, in good agreement with the experimental value of 5.43 Å, and the average Si-Si bond length is 2.35 Å. Polysilane (Si\(_2\)H\(_6\)) has a layered structure, composed of corrugated H-terminated Si(111) planes (Figure 1a). Within the Si layers, each Si atom is bonded to three neighboring Si atoms, forming a honeycomb geometry. The forth Si bond, perpendicular to the (111) plane, is saturated by H. The optimized Si-Si bond lengths are 2.36 Å, and Si-H bond lengths are 1.50 Å. The
adjacent Si(111) layers in polysilane are bound to each other by weak van der Waals (vdW) forces. It is known that PBE calculations usually are unable to describe weak dispersive interactions between the layers, resulting in overestimated out-of-plane lattice parameter (as has been demonstrated for graphite, MoS$_2$ and BN).$^{22}$ The effect of vdW interactions in polysilane is taken into account by using the semi-empirical correction scheme of Grimme (DFT-D), which has been proven to successfully describe the structure of layered materials.$^{23}$ Results obtained with PBE and PBE+vdW techniques are compared in Table 1. The PBE calculations produce an overestimated interlayer spacing of 6.1 Å (see Figure 1a). In contrast, PBE+vdW calculations show an optimal interlayer spacing of 5.45 Å, close to the experimental value of 5.5 Å.$^{37}$ The in-plane lattice parameter, governed mainly by strong covalent interactions between Si atoms, is reproduced with a good accuracy by both PBE and PBE+vdW methods, $a = 3.84$ Å.

A unique feature of silicene, a single-layer Si honeycomb structure, is its low-dimensional buckling distortion, as shown in Figure 1b. In contrast to graphene, the $\pi-\pi$ overlap in silicene is very weak due to the increased interatomic distance. The poor bonding leads to an unstable planar structure, but silicene can gain extra stability by buckling.$^{74, 75}$ The calculated sum of the bond angles at each Si atom in silicene is 324°, which is close to the idealized value of 328° for the $sp^3$ tetrahedral configuration. Therefore, H-passivated silicene is expected to combine beneficial properties of single-layer materials (i.e. high surface area without dangling bonds) and a tetrahedral local configuration, which is more natural and stable in silicon. Experimentally, single-layer H-passivated silicene has been derived from polysilane by exfoliation method.$^{39-41, 76}$

Due to experimental availability and stability, we focus on H-passivated silicene in this study. In the following discussion, we refer to layered polysilane as "polysilane" and single-layer H-passivated silicene as "silicene".

### Table I Structural properties of single-layer H-passivated silicene, layered polysilane and bulk silicon

<table>
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<tr>
<th>Method</th>
<th>a (Å)</th>
<th>d (Å) (interlayer spacing)</th>
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<tr>
<td>Silicene</td>
<td>PBE</td>
<td>3.84</td>
</tr>
<tr>
<td>Polysilane</td>
<td>PBE</td>
<td>3.84</td>
</tr>
<tr>
<td></td>
<td>PBE+vdW</td>
<td>3.84</td>
</tr>
<tr>
<td></td>
<td>Exp.$^a$</td>
<td>3.83</td>
</tr>
<tr>
<td>Bulk Silicon</td>
<td>PBE</td>
<td>5.46</td>
</tr>
<tr>
<td></td>
<td>Exp.$^a$</td>
<td>5.43</td>
</tr>
</tbody>
</table>

$^a$ Ref.$^{37}$

### Na and Li insertion in bulk Si

Before we address Na insertion in layered Si nanomaterials, we first examine the insertion properties of Na and Li atoms in the Si bulk crystal as a reference. We perform structure optimizations starting with different initial positions of the alkali atom inside a 64-atoms Si diamond cell. The calculated binding energies and the nearest Na/Li-Si distances are summarized in Table 2. Both Na and Li energetically favor a tetrahedral interstitial configuration (Td, see Fig. 2a) with four nearest Si neighbors inside the bulk Si crystal, in agreement with experimental studies.$^{77}$ However, we find significant differences in the binding energies of Na and Li. The Li binding energy is negative (~1.41 eV, consistent with recent theoretical calculations$^{22, 57}$), denoting favorable interaction between Li and the Si bulk. In contrast, binding energy of Na is positive (+0.60 eV), indicating that Na insertion in bulk Si is not energetically feasible, consistent with recent studies.$^{23}$ The large difference in binding energies of Na and Li is a direct consequence of a much greater stress/strain associated with the Na insertion. Since Na has a larger atomic radius than Li, its insertion leads to larger displacements of neighboring Si atoms (0.15 vs. 0.08 Å for Na and Li, respectively). We also find a smaller charge transfer in the Na-Si system as compared with Li-Si (+0.75|e| and +0.84|e| for Bader charges on Na and Li atoms at Td sites, respectively).

Large deformations and less active charge transfer may be responsible for the unfavorable Na insertion in bulk Si crystal. Besides insertion energetics, slow Na diffusion in bulk Si may seriously hinder its application in Na-ion batteries, as suggested in a recent study.$^{23}$ Single Na atom diffusion in Si bulk occurs in the form of jumps between neighboring Td sites through Hex intermediate. The calculated barrier for Na diffusion (1.06 eV) is much larger compared to that for Li diffusion (0.61 eV).

