Interfacial regulation of aqueous synthesized metal-semiconductor hetero-nanocrystals

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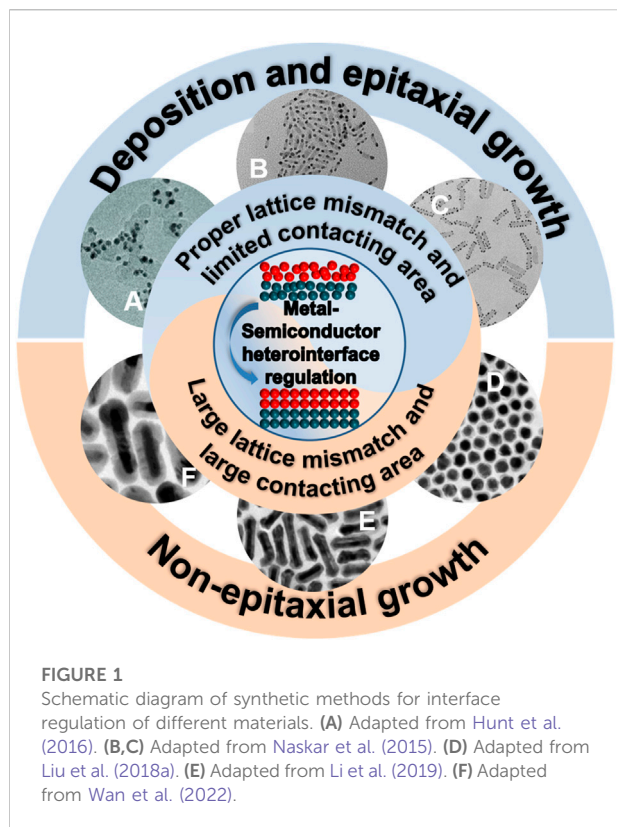
Integrating metal and semiconductor components to form metal-semiconductor heterostructures is an attractive strategy to develop nanomaterials for optoelectronic applications, and the rational regulation of their heterointerfaces could effectively influence their charge transfer properties and further determine their performance. Considering the natural large lattice mismatch between metal and semiconductor components, defects and low crystalline heterointerfaces could be easily generated especially for heterostructures with large contacting areas such as core-shell and over quantum-sized nanostructures. The defective interfaces of heterostructures could lead to the undesirable recombination of photo-induced electrons and holes, which would decrease their performances. Based on these issues, the perspective focusing on the most recent progress in the aqueous synthesis of metal-semiconductor heterostructures with emphasis on heterointerface regulation is proposed, especially in the aspect of non-epitaxial growth strategies initiated by cation exchange reaction (CER). The enhanced optoelectronic performance enabled by precise interfacial regulations is also illustrated. We hope this perspective could provide meaningful insights for researchers on nano synthesis and optoelectronic applications.

KEYWORDS

metal-semiconductor, heterostructure, lattice mismatch, cation exchange, interfacial

Introduction

Colloidal nanocrystals (NCs) have been widely investigated both in basic research and applications in the past few decades (Tan et al., 2017; Clark et al., 2019; Huang et al., 2020; Acharya et al., 2021; Goldzak et al., 2021; Guntern et al., 2021; Ondry et al., 2021; Liu Z. et al., 2022; Coropceanu et al., 2022; Li and Wang, 2022; Wang and Dou, 2022; Zhang et al., 2022; Zhu et al., 2022), in which metal-semiconductor heteronanocrystals (HNCs)

FIGURE 1
Schematic diagram of synthetic methods for interface regulation of different materials. **(A)** Adapted from Hunt et al. (2016). **(B,C)** Adapted from Naskar et al. (2015). **(D)** Adapted from Liu et al. (2018a). **(E)** Adapted from Li et al. (2019). **(F)** Adapted from Wan et al. (2022).

