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硫化氢在果蔬贮藏保鲜中的应用及机制研究进展

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摘 要：硫化氢（H_2S）被认为是继一氧化氮（NO）和一氧化碳（CO）之后的第3种气体信号分子，近年来，研究证明H_2S在果蔬成熟衰老和抗病应答中具有重要的调控作用。结合最新的研究成果和课题组的研究工作，总结了H_2S在果蔬贮藏保鲜上的应用，以及从呼吸与能量代谢、乙烯调控、活性氧代谢、细胞壁降解、信号分子互作以及蛋白质翻译后修饰等方面概述了其可能的作用机制，并展望了H_2S在调控果蔬成熟衰老机制上的研究方向，为H_2S在果蔬贮藏保鲜上的应用提供理论依据。

关键词：果蔬；H_2S；保鲜；抗病性

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Application and regulation of hydrogen sulfide in storage of fruits and vegetables

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Abstract: In recent years, hydrogen sulfide (H_2S), as an emerging endogenous gas signal molecule after nitric oxide (NO) and carbon monoxide (CO), has attracted more and more attention of researchers. In people’s traditional concept, H_2S is a colorless, highly corrosive gas with the smell of rotten eggs. However, researchers found that low concentrations of H_2S have a positive effect in cells, studies have shown that H_2S has the functions of inducing seed germination, promoting the growth and development of roots, stems, leaves and other organs, and enhancing resistance to biotic and abiotic stresses. In recent years, there have been many researches on the preservation and disease resistance of fruits and vegetables, which started with Hu’s research on strawberries in 2012, and then applied to various fruits and vegetables, and attracted wide attention from scholars in postharvest physiology of fruits and vegetables. As a signal molecule, the application concentration of exogenous H_2S is very low, so the treated fruit and vegetable products are safe. Some studies have shown that the exogenous H_2S treatment plays a positive role in the preservation of postharvest fruits and vegetables like kiwifruit, mulberry, banana, sweet cherry, hawthorn fruit, strawberry, litchi, broccoli, daylily flower, pak choy, sweet potato, pear, lotus root, apple and so on. During postharvest storage, fruits and vegetables will be affected by fruit softening, decay, and pathogen infection, which will lead to the decline of fruit quality and shortening of shelf life. The latest research showed that H_2S treatment could significantly delay fruit ripening and senescence. The quality of postharvest fruits and vegetables is reflected by color, firmness, soluble solid

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content (SSC), titratable acid (TA) and vitamin C (Vc) content. Some studies have shown that exogenous H_2S treatment could maintain the SSC, Vc and chlorophyll content, and inhibit the decrease of firmness. From the perspective of postharvest physiology, the researchers elaborated the role of H_2S in the process of fruits and vegetables metabolism, and discussed the regulation mechanisms of H_2S on postharvest fruits and vegetables preservation from the aspects of respiration, energy metabolism, plant hormones, active oxygen system. At the same time, exogenous H_2S treatment could also regulate the postharvest physiology of fruits and vegetables by affecting gene expression, signal transduction and protein modification. The main enzymes related to energy metabolism are ATPase, succinate dehydrogenase (SDH) and cytochrome c oxidase (CCO). Through the regulation of these enzymes' activities, H_2S treatment could affect the energy metabolism of cells and delay fruit senescence. Ethylene as an important plant endogenous hormone plays important roles in a multitude of physiologic processes, including growth, development, maturation, and senescence. Studies have shown that H_2S treatment could inhibit ethylene biosynthesis by suppressing the gene expression of key enzymes including ACC synthase (ACS) and ACC oxidase (ACO) thus slow down the ripening and senescence of postharvest fruits and vegetables. Antioxidant system in plants could keep a delicate balance between reactive oxygen species (ROS) production and scavenging, thereby maintain ROS at a non-toxic level. Exogenous H_2S treatment could delay senescence of postharvest fruits and vegetables by regulating the activities of antioxidant enzymes such as superoxide dismutase (SOD), peroxidase (POD), catalase (CAT), ascorbic acid peroxidase (APX) and glutathione reductase (GR). Reduced glutathione (GSH) and ascorbic acid (AsA) are important non-enzymatic substances for scavenging ROS, which directly or indirectly quench highly active oxygen free radicals through a variety of ways. Exogenous H_2S treatment reduced the loss of non-enzymatic antioxidants and the damage of reactive oxygen species to postharvest fruits and vegetables. Softening is a typical characteristic of fruit ripening and senescence, so maintaining high firmness or reducing softening degree is one of the main goals to prolong the storage life of postharvest fruits and vegetables. The degradation of cell wall has a great influence on fruit ripening and softening. H_2S not only participates in the endogenous sulfur metabolism of plants, but also interacts with other signal molecules like Ca^{2+}, nitric oxide (NO), carbon monoxide (CO), salicylic acid (SA) and jasmonic acid (JA). It is also related to protein sulfhydrylation modification, but the related mechanism is not clear and needs further study. In this paper, the effects of H_2S on the preservation and disease resistance of fruits and vegetables, as well as its regulation mechanism on the ripening and senescence of fruits and vegetables were summarized. Combined with the latest research progress at home and abroad and our own research work, the mechanism of H_2S regulation on the ripening and senescence of postharvest fruits and vegetables was summarized, to provide reference for further study of H_2S. In the future, we suggest to focus on the interaction of endogenous H_2S with other signal molecules on the postharvest preservation and disease prevention mechanisms of fruits and vegetables. As a relatively new field of plant metabolism, protein disulfide (Cys-SSH) needs further exploration in the metabolic pathway of postharvest fruits and vegetables.

