Micromechanism Study of Strengthening Effect of Copper on Gold Thiosulfate Leaching

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ABSTRACT: To study the effect of copper on gold thiosulfate leaching, the gold dissolution of three different sample powders (gold, gold/copper, and gold/copper oxide) in a solution of 5 mM Cu$^{2+}$, 0.4 M ammonia, and 0.1 M thiosulfate was studied. Scanning electron microscopy analysis showed no sulfur passivation on the gold surface, and there were more prominent corrosion pits on the gold surfaces of samples that were ground with copper or copper oxide. The Evans diagrams showed that copper and copper oxide can promote both the anode and cathode processes of gold dissolution. Based on first principle simulations, copper and copper oxide exhibited the ability to disrupt the stability of gold surface atoms and cause different degrees of relaxation. Both copper and copper oxide reduce the d-band center of the gold surface atoms and the adsorption between gold and thiosulfate. In addition, the bond length of the S−S bond of thiosulfate adsorbed onto the gold surface was longer when copper or copper oxide were not present. According to the change in the potential surface energy, the energy barriers for gold atom dissolution from gold, gold/copper, and gold/copper oxide surfaces were 1.79, 0.72, and 1.01 eV, respectively.

1. INTRODUCTION

As the oxidation catalyst of the gold thiosulfate leaching process, Cu$^{2+}$ is very important for the dissolution process of gold. Copper ions are a very effective oxidant for the dissolution of gold, regardless of whether in the traditional ammonia system $\text{1,5}$ or in the new ethylenediamine $\text{6,7}$ and citric acid systems. $\text{8}$

The dissolution of gold in copper ammonium thiosulfate solution is an electrochemical process. The oxidation of gold occurs in the anode area, as shown in eq 1, and the reduction of copper ions occurs in the cathode area, as shown in eq 2. The resulting Cu($S_2O_3)_3^-$ reacts with dissolved oxygen to form Cu(NH$_3$)$_4^{2+}$, as shown in eq 3. Thus, the copper ion can catalyze the dissolution of gold. In addition to copper ions, cobalt and nickel ions can also be used as catalysts for gold leaching in thiosulfate solution. $\text{3−5}$

\[
\text{Au} + 2S_2O_3^{2−} \rightarrow \text{Au(S}_2\text{O}_3)_2^{3−} + e^− \quad (1)
\]

\[
\text{Cu(NH}_3\text{)}_4^{2+} + 3S_2\text{O}_3^{2−} + e^− \rightarrow \text{Cu(S}_2\text{O}_3)_3^{5−} + 4\text{NH}_3 \quad (2)
\]

\[
4\text{Cu(S}_2\text{O}_3)_3^{5−} + 16 + \text{O}_2 + 2\text{H}_2\text{O} \rightarrow 4\text{Cu(NH}_3\text{)}_4^{2+} + 4\text{OH}^− + 12S_2\text{O}_3^{2−} \quad (3)
\]

Copper ions not only act as an oxidant but also affect the anodic dissolution of gold. Numerous scholars have studied the effect of Cu$^{2+}$ on the dissolution of gold from various perspectives. Smith et al. $\text{9}$ and Nicol et al. $\text{10}$ found that Cu$^{2+}$ is beneficial to removal of sulfur-containing adsorbates on gold surfaces, thus increasing gold dissolution. In another study,

Accepted: November 26, 2020
Published: December 7, 2020

Received: September 16, 2020
Zhang and Nicol\textsuperscript{11} found that copper ions can promote gold dissolution in alkaline sodium thiosulfate solutions using electrochemical technology. When the electrode potential is maintained at 0.3 V, the addition of copper ions can improve the gold dissolution rate. It is suggested that the formation of a Cu\textsuperscript{2+}\text{−}S\text{2O}\text{3}\text{−}\text{−}O\text{2} intermediate, which is easier to reduce than oxygen, or a mixed complex of (Au, Cu) (S\text{2O}\text{3})\text{2}\text{−} may promote the cathodic process of gold dissolution. It has been shown that copper can promote the dissolution of gold when gold powder is milled with copper (the ion, metal, or oxide form) during leaching. By calculating formation equilibrium constants, Senanayake\textsuperscript{12} discovered low-concentration copper complexes, such as Cu(S\text{2O}\text{3})\text{2}, Cu(S\text{2O}\text{3})\text{2}\text{−}, and Cu(OH)\text{3}\text{−} in the solution. According to Gibbs free energy calculations, these complexes can react with gold to form Au(S\text{2O}\text{3})\text{2}\text{−}, which can promote gold dissolution. Furthermore, Breuer and Jeffer\textsuperscript{13} tested different oxidants (oxygen, cobalt ions, and copper ions) in a solution of sodium thiosulfate and ammonia. The mixed potential remained constant, and the copper ions proved to be the most effective oxidant. Even in a system with only thiosulfate in solution, the addition of a small amount of copper ions can still promote the dissolution of gold.\textsuperscript{11,14}