are attracting more attention due to their functional coupling between different substances (Wang et al., 2014; Strobbia et al., 2015; Kamarudheen et al., 2020; Kumar et al., 2020; Wang et al., 2021; Yin et al., 2022). In particular, the core-shell structure, in which the metal core is completely encapsulated by the semiconductor shell, achieves the greatest degree of heterogeneous contact interface, and thus hopefully achieves the greatest degree of functional coupling (Naya et al., 2018; Das et al., 2020). Besides, the core-shell structure has various morphologies, including nanoparticles, nanopolyhedron, nanorods, *etc.* The controllable morphologies are conducive to controlling its physical and chemical properties. To date, metal-semiconductor HNCs have exhibited high performance in many fields, such as photocatalysis (Kumar et al., 2020), sensors (Strobbia et al., 2015), biomedical treatment (Wang et al., 2021), *etc.* However, the properties of metal-semiconductor HNCs are affected by various factors such as morphology, size, and composition among which the heterointerface should also be considered (Liu and Zhang, 2020; Zhang et al., 2021). The high crystallinity and the well-defined heterointerface of the metal-semiconductor heterostructure could facilitate carrier migration, thereby enhancing the optoelectronic properties of the material. Therefore, the interface regulation of metal-semiconductor HNCs has been widely concerned by researchers (Liu and Zhang, 2020; Song et al., 2020; Zhang et al., 2021). As shown in Figure 1, an issue in interface

regulation is the large lattice mismatch when forming heterointerfaces due to the inherent difference in lattice constants between different materials, especially when constructing metal-semiconductor core-shell structures. In this perspective, we summarize the effect of lattice mismatch on the synthesis of metal-semiconductor HNCs and the progress have been made in the construction of well-interfaced metal-semiconductor HNCs, especially the non-epitaxial growth strategies induced by cation exchange reaction (CER). And then, the influence of interface regulation on performance is introduced. Finally, some existing problems and challenges in heterogeneous interface regulation engineering are concluded.

Lattice mismatch at metal-semiconductor heterointerfaces

Due to the different lattice constants of the different materials, stress will be generated near the growth interface, and then a crystal defect-misfit dislocation will be generated when another material is selectively grown on a certain crystalline substrate, called lattice mismatch (Gabrys et al., 2018; Chen et al., 2020). The lattice mismatch between metal-metal heterostructures and semiconductor-semiconductor heterostructures is usually less than 20% due to the two similar crystal structures of materials involved. However, for metal-semiconductor heterostructures, due to the obviously differentiated crystal structure, the lattice mismatch is often more than 20% (Liu and Zhang, 2020). The large lattice mismatches could lead to defects at the heterointerfaces and thus affect charge transport and utilization. Therefore, the construction of well-defined heterointerfaces is crucial for the overall application of heterostructures (Weng et al., 2014; Jang et al., 2017; Zhou et al., 2022). In the past decade, researchers have made great efforts to modulate the heterointerfaces and some low defect interfaces were fabricated by epitaxial growth with various morphologies (Bian et al., 2015; Fan et al., 2015; Jing et al., 2016; Xiong et al., 2017; Ding et al., 2022). However, Royer et al. proposed the premise of epitaxial growth is that the lattice mismatch between the two different components is less than 15% (Tan et al., 2018), and the core-shell heterostructure is more demanding, which should be less than 5% (Fan et al., 2008). Thus the epitaxial growth method is limited in the synthesis of core-shell heterostructures with fully contacted heterointerface and atomic-designed interfaces under large lattice mismatch, such as metal-semiconductor core-shell NCs. For example, in 2008, Chen et al. (2008) proposed the epitaxial growth of CdS semiconductors on Au cores. However, due to the natural large lattice mismatch between metals and semiconductors, the heterointerface of the synthesized Au@CdS core-shell NCs was not clear and had many defects. To overcome this challenge, CER facilitated non-epitaxial growth was developed in recent years, which enabled the synthesis of metal-semiconductor core-

shell NCs with a single crystalline semiconductor shell and atomically clean heterointerface. In the next section, the metal-semiconductor heterostructures with considered interface enabled by epitaxial growth strategy will be first discussed. Then, a non-epitaxial growth strategy for the synthesis of metal-semiconductor core-shell nanostructures with an engineered interface will be emphasized.