Key words: Fruits and vegetables; H_2S; Preservation; Disease resistance

硫化氢（H_2S）是次于一氧化氮（NO）和一氧化碳（CO）的第3种内源性信号气体递质，是一种无色、具有臭鸡蛋气味的强腐蚀性气体。近些年的研究发现H_2S与NO和CO具有相似的性质，低浓度H_2S在细胞中产生积极作用，能够调控植物中各种生理反应[1]。大量研究表明，H_2S具有诱导种子萌发，促进根、茎、叶等器官的生长和发育，增强非生物胁迫耐受性等功能[2]。近年来，H_2S在果蔬保鲜和抗病性方

面也有诸多研究，H_2S处理对采后果蔬通过调控活性氧体系，减缓呼吸作用和能量代谢来延缓果实衰老，还与其他信号分子，衰老基因表达和蛋白质S-巯基化修饰有关联[3]。笔者概述了H_2S对果蔬保鲜和抗病性的影响以及对果蔬成熟和衰老的调控机制，并结合国内外最新研究进展和笔者的研究工作，总结了H_2S调控采后果蔬成熟和衰老的作用机制，以期为H_2S更深入研究提供参考。

1 H_2S在果蔬采后贮藏保鲜中的应用

H_2S对果蔬采后贮藏保鲜最早开始于2012年Hu等[4]对草莓的研究，随后应用研究于各类果蔬中，在果蔬采后生理学上受到学者的广泛关注。外源H_2S施用浓度很低，对处理后的果蔬产品安全无毒害作用，大量研究表明外源H_2S处理采后猕猴桃[5]、桑葚[6]、香蕉[7]、甜樱桃[8]、山楂[9]、草莓[10]、荔枝[11]、西兰花[12]、黄花菜[13]、白菜[14]、甘薯[15]、梨[16]、莲藕[17]、苹果[18]等果蔬有较好的保鲜效果。可溶性固形物和可滴定酸含量是影响采后果实品质的主要因素。研究表明，H_2S处理猕猴桃可保持可溶性固形物水平并抑制硬度和叶绿素含量的降低[5]。在对桑葚的研究中发现，H_2S熏蒸后可以通过增加D-半胱氨酸脱硫酶(D-DES)和L-半胱氨酸脱硫酶(L-DES)的活性来显著提高内源性H_2S含量，从而降低果实的呼吸速率，减少花色苷含量，大大减慢桑葚的成熟速度[6]。Deshi等[11]在真空下用1和2 mmol·L^{-1}的NaHS溶液浸泡荔枝后发现经NaHS溶液处理能显著抑制荔枝果皮褐变，降低果实失重率，保持荔枝的采后品质。Li等[12]发现西兰花采后贮藏3 d后迅速成熟并发黄，而经过不同浓度的H_2S供体NaHS溶液处理后减轻了西兰花的黄变现象。鲜切果蔬随着贮藏时间的增加褐变程度持续增加，15 μL·L^{-1} H_2S处理显著抑制鲜切莲藕切片褐变的加重，Sun等[17]和Zheng等[18]对鲜切苹果的研究发现，用浓度高于0.4 mmol·L^{-1} NaHS溶液释放的H_2S气体熏蒸处理果实对褐变、衰老和腐烂有明显的抑制效果。