The dissolution process is a chemical reaction at the solid–liquid interface; therefore, the structural change of the solid surface often affects the whole reaction.\textsuperscript{15,16} CeO\text{2} rods with (1\text{ 0} 0)/(1\text{ 1} 0) exposed surfaces have stronger Pt nanocrystal capture ability and catalytic performance for methanol oxidation than CeO\text{2} plates and CeO\text{2} cubes with (1\text{ 1} 1) and (1\text{ 0} 0) faces.\textsuperscript{17,18} Zhuang and co-workers\textsuperscript{19} observed that the interaction between oxygen and the Ni surface after 3d metal modification was significantly weakened. For example, the desorption temperature of oxygen on the surface of a Ni–Cr catalyst decreased by 130 °C, which was not observed with pure Ni. This entire reaction was affected by changes in the electronic orbit on the solid surface, whether it was changes to the crystal structure of the solid or modifications of other elements on the solid surface.\textsuperscript{20–23} This causes the adsorbed molecules to decompose or atoms to dissociate from the bulk solid surface.\textsuperscript{24,25}

The aforementioned studies about gold leaching have investigated the effects of copper ions on the dissolution of gold with respect to changes in the copper ion complex or the passivation of the gold surface. However, the micromechanism behind copper promoting gold atom dissolution has not been reported, especially when changes to the electronic structure of the gold surface were caused by copper powder or copper oxide powder. In this paper, the electronic structure of the gold and the energy changes in the different intermediates during the gold dissolution were analyzed by first principle simulations. The results of this work elucidated the micromechanism behind the promotion of gold dissolution in thiosulfate solution by copper.

2. RESULTS AND DISCUSSION

2.1. Dissolution Study. 2.1.1. Gold Leaching and Changes in the Copper and Thiosulfate Ion Concentrations. Figure 1 illustrates the gold leaching percentage in the copper, ammonia, and thiosulfate solution. The leaching percentage reached 68% within 6 h for the experiments using 10 mg of gold powder. When the gold powder was ground with copper or copper oxide, leaching rates of 88 and 82%, respectively, were obtained. These results show that the presence of copper or copper oxide increases gold dissolution during thiosulfate leaching and are consistent with results reported by Zhang and Nicol.\textsuperscript{11}

\[
\begin{align*}
\text{Cu} + 2\text{NH}_3 &= \text{Cu(\text{NH}_3)\text{2}+} + e^- \quad \Phi = -0.12 \text{ V} \\
\text{CuO} + 4\text{NH}_3 + \text{H}_2\text{O} &= \text{Cu(\text{NH}_3)\text{4}+} + 2\text{OH}^- \\
\Delta G &= 47.2 \text{ kJ/mol}
\end{align*}
\]

Here, $\Phi$ was calculated using $\Phi^{0}[\text{Cu}^+/\text{Cu}]-0.0591 \log[\beta]$, and $\Delta G$ was calculated using the values reported by Liu et al. under the condition 298 K and 1 atm.\textsuperscript{26}

Using eq 4, the redox potential of Cu(\text{NH}_3)\text{2}+ was determined to be -0.12 V, while that of Cu(\text{NH}_3)\text{4}+ was 0.24 V.\textsuperscript{27} These values confirm that copper powder can be dissolved in the leaching solution. Although the Gibbs free energy of eq 5 is positive, there are cases of ammonia leaching of copper oxide in actual production;\textsuperscript{28} therefore, copper oxide may also be dissolved in solution. The effects that copper and copper oxide have on the changes in the copper ion concentrations are shown in Figure 2. The results show that the copper ion concentration in the three groups of experiments was approximately the same. This is because, only small amounts of copper powder and copper oxide were added. Because of the reaction between copper ion and thiosulfate, as shown in eq 2, the concentration of copper ions will decrease with the prolonged leaching time.\textsuperscript{4,29} In
addition, the thiosulfate concentrations for the three reaction systems were very similar.