### Table II Li and Na binding energies, nearest Li-Si and Na-Si distances and Bader charges in Si bulk, polysilane and silicene

<table>
<thead>
<tr>
<th></th>
<th>E, eV</th>
<th>$d_{Li-Si}$, Å</th>
<th>q</th>
<th>E, eV</th>
<th>$d_{Na-Si}$, Å</th>
<th>q</th>
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<tr>
<td>Bulk</td>
<td>-1.41</td>
<td>2.45</td>
<td>+0.84</td>
<td>e</td>
<td></td>
<td>+0.60</td>
</tr>
<tr>
<td>Polysilane</td>
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<td>3.25</td>
<td>+0.91</td>
<td>e</td>
<td></td>
<td>-0.57</td>
</tr>
<tr>
<td>Silicene</td>
<td>-0.90</td>
<td>2.63</td>
<td>+0.88</td>
<td>e</td>
<td></td>
<td>-0.32</td>
</tr>
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</table>

**Fig. 2** (a-b) Stable Na/Li insertion sites in bulk Si: (a) tetrahedral (Td), and (b) hexagonal (Hex). (c) Energy profile for (Td$\rightarrow$Hex$\rightarrow$Td) diffusion path in Si bulk.
Na and Li insertion in layered polysilane and single-layer silicene

The above challenges can be tackled by rational engineering of anode morphology and structure. We first examine possible sites for the Na and Li insertion in the layered structure of polysilane. Our calculations show that both Na and Li prefer the position just above the center of Si₆ hexagonal ring, denoted as hollow site (H, see Figure 1c). Such behavior is typical for the ionically bound impurities which usually prefer adsorption sites of high coordination on semiconductor surfaces. Importantly, we find that both Na and Li have negative binding energies equal to -0.57 and -1.01 eV, respectively. This implies that Na insertion in polysilane is energetically favorable, which is an important advantage over Si bulk. The nearest Na-Si distances in layered polysilane are much larger than in Si bulk (3.34 Å vs. 2.52 Å) providing more interstitial space and efficient stress relaxation. The structural distortions caused by Na insertion in polysilane are found to be small. For instance, the interlayer distance changes only by ~2% upon Na insertion (at NaSi₂H₂ ratio). This differs from the alkali-intercalated graphite, where a large Li-driven interlayer shift (~10.5% in LiC₆) can be observed during Li-ion battery cycling. This result suggests that good structural stability and reversibility upon cycling may be achieved in layered polysilane anodes.

When layered polysilane is exfoliated into single-layers, there are two representative adsorption sites on the H-passivated silicene surface, namely, the hollow site above the center of Si₆ hexagon (H) and the top site above the Si atom (T) (Figure 1c). Both sites have nearly equal Na binding energies (difference around 0.04-0.05 eV). Importantly, Na binding energy in silicene is negative (Table 2), denoting energetically favorable Na adsorption, similar as in polysilane. We note that Na-host and Li-host interactions are enhanced in layered polysilane as compared with single-layer silicene. This is a direct sequence of a stronger Coulomb interaction and charge transfer between adjacent Si layers and the Na/Li atom. For instance, a Bader charge analysis shows charges of +0.86 and +0.79|e| on Na atom in polysilane and silicene, respectively. Similar observations were reported for Li-graphene system, where it was concluded that the weakened Li-graphene interaction may result in a formation of metal clusters and deactivation of anode material. Hence, similar to the single layer graphene/graphite, silicene is expected to have a smaller storage capacity as compared with layered polysilane.

Electronic structure

The binding mechanism between a Na atom and the layered Si hosts is examined via electronic structure analysis. The calculated density of states (DOS, see Figure 3a) suggests that pristine layered polysilane is a semiconductor with a band gap of 2.10 eV, in fair agreement with previous theoretical studies. Note that PBE calculations usually underestimate the band gap, as in the case of bulk Si. The insertion of Na atoms does not significantly change the overall DOS of layered polysilane host (Figure 3b). The adsorbed Na atom transfers its partial charge to Si but does not create an extra level inside the band gap. Na makes two main contributions to the total DOS: one is located deep in the valence band while the other is around the Fermi level in the conduction band as shown in Figure 3c. Due to the charge transfer from Na to polysilane, the Fermi level is shifted into the bottom of the conduction band. Although the pristine polysilane host is a semiconductor, the Na-inserted polysilane has electronic states at the Fermi level. This may possibly lead to an improved electron conductivity of polysilane anode which is beneficial for battery application. This finding is good agreement with the experimental work by McDowell et al., which showed that single Si nanowires in the lithiated state exhibit conductivities two to three orders of magnitude higher than in the pristine (delithiated) state. In order to estimate the amount of charge transfer, we performed a Bader charge analysis based on integration of the charge density over a grid in real space. Our calculations suggest that Na and Li atoms transfer 0.86 and 0.91|e| to polysilane host, respectively. These findings suggest that Na atom becomes almost completely ionized by transfer of its 3s valence electron to polysilane, and the bonding between alkali atom and polysilane host is mainly ionic with a small part of covalence (alternatively, it may be treated as covalent polar).