H_2S处理不仅能延缓衰老，还能抑制采后果蔬病害的发生，防止微生物侵染，其抗菌作用近年来也逐渐被人们重视。研究表明，Tang等[15]采用浓度为2 mmol·L^{-1}的NaHS处理鲜切甘薯能够有效抑制果实的黑腐病和软腐病，延缓甘薯的腐烂程度。H_2S处理显著抑制黑曲霉和意大利青霉孢子萌发和菌丝生长[19]。Hu等[16]通过H_2S处理鲜切梨发现H_2S能有效抑制鲜切梨黑曲霉和青霉的孢子生长，较好保持了梨果实在贮藏期间的品质。综上所述，硫化氢处理果蔬保鲜的因素主要包括对可溶性固形物水平的保持，抑制硬度的降低，减少花色苷含量，降低果实的呼吸速率，防止鲜切果蔬褐变的加重，抑制果实病害的发生，维持采后果蔬较好的品质。表1汇总了H_2S对采后果蔬保鲜效果的影响。

表1 H_2S对采后果蔬保鲜效果的影响

Table 1 Effect of H_2S on preservation of postharvest fruits and vegetables

分类 Classification	果蔬种类 Type of fruits and vegetables	处理方法 Treatment method	保鲜效果 Preservation effect
水果 Fruits	猕猴桃[5] Kiwifruit	15、30、45、90、180和1000 μmol·L^{-1}的H_2S溶液中浸泡 Dipping into 15、30、45、90、180 and 1000 μmol·L^{-1} H_2S solution	维持较高的可滴定酸和维生素C含量，抑制了叶绿素和硬度的降低 Maintained higher titratable acid (TA) and Vitamin C, inhibited the decrease in chlorophyll content and firmness
	桑葚[6] Mulberry	0、0.4、0.8(最佳)、1.2和1.6 mmol·L^{-1}的NaHS溶液释放的H_2S气体进行熏蒸 Fumigation with H_2S gas released from NaHS solutions of 0、0.4、0.8(optimum)、1.2 and 1.6 mmol·L^{-1}	显著减缓桑葚的成熟速度，并降低呼吸强度和花色苷含量 Significantly slow down the ripening rate of mulberry fruit and reduce the respiratory intensity and anthocyanin content
	香蕉[7] Banana	0.1、0.3、0.5(最佳)、0.7和1.0 mmol·L^{-1}的NaHS溶液释放的H_2S气体熏蒸 Fumigation with H_2S gas released from NaHS solutions of 0.1、0.3、0.5(optimum)、0.7 and 1.0 mmol·L^{-1}	保持较高的亮度和果皮紧实度 Maintained higher values of lightness and peel firmness
	甜樱桃[8] Sweet cherry	0.8和1.6 mmol·L^{-1}的NaHS溶液释放的H_2S气体熏蒸 Fumigation with H_2S gas released from NaHS solutions of 0.8 and 1.6 mmol·L^{-1}	维持较高的硬度和较低的呼吸速率，显著抑制茎褐变、腐烂和点蚀的发生 Maintained greater firmness and lower respiration rate, significantly suppressed stem browning, decay, and pitting incidences
	山楂[9] Hawthorn	0.5、1、1.5和3 mmol·L^{-1}的NaHS溶液释放的H_2S气体熏蒸 Fumigation with H_2S gas released from NaHS solutions of 0.5、1、1.5 and 3 mmol·L^{-1}	保持膜的完整性,在冷藏期间保持营养品质 Maintained membrane integrity, preserve nutritional quality during cold storage