2.1.2. Scanning Electron Microscopy Characterization of Gold Powders after Leaching.

The microscopic appearance of gold powder after leaching is presented in Figure 3. Numerous corrosion pits were observed on the gold surface, and while the surface primarily consisted of gold, small amounts of oxygen were also present. However, sulfur signals were not detected in the element distribution mapping of the sample. More noticeable corrosion edges and larger corrosion pits were observed on the gold surface of the gold/copper powder (Figure 3b) than on the surface of the fresh gold powder sample. Furthermore, the weight percentage of oxygen was higher on the surface of the gold/copper sample than on the surface of the fresh gold powder. Additionally, there were no copper signals observed on the gold surface, indicating that the copper powder in the sample had dissolved in the leaching solution. The amount of copper powder added was only 2 mg, with a corresponding molarity of only 0.03 mmol, so the copper ion concentrations of different experiments presented in Figure 2 are very similar.

Element distribution mapping of the gold/copper oxide sample was recorded, and 24.71% copper was observed. Furthermore, large corrosion pits and obvious corrosion edges on the sample surface were also seen (Figure 3c). It seems that the corrosion process proceeds along the edge of the copper-covered area. According to the scanning electron microscopy (SEM) characterization results, there was no passivation material containing sulfur on the surface of the gold. After leaching, more obvious corrosion pits were seen on the gold surfaces of the gold/copper and gold/copper oxide samples than on those of the pure gold sample.

2.2. Electrochemical Study. According to the Tafel curve, the open circuit potential of different systems can be easily obtained.30,31 Figure 4 illustrates that the open circuit potential of the gold powder is 0.15 V. This potential changes to −0.1 and 0.1 V, respectively, when the copper powder and copper oxide are present. These results show that the dissolution process of gold is promoted with the addition of copper or copper oxide, which strengthen the anode reaction process.32 Copper can dissolve in leaching solutions, and Drissi-Daoudi et al.33 found that the potential of copper oxidation to univalent copper ions was −0.32 V (relative to saturated calomel electrode), which is close to the −0.1 V (relative to standard hydrogen electrode) value. Therefore, the enhancement effect of the anode process of Au–Cu electrodes may be partly due to the dissolution of copper. To eliminate the interference of copper oxidation in the anode process, we tested the anode and cathode processes of gold dissolution and determined the open circuit potentials and current densities of gold dissolution on different electrodes using Evans diagrams (Figure 5).13,34

Figure 3. Scanning electron micrographs of gold powder and element distribution mapping: (a) gold powder sample before leaching; (b) gold powder sample after leaching; (c) gold/copper powder sample after leaching; (d) gold/copper oxide sample after leaching.

Figure 4. Tafel representation of the linear sweep voltammetry of different electrodes at a positive scanning rate of 10 mV/s in a solution of 5 mM Cu^{2+}, 0.4 M NH₃, and 0.1 M thiosulfate.
It can be seen from Figure 5 that the presence of copper powder or copper oxide strengthens the anode and cathode processes of gold leaching. The open circuit potential at the gold electrode was 0.18 V, which is slightly higher than that of the actual leaching system (0.15 V, Figure 4). This lower value of the actual system is because of the presence of copper ions, while the anode process measured in Figure 5 includes only the oxidation process of gold in the thiosulfate solution. Because copper ions are removed from the solution, the open circuit potential obtained by the Evans diagram is higher than that measured in the actual system. This result confirms that copper ions can promote the anodic process of gold leaching.

As shown in Figure 5b, the open circuit potential of the Au–Cu electrode is –0.05 V. Compared with the potential of the actual leaching system (–0.1 V), the open circuit potential of the Au–Cu electrode is shifted positive, indicating that the oxidation of copper interferes with the measurements recorded in Figure 4. The open circuit potential of the Au–CuO electrode obtained by the Evans diagram is relatively the same as the measured value of the actual leaching system (approximately 0.1 V). The effects of copper and copper oxide on the open circuit potentials and leaching currents of gold dissolution are summarized in Table 1. Copper and copper oxide cause the open circuit potential of gold to decrease by 0.23 and 0.08 V, respectively. Moreover, they cause the leaching current of gold to increase from 0.08 to 0.45 and 0.12 mA cm$^{-2}$, respectively.