Deposition and epitaxial growth of heterostructures

In recent years, tremendous progress has been made in the synthetic control of NCs, including size, morphology, composition, and so on (Costi et al., 2010; Hunt et al., 2016; Jansons and Hutchison, 2016; Ma et al., 2016; Nasilowski et al., 2016; Liu et al., 2021; Adenle et al., 2022; Liu et al., 2022a; Zheng et al., 2022). As an important component of NCs, heterostructures have also been extensively studied, and the main synthesis methods include epitaxial growth, deposition, etc (Mokari et al., 2004; Sun et al., 2009; Carbone and Cozzoli, 2010; Yang and Ying, 2011; Chen et al., 2012; Ji et al., 2022; Yang et al., 2022). The epitaxial growth method refers to the reaction of growing a crystalline material on another crystalline substrate with a well-defined surface, which follows the similar crystal orientation or lattice spacings (Tan et al., 2018). For example, Mokari et al. (2004) reported the controlled growth of Au on CdSe nanorod tips to obtain the Au-tipped-CdSe nanorods with well-defined heterointerface, making a breakthrough in metal-semiconductor heterostructure synthesis. They utilized a simple one-pot method to achieve the controllable growth of Au tips and the size of Au was controlled by the concentration of reactants. Yang and Ying (2011) further investigated the preparation of metal-semiconductor heterostructures in aqueous solvents. They first derived aqueous-dispersible Ag_2S NCs by a room-temperature method and used them as the seed to realize the epitaxial growth of noble metals by reducing metal precursors in solution. In addition to epitaxial growth, heterostructures can also be synthesized by deposition. Chen et al. (2012) proposed non-selective electrochemical deposition of Au on ZnO nanorods. The deposited Au particles had good crystallinity and a clear boundary with ZnO nanorods. The formation of heterointerfaces facilitates the functional coupling of materials, enhancing their application performance. However, such heterostructure with a smaller heterointerface mentioned above could be limited in performance improvement. Metal-semiconductor core-shell NCs in which the inner metal core is uniformly coated with one or more semiconductor shell layers, thus the various components have a large contact area (Carbone and Cozzoli, 2010). Sun et al. (2009) proposed a hydrothermal method to fabricate gold@sulfide semiconductor core-shell structures. However, due to the large lattice mismatch between metals and semiconductors, the core-shell structures

synthesized by epitaxial growth have relatively poor crystallinity and severe heterointerface defects. General metal-semiconductor heterostructures can make use of epitaxial growth, deposition, and other methods to obtain ideal products (Mokari et al., 2004; Meyns et al., 2010; Chen et al., 2012; Liu et al., 2013; Schlicke et al., 2013; Naskar et al., 2015; Zeng et al., 2019), but for core-shell, yolk-shell, and other materials with large hetero contact areas, it is still necessary to develop new synthesis methods that can obtain heterogeneous interface with high crystallinity and low defect (Figuerola et al., 2010; Meyns et al., 2010; Liu et al., 2018b).