表1（续）

Table 1　continued

分类 Classification	果蔬种类 Type of fruits and vegetables	处理方法 Treatment method	保鲜效果 Preservation effect
	草莓[10] Strawberry	0.4、0.8、1.6和3.2 mmol·L-1 的NaHS溶液释放的H_2S气体熏蒸 Fumigation with H_2S gas released from NaHS solutions of 0.4、0.8、1.6 and 3.2 mmol·L-1	保持较高的果实硬度(FF)和可滴定酸(TA)含量，以及较低的腐烂程度 Maintained higher fruit firmness (FF) and titratable acidity (TA) as well as lower decay
	荔枝[11] Litchi	在真空下用1和2 mmol·L-1的NaHS溶液浸泡 Infiltration with NaHS solutions (1 and 2 mmol·L-1) under vacuum (0.01 MPa)	显著降低了水分损失和果皮褐变 Significantly reduced weight loss and pericarp browning
蔬菜 Vegetables	西兰花[12] Broccoli	0、0.4、0.8、1.2、1.6、2、2.4、2.8和3.2 mmol·L-1的NaHS溶液释放的H_2S气体熏蒸 Fumigation with H_2S gas released from NaHS solutions of 0、0.4、0.8、1.2、1.6、2、2.4、2.8 and 3.2 mmol·L-1	减轻采后黄变和腐烂程度 Alleviates the postharvest yellowing and rotting rate
	黄花菜[13] Daylily flower	0、0.8、1.6、2.4、3.2、4.0、4.8和5.6 mmol·L-1的NaHS溶液释放的H_2S气体熏蒸 Fumigation with H_2S gas released from NaHS solutions of 0、0.8、1.6、2.4、3.2、4.0、4.8 and 5.6 mmol·L-1	维持能量状态，降低呼吸频率 Sustained the energy status, and decreased the respiration rate
	白菜[14] Pak choy	0、50、100和250 μL·L-1的H_2S气体熏蒸 Fumigation with 0、50、100、250 μL·L-1 H_2S gas	抑制绿色损失和呼吸作用 Inhibited the loss of green color and respiration
鲜切果蔬 Fresh-cut fruits and vegetables	鲜切甘薯[15] Fresh-cut Sweetpotato	0、0.5、1.0、1.5、2.0、2.5 mmol·L-1的NaHS溶液释放的H_2S气体熏蒸 Fumigation with H_2S gas released from NaHS solutions of 0、0.5、1.0、1.5、2.0、2.5 mmol·L-1	保持较高的还原糖水平,有效缓解衰老和腐烂 Maintained significantly higher levels of reducing sugar, effectively alleviated the senescence and decay
	鲜切梨[16] Fresh-cut pears	0、0.5、1.0、1.5、2.0、2.5、3和3.5 mmol·L-1的NaHS溶液释放的H_2S气体熏蒸 Fumigation with H_2S gas released from NaHS solutions of 0、0.5、1.0、1.5、2.0、2.5、3 and 3.5 mmol·L-1	保持较高水平的还原糖和可溶性蛋白质,降低果实腐烂程度 Maintained higher levels of reducing sugar and soluble protein, reduced the rot index
	鲜切莲藕[17] Fresh-cut lotus root	0、10、15、20 μL·L-1的H_2S气体熏蒸 Fumigation with 0、10、15、20 μL·L-1 H_2S gas	显著抑制褐变程度的加重 Significantly inhibited the increase of browning degree
	鲜切苹果[18] Fresh-cut apple	0、0.2、0.4、0.6、0.8和1.0 mmol·L-1的NaHS溶液释放的H_2S气体熏蒸 Fumigation with H_2S gas released from NaHS solutions of 0、0.2、0.4、0.6、0.8 and 1.0 mmol·L-1	防止褐变、衰老和腐烂，还原糖和可溶性蛋白含量明显增加 Protection against browning, senescence and rot，reducing sugar content and soluble protein content continually decreased