To study the effect of copper and copper oxide on the gold dissolution process, the apparent activation energy of the gold dissolution reaction was also investigated. Linear sweep voltammetry curves were measured at different temperatures (Figure 6). The current density of 0.18 V was chosen to represent the rate of gold dissolution of the gold electrode, while a current density at –0.05 V was chosen for the gold/copper electrode; 0.10 V was chosen for the gold/copper oxide electrode. Equations 6 and 7 were used to calculate the apparent activation energy ($E_a$) for the gold dissolution reaction.

\[
j = F\alpha \exp \left(-\frac{E_a}{RT}\right)
\]

\[
E_a = -2.303R\frac{\delta \log j}{\delta (1/T)}
\]

where $j$ is the current density value, $F$ is the Faraday constant (96,485.3 C/mol), $k$ is the reaction constant, $\alpha$ is the reactant activity, $R$ is the gas constant (8.314 J/mol K), and $T$ is the thermodynamic temperature.

Figure 6 shows that temperature has an obvious effect on the anodic process of gold dissolution, and there is a current peak at –0.05 V on the gold/copper electrode. The relationship between the $j$ of the gold dissolution process and temperature under different electrode systems is shown in Figure 7. According to the fitting results, the $\delta \log j/\delta \log (1/T)$ values

![Figure 5](https://dx.doi.org/10.1021/acsomega.0c04544)

**Figure 5.** Evans diagrams of different work electrodes. Anode sweep curves had a positive scanning rate of 10 mV/s in a 0.1 M thiosulfate solution, cathode sweep curves had a negative scanning rate of 10 mV/s in a 5 mM Cu$^{2+}$ and 0.4 M NH$_3$ solution; (a) gold electrode; (b) gold/copper electrode; (c) gold/copper oxide electrode.

| work electrodes          | open circuit potential/V | leaching current/mA cm$^{-2}$ |
|--------------------------|--------------------------|-------------------------------|
| gold                     | 0.18                     | 0.08                          |
| gold/copper              | –0.05                    | 0.45                          |
| gold/copper oxide        | 0.10                     | 0.12                          |

(31804)
are $-2.81$, $-2.12$, and $-2.43$ for the gold, gold/copper, and gold/copper oxide electrodes, respectively. Additionally, $E_a$ values of the gold dissolution process can be calculated using eq 7 for each of the electrodes, giving values of 53.8, 40.6, and 

Figure 6. Linear sweep voltammetry curves of different working electrodes at a positive scanning rate of 10 mV/s in 0.1 M thiosulfate solution at different temperatures.

Figure 7. Fitting relationship between gold leaching current density and temperature of different electrodes.
46.5 kJ/mol, for the gold, gold/copper, and gold/copper oxide electrodes, respectively. Based on these results, we concluded that the appearance of copper or copper oxide can reduce the $E_f$ of gold dissolution.

### 2.3. Micromechanism Study

The dissolution of gold reflects the adsorption effect at the solid–liquid interface. During adsorption, bonding between the solid surface and the adsorbate molecules occurs, which destroys the stability of the adsorbed molecules and the solid surface structure. However, limited studies have been conducted on thiosulfate adsorbed onto different gold surfaces and the influence that this adsorption effect has on the thiosulfate molecular and gold surface structure.

We have established the calculation model as shown in Figure 8 to study changes in the d-band density of the first-layer atoms on the surface of gold. Figure 8 shows the change of the gold surface after structural optimization. Copper alters the relaxation state of gold atoms in the first layer, and when copper oxide is present, this relaxation phenomenon becomes more apparent. In addition, the second layer of gold atoms demonstrates an external diffusion trend, as shown in Figure 8c. The density of d-band states of the first-layer surface atoms is shown in Figure 9. With copper or copper oxide present, the width of the d-band increases, the delocalization improves, and the density of the states at the Fermi level decreases. The d-band center of the first-layer atoms on Au(111) is $-3.01 \text{ eV}$, but when copper and copper oxide are present, this value becomes $-3.30$ and $-3.20 \text{ eV}$, respectively. Copper and copper oxide decrease the d-band centers of atoms on the surface of gold, which is consistent with other related scholars and indicates that the reactivity of the gold surface may be decreased.