Na diffusion

Fast Na diffusion is of key importance for the performance of Na-ion batteries since it determines charge/discharge rates of the battery. In certain applications of rechargeable batteries, such as grid/bulk storage, high rate capability is more critical than energy capacity. In the dilute regime, the diffusivity is proportional to the activation energy (i.e. energy barrier) according to classical Arrhenius equation:

![Fig. 3 Density of states of (a) pristine layered polysilane and (b) Na-polysilane. (c) Partial density of states of inserted Na atom in layered polysilane. The Fermi level is shown by dotted lines. The origin is at the valence band maximum of the pristine structure.](image_url)
where \( k_B \) is the Boltzmann constant and \( T \) is the temperature. Accordingly, the intrinsic Na diffusivity in the given anode material can be evaluated by calculating the energy barrier \( (E_{\text{barrier}}) \) with theoretical techniques, such as the nudged elastic band (NEB) method.\(^5\)

As shown in the above discussion, Na diffusion inside bulk Si crystal encounters a large energy barrier of >1eV, which may represent a significant rate limitation. It is, therefore, desirable to examine whether Na diffusion can be facilitated by using layered structures of silicon. In polysilane, the diffusion of alkali atom occurs in the empty interstitial space between the adjacent layers by moving from one stable hollow (H) site to another. We find that the transition state for the diffusion lies at a high-symmetry point where Na is located between two hydrogen atoms. At this site, the alkali atom is located above the mid-point of the Si-Si bond (B, see Figure 1c). The calculated diffusion path \((H \rightarrow B \rightarrow H)\) and the corresponding energy profile are shown in Figure 4. The computed energy barrier for Na diffusion in polysilane is only 0.41 eV, which is a significant improvement over Na diffusion in bulk Si (1.06 eV). Similarly, we find that the energy barrier for Li diffusion is reduced in polysilane as well (0.34 eV in polysilane vs. 0.56 eV in bulk). The reduced activation energy for Na diffusion will lead to improved diffusion rates according to Eq. (2) and, hence, charge/discharge rates of the batteries. This trend compares well with the available experimental measurements of Li diffusion coefficients in layered polysilane and Si powder.\(^3\)

We then investigate how the exfoliation of polysilane into single-layers affects Na and Li diffusion rates. The diffusion of Na on the surface of single-layer silicene occurs in the form of jumps between the neighboring hollow surface sites as shown in Figure 5. Our calculations suggest that the diffusion path goes through an intermediate state located on top of a Si atom, i.e. a T surface site. The calculated energy barrier for Na diffusion on silicene is only 0.12 eV, much lower than in Si bulk (1.06 eV) and lower than in polysilane (0.41 eV). The calculated energy barrier for Li diffusion on silicene is 0.21 eV. Interestingly, the surface diffusion barrier in silicene decreases with cation size \( E_{\text{barrier}}(\text{Na}) < E_{\text{barrier}}(\text{Li}) \), similar to the diffusion of alkali atoms (e.g. Li, Na and K) on graphene.\(^6\) This trend is opposite to bulk and polysilane cases where Li has the lowest migration barrier.

These results suggest that alkali atom diffusion in polysilane and silicene is mainly governed by the following factors: (1) in polysilane and bulk, diffusion is controlled by the available interstitial space and free volume, which promotes migration of smaller Li atoms; (2) on the silicene surface, Li atoms experience a stronger potential than Na. Li experiences a more corrugated potential in the hexagons of silicene due to its smaller ionic radius and smaller Li-silicene distance compared with Na (Table II). As the alkali atom radius increases (from Li to Na), the distance to the surface increases, and the effect of the corrugation of the silicene is reduced. Therefore, the surface diffusion barrier is correlated with atomic radius, promoting fast Na diffusion.
Conclusions

We have performed first-principles calculations on layered forms of silicon – polysilane and silicene – as potential anode materials for Na-ion batteries. Bulk Si has been previously identified as not a suitable material for Na-ion batteries due to unfavorable Na insertion energetics and slow Na kinetics. However, we have shown that by rational design of Si-based structure and morphology, the above challenges can be efficiently resolved. In particular, we have shown that:

1) Na insertion in layered polysilane and silicene is exothermic with negative (favorable) single Na atom binding energies of -0.57 and -0.32 eV, respectively (in contrast to unfavorable Na binding energy of +0.60 eV in bulk Si).

2) Although the pristine layered polysilane host is semiconductor, the Na-inserted polysilane has electronic states at the Fermi level. This may lead to an improved electron conductivity of polysilane anode which is beneficial for battery application.

3) The diffusion barrier for Na migration has been reduced from 1.06 eV in the Si bulk to 0.41 eV in layered polysilane suggesting much facilitated Na diffusion rates.

The above improvements can be attributed to a beneficial architecture of polysilane and silicene. Due to the large surface area, large available free volume, and low activation energy for Na diffusion, layered polysilane may be a promising anode material for Na-ion batteries. We expect that our theoretical results will inspire further experimental studies.

Notes and references

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