Non-epitaxial growth induced by cation exchange

To realize the precise control and synthesis of metal-semiconductor core-shell heterostructure interfaces, researchers have made great efforts. As an important method for the synthesis and post-processing of colloidal NCs in recent years, CER can achieve topological conversion in most cases, and the anion framework remains intact to maintain the overall morphology of the structure (De Trizio and Manna, 2016; Li et al., 2020). In 2010, Zhang et al. proposed the synthesis of metal-semiconductor core-shell NCs with single crystalline shell under large lattice mismatch by CER facilitated non-epitaxial growth strategy (Zhang et al., 2010a). The non-epitaxial growth strategy was enabled by the transformation of shell components by guest ions and ligands-induced CER, achieving the indirect growth of single crystal semiconductor shell on the metal core. As shown in Figure 2A, first, an Ag shell with a small lattice mismatch was epitaxially grown on the metal core, and then the core-shell NCs suffered a controlled sulfidation to transform the Ag shell into an amorphous Ag_2S shell. Finally, the amorphous Ag_2S shell was converted into a single-crystalline semiconductor shell by utilizing the CER induced by the phosphine ligand. According to the theory of hard and soft acids and bases, tributylphosphine was a soft base that had different coordination abilities with metal ions. In this typical reaction, the tributylphosphine would coordinate with soft acid Ag^+ in the amorphous Ag_2S shell preferentially, which induced the CER between the Cd^{2+} in solution and Ag^+ in the shell forming single-crystalline CdS shell with low defect heterointerfaces. The as-prepared core-shell nanoparticles at quantum scale with low defect heterointerfaces and single-crystal semiconductor shells. In recent years, researchers further developed the interface-controlled synthesis of a variety of metal-semiconductor heterostructures through the non-epitaxial growth strategy initiated by CER (Li et al., 2011; Gui et al., 2015; Liu et al., 2018a; Lim et al., 2018; Li et al., 2019; Su et al., 2021; Wan et al., 2022). In 2015, Gui et al. (2015) used different phosphines to regulate the thermodynamic and kinetic parameters of the CER, which could precisely regulate of
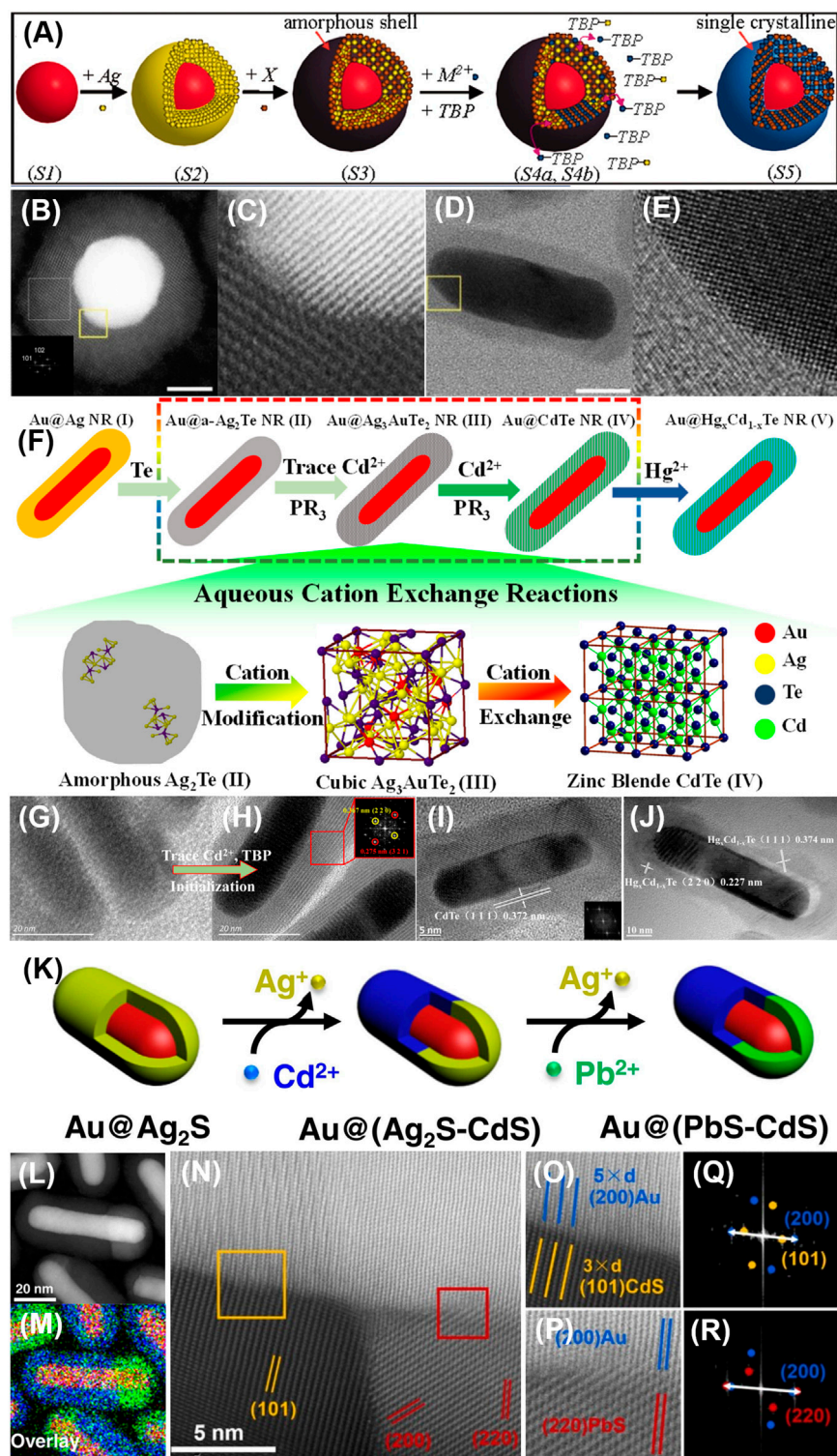
FIGURE 2
(A) Schematic of Nonepitaxial growth process. Adapted from Zhang et al. (2010a). **(B,C)** HAADF–STEM and HRTEM images of prepared spherical Au@CdS NCs. **(D,E)** HRTEM images of prepared rod-like Au@CdS NCs. Scale bar 10 nm. **(C,E)** are magnified images corresponding to the areas enclosed by the yellow squares in **(B,D)**, respectively. Adapted from Liu et al. (2018a). **(F)** Scheme of aqueous cation-exchange reactions to realize multi-step Au@telluride NR transformations. **(G,H)** HRTEM images of Au@Ag₂Te and Au@Ag₃AuTe₂ NRs. The Fourier transform from the shell (inset in H) shows the expected crystal structure of Ag₃AuTe₂. **(I)** HRTEM image of Au@CdTe NRs. Fourier transform in the inset demonstrates the