The effect that these changes in the d band densities have on thiosulfate adsorption to the gold surfaces was also studied. During the process of gold leaching, we had hoped that the adsorption effect between the gold surface and thiosulfate could destroy the bonding between gold atoms on the surface, while the thiosulfate molecules remained stable. Figure 10 shows the adsorption geometry of thiosulfate on different gold surfaces. Because of its high d-band center, the gold atoms on the surface have high reactivity (Figure 10a). The relaxation degree of the gold atoms on the surface is the most prominent after adsorption. In addition, the effect of adsorption on the structure of thiosulfate is also very significant and the S–S bond length becomes $3.489 \text{ Å}$. When copper atoms are present on the gold surface the S–S bond length becomes $3.080 \text{ Å}$, and in the presence of copper oxide, the S–S bond length decreases even further to $1.904 \text{ Å}$, which is close to the S–S bond length of thiosulfate by itself ($1.881 \text{ Å}$). This indicates that the adsorption effect is weakest on the structure of thiosulfate and predominantly affects the bonding of gold atoms on the surface, as shown in Figure 10.

The aforementioned results demonstrate that although the high d-band center and reaction activity of gold atoms on the surface can strengthen the adsorption effect on thiosulfate, the dissolution of gold is not accelerated. This could be ascribed to the damage degree of the S–S bond being greater than in the absence of copper or copper oxide on the gold surface (Figure 10). The destruction of thiosulfate stability caused by strong adsorption may be the reason for the passivation of gold surfaces. Some scholars have found that the addition of copper ions can negate this passivation phenomenon on the surface of gold, which may be related to the reduced d-band center and reaction activity of gold surface atoms. In addition, the higher reaction activity of gold surfaces not only affects the stability of thiosulfate but also affects the stability of polythionates in gold leaching solutions, which promotes their decomposition. It has been reported that polythionates decompose on the surface of gold, generate different sulfur species, and inhibit the dissolution of gold.

The dissolution process of gold proceeds as follows: thiosulfate first adsorbs onto the gold surface, followed by the combination of thiosulfate and gold atoms that subsequently forms free radicals, and finally, the separation of these radicals from the gold surface and their combination with thiosulfate in solution results in stable complex ions.
Therefore, not only do we pay attention to the process of thiosulfate adsorption on gold surfaces but also study the dissociation process of gold atoms from the surface (Figure 11).

\[
\text{Au} + \text{S}_2\text{O}_3^{2−} \rightarrow \text{AuS}_2\text{O}_3^{2−}(\text{ads}) \\
\text{AuS}_2\text{O}_3^{2−}(\text{ads}) \rightarrow \text{AuS}_2\text{O}_3^{−}(\text{ads}/\text{aq}) + e^{-} \\
\text{AuS}_2\text{O}_3^{−}(\text{ads}/\text{aq}) + \text{S}_2\text{O}_3^{2−} \rightarrow \text{Au(S}_2\text{O}_3)_2^{3−}(\text{aq})
\]

Figure 11. Reaction path of gold dissolution from the gold surface.

We have studied the energy changes of two intermediate states that exist during the process of gold dissolution. The reaction path is shown in Figure 11. According to the trend of energy changes, the energy barrier of gold dissolution can be obtained.\(^{12}\) TS1 represents the structure of thiosulfate adsorbed on the gold surface, and TS2 corresponds to the structure of gold atoms dissociated from the surface. The reaction paths of gold dissolution when copper or copper oxide exist on the surface are shown in the Figures 12 and 13. As demonstrated in Figure 11, it is necessary for the reaction to overcome the energy barrier of 1.79 eV from the initial state of the gold surface to the departure of the intermediate through thiosulfate adsorption. In the presence of copper and copper oxide, the energy barrier becomes 0.72 and 1.01 eV, respectively. Copper and copper oxide decrease the energy barrier of gold dissolution and promote gold leaching.

3. CONCLUSIONS

The micromechanism of copper and copper oxide on the dissolution of gold in a copper, ammonia, and thiosulfate solution was studied. When grinding 10 mg of gold powder with either 2 mg of copper or copper oxide, the gold leaching percentages increased by 20 and 14%, respectively, over 6 h. The concentrations of the copper and thiosulfate ions in the leaching solution exhibited negligible changes among the different experimental groups. After leaching, SEM characterization showed that there were more apparent corrosion pits on the gold surface being ground with copper or copper oxide. Furthermore, when copper and copper oxide were present the open circuit potential was shifted from 0.18 to -0.05 and 0.1 V, respectively, and the leaching current was increased from 0.08 to 0.45 and 0.12 mA cm\(^{-2}\), respectively. The presence of copper or copper oxide increased the relaxation of atoms on the surface of gold but reduced the central energy level of the d-band from \(-3.01\) to \(-3.30\) and \(-3.20\) eV, respectively. On the gold surface, the S−S bond length in thiosulfate was 3.489 Å, but when copper and copper oxide were present on the gold surface, this bond length became 3.080 and 1.881 Å, respectively. This indicates that copper and copper oxide can reduce the damage that the adsorption effect has on the stability of thiosulfate. When the atoms on the surface of gold dissolved in the thiosulfate solution, the energy barrier that the reaction had to overcome is 1.79 eV, and when copper and copper oxide were present, this energy barrier decreased to 0.72 and 1.01 eV, respectively.

4. EXPERIMENTAL SECTION

The gold powder (44−74 μm), copper powder (<44 μm), and copper oxide (<44 μm) used in this study are all 99.99% pure. The sodium thiosulfate, copper sulfate pentahydrate, ammonia (25%), hydrogen peroxide, nitric acid, and hydrochloric acid are analytically pure. Deionized water was used to prepare the solutions. A mixture of copper (2 mg) and gold (10 mg) powders were ground in an agate mortar for 5 min to acquire the gold/copper sample. A mixture of copper oxide (2 mg) and gold (10 mg) powder were ground in an agate mortar for 5 min to acquire gold/copper oxide samples. To avoid the interference caused by changes in the gold particle size during the grinding process, fresh gold powder (10 mg) was also ground for 5 min for the leaching experiments.

Hydrogen peroxide and hydrochloric acid were added to the solution samples in sequence, and then, the solutions were each boiled for 5 min. Atomic absorption spectroscopy was then used to determine the concentration of gold in each sample. The concentration of thiosulfate ions was determined using the iodometric method,\(^{43}\) and the absorbance of the Cu(NH₃)₄²⁺ complex was measured at 605 nm using a UV−vis spectrophotometer. All measured values were corrected for the background absorbance of the other reagents. The morphology of the reagents...
Quantum chemical calculations were performed using the Materials Studio program CASTEP,\textsuperscript{31,37,44,45} which is a software program theoretically based on density functional theory. Within the generalized-gradient approximation, the Perdew–Burke–Ernzerhof function is adopted as the exchange–correlation function. The interaction between valence electrons and the ion core is described by an ultrasoft pseudopotential. The convergence tolerances for geometry optimization calculations were as follows: 0.002 Å for the maximum displacement, 0.05 eV/Å for the maximum force, 2.0 × 10\(^{-5}\) eV/atom for the energy, 2.0 × 10\(^{-6}\) eV/atom for the self-consistent field, and 351.0 eV for the plane-wave cut-off. Three layers of (1 1 1) crystal surfaces were used to simulate an actual gold surface. The Cartesian coordinates of the gold atoms in the bottom surface were fixed as a constant during the geometry optimization. For the Au (1 1 1) surface, a \(2 \times 4 \times 1\) supercell with periodic boundary conditions on the \(x\) - and \(y\) -axes was used to model the infinite sheet. The vacuum thickness in the direction perpendicular to the (1 1 1) surface was 15 Å.

The leaching of gold was carried out in a 250 mL conical flask, and the solution consisted of 200 mL of 5 mM Cu\(^{2+}\), 0.4 M NH\(_3\), and 0.1 M thiosulfate. A magnetic stirrer was used to maintain the rotation speed at 300 rpm, and the reaction temperature was 23 ± 1 °C.

![Figure 14. Image of the working electrodes. (Photograph courtesy of Yanhe Nie. Copyright 2020.)](image)

**Acknowledgments**

This work was financially supported by the Key Scientific and Technological Project of Henan Province (182102210056), the Fundamental Research Funds for the Universities of Henan Province (NSFRF180333 and NSFRF200311), and the Doctoral Foundation of Henan Polytechnic University (B2018-43).

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