(Continued)

FIGURE 2 (Continued)
high crystallinity of the shell. **(J)** HRTEM image of Au@Hg$_x$Cd$_{1-x}$Te NRs. Adapted from Li et al. (2019). **(K)** Schematic illustration of the synthetic process for Au@ (PbS-CdS) based on partial cation exchange. **(L,M)** HAADF-STEM images with corresponding EDS mapping. **(N)** HAADF-STEM image of the interfaces in Au@ (PbS-CdS). **(O)** Magnified image of the area denoted by the yellow square in panel **(N)** with **(Q)** corresponding FFT patterns. **(P)** Magnified image of the area denoted by the red square in panel **(C)** with **(R)** corresponding FFT patterns. Adapted from Wan et al. (2022).

crystallinity and composition of metal/semiconductor core-shell and doped NCs. They systematically studied the roles and basic reaction mechanisms of different phosphine ligands, providing a theoretical basis for the regulated synthesis of multicomponent heterostructures. And then, In 2018, Liu et al. extended the non-epitaxial growth strategy initiated by CER to the aqueous phase, and successfully synthesized anisotropic metal@semiconductor core-shell nanorods (Figures 2B–E) (Liu et al., 2018a). The characterizations such as spherical aberration electron microscopy and transient absorption confirm the formation of low-defect hetero-interface and the high efficiency of hot electron injection, which have obvious advantages compared with the samples prepared by epitaxy. Subsequently, Li et al. (2019) further extended the aqueous non-epitaxial growth method to the synthesis of metal@telluride heterostructure and regulated the heterointerface by utilizing localized ion diffusion. They achieved the change from binary shell to multi-component shell, and the high crystallinity of the shell layer is maintained (Figures 2F–J). In 2022, Wan et al. (2022) successfully synthesized ternary heterostructures, taking the research of aqueous non-epitaxial growth one step forward. The n-metal-p Janus plasmonic HNCs were synthesized (Figures 2K–R), elucidating the mechanism of hot electrons and hot holes in the p-n junction. With the deepening of research, the diversity of materials that can be synthesized by non-epitaxial growth methods induced by CER is becoming more and more abundant.

Precise interface control facilitates application

Precise interface regulation of heterostructure offers a rational strategy for arising materials with improved performance of photoelectric catalytic, conversion, biological detection, photothermal therapy, *etc.* For metal-semiconductor heterostructures, the heterointerface is an important factor affecting various aspects of the performance (Liu and Zhang, 2020; Zhang et al., 2021). Interface defects accelerate carrier recombination and inhibit optoelectronic properties of heterostructures, thus severely degrading application performance (Khon et al., 2011). The non-epitaxial growth strategy initiated by CER can tune the heterointerface to form a well-defined heterointerface between two substances with high crystallinity, which provides a theoretical basis for the construction of materials with excellent performance (Zhang

et al., 2010b; Khon et al., 2011; Yu et al., 2015). Liu et al. utilized the non-epitaxial growth method and seeded growth method to fabricate Au@CdS heterostructures with similar composition and morphology, which has an atomically clean interface and an interface with many defects, respectively (Liu et al., 2018a). The photocatalytic hydrogen evolution performance of Au@CdS was tested under visible light ($\lambda >$ 420 nm). The as-prepared metal-semiconductor NCs exhibited two to three orders of magnitude higher photocatalytic H$_2$ evolution activity than those fabricated by conventional methods. Moreover, the quantum yield of hot electron injection was estimated at ~ 48% measured by Mid-IR femtosecond transient absorption spectroscopy. The results showed that Au@CdS synthesized by non-epitaxial growth exhibits higher hot electron injection efficiency and better photocatalytic hydrogen evolution performance. Li et al. (2019) proposed a continuous CER in the aqueous phase to realize the transformation of the shell from amorphous to crystalline and from binary to ternary phase, finally the synthesized Au@Hg$_x$Cd$_{1-x}$Te with high crystallinity. The synthesized heterostructures have well-controlled shell composition and thickness, enabling tunable surface plasmon resonance properties in the NIR region. They fabricated a hybrid photodetector structure by loading hetero nanorods on graphene, and the photocurrent response under different wavelengths of light was studied. The assembled device showed high photoresponsivity of visible to NIR broadband detection from 10^3–10^7 A/W. In addition, the precise regulation of heterointerfaces also has an important impact on biomedicine, solar energy utilization, etc (Wang et al., 2011; Zhang et al., 2012; Strobbia et al., 2015; Ji et al., 2016; Wang et al., 2021), which can guide performance improvement.

Discussion

Heterointerface regulation of metal-semiconductor heterostructures remains a challenging research task. The traditional epitaxial growth strategy depends on the lattice matching between different crystals, and can only build a good heterointerface under the condition of small lattice mismatch or small heterostructure contact area. While the non-epitaxial growth strategy initiated by CER is based on the topological transformation of the shell, which realizes the synthesis of metal-semiconductor core-shell heterostructures

with clear heterointerface under large lattice mismatch. In this Perspective, we first briefly introduced the effect of lattice mismatch on the regulation of heterointerfaces and then illustrated the progress in the controllable synthesis of heterostructures with well-defined heterointerface, especially the synthesis of metal-semiconductor core-shell heterostructures by a non-epitaxial growth strategy initiated by a CER. Metal-semiconductor heterodimers, metal-tip semiconductor structures, and so on, which without continuous interfaces between different components were synthesized by metal deposition, epitaxial growth, *etc.* However, methods such as epitaxial growth and metal deposition have some limitations when constructing metal-semiconductor core-shell heterostructures because of the lattice mismatch. The non-epitaxial growth strategy could effectively avoid the defective structure caused by large lattice mismatch and expands the range of achievable compositions. Metal-semiconductor core-shell heterostructures were synthesized *via* a cation-exchange-initiated non-epitaxial growth strategy, forming a continuously extended low-defect heterointerface between the metal-semiconductor and facilitating carrier migration. Finally, we summarized the effects of heterogeneous interface regulation on application performance, such as photocatalysis, sensors, solar cells, biomedical treatment, *etc.* Clear heterointerface and high crystallinity components are conducive to carrier transport and utilization, which can greatly improve their optoelectronic performance.

Although great progress has been made in the interfacial regulation of heterostructures in recent years, there are still many issues that require further research. Firstly, in addition to interface regulation, surface regulation is also an important factor affecting the optoelectronic and catalytic properties of colloidal NCs. Low-defect heterointerfaces facilitate carrier migration, while for surface regulation, amorphous surfaces have stronger electron transfer and substrate adsorption effects than highly crystalline surfaces. Hence, the surface-interface synergistic regulation of metal-semiconductor heterostructures is a very promising direction to enhance their application performance. Second, the regulated synthesis of multilevel interfaces still needs further investigation. To date, the research on core-shell structures has mainly focused on binary heterointerfaces, multiple-coated heterostructures are rarely reported. Functional coupling of materials brought about by multi-level heterointerfaces is expected to achieve breakthroughs in application performance. Finally, for a wider range of applications, the preparation of macroscopic and large-scale devices has also attracted much attention. Achieving functional applications will bring a big step forward in the field of metal-semiconductor heterostructures.

Data availability statement

The original contributions presented in the study are included in the article/supplementary material, further inquiries can be directed to the corresponding authors.

Author contributions

XL and JZ supervised the project. SL contributed to most of the writing, XL and SS revised the manuscript. All authors listed approved it for publication and made a substantial and intellectual contribution to this work.

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Conflict of interest

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