2　H_2S对果蔬成熟与衰老的调控机制

2.1　H_2S对果蔬呼吸作用和能量代谢的调控

呼吸作用是采后果蔬重要的生理特性，细胞能量供应是控制成熟和衰老的关键因素，采后果蔬的生理活动离不开呼吸作用和能量代谢。呼吸作用所释放的能量主要通过ATP的形式贮存在植物体内，还有一部分以呼吸热的形式释放到环境中[20]。研究表明用浓度为0.8 mmol·L-1的NaHS处理桑葚后，在贮藏6 d期间，显著抑制桑葚果实的呼吸强度，且在第4天呼吸高峰明显降低，证实了呼吸强度减少与延缓衰老密切相关[6]。能量水平的变化与能量代谢息息相关，与能量代谢有关的酶主要有：三磷酸腺苷酶（ATPase），琥珀酸脱氢酶（SDH）和细胞色素氧化酶（CCO），这些酶同时也是线粒体内膜的关键酶，参与ATP的合成[21]。有研究表明，在冷藏和成熟阶段，H_2S处理增强了氢离子ATP酶（H^+-ATPase），钙离子ATP酶（Ca^{2+}-ATPase）、细胞色素氧化酶（CCO）和琥珀酸脱氢酶（SDH）的活性，通过调控ATP、ADP、AMP含量影响细胞中的能量状态，从而抑制香蕉果实冷害的发生[22]。果实衰老是一个需要能量的过程，其基本特征主要是细胞膜的降解，果实细胞组织ATP含量和能量水平的平衡能够增强细胞膜自身的修复功能，保持果实组织细胞膜的完整性，延缓衰老。经过H_2S处理后的黄花菜，对照组与处理组在贮藏期内随着时间的增加呼吸速率均增加，相比之下，H_2S处理后果蔬呼吸速率显著减弱，可能是由于内源性H_2S合成浓度的增加提供足够的可用能量（ATP），所以呼吸作用被抑制，呼吸速率相应降低[3,13]。反之，贮藏后期能量若出现供应不足，随着

呼吸速率升高，在呼吸过程中放出大量呼吸热将引起温度升高，不利于果蔬的贮藏[23]。H_2S处理通过抑制果蔬呼吸速率并调控能量代谢相关酶活性来维持较低的能量水平，从而延缓果蔬衰老。

2.2 H_2S对果蔬中乙烯的调控

乙烯作为一种重要的植物内源激素，也是一种熟知的信号分子，对采后果蔬的生长发育、成熟衰老及信号传导发挥着重要的作用。采后果蔬随着贮藏时间加长，乙烯合成速率增长，内源乙烯浓度增加，呼吸作用加速，从而使果蔬的耐贮性降低。有研究表明与对照叶片相比，通过250 μL·L^{-1} H_2S熏蒸处理，白菜产生的乙烯速率明显降低[24]。在植物体内，乙烯的合成主要是由SAM合成酶催化蛋氨酸（Met）合成S-腺苷蛋氨酸（SAM），SAM在ACC合成酶（ACS）催化下生成1-氨基环丙烷-1-羧酸（ACC），最后经过ACC氧化酶（ACO）作用生成乙烯。其中，ACS和ACO在果蔬细胞中的生理活性影响了乙烯的生成速率，对乙烯的合成起到关键作用。通过对香蕉[25]、猕猴桃[26]等跃变型水果进行H_2S处理，发现与单独乙烯处理相比，乙烯与H_2S联合处理降低了乙烯合成基因*MaACS1*、*MaACS2*、*MaACO1*和果胶裂解酶*MaPL*的表达，而乙烯受体基因*MaETR*、*MaERS1*和*MaERS2*的表达增强。研究表明，H_2S可以拮抗乙烯，并通过减少ROS的积累来推迟采后番茄的成熟和衰老[27]。笔者课题组通过对H_2S处理后的猕猴桃进行转录组学分析，发现8个基因与乙烯信号传递途径有关，H_2S下调了乙烯受体基因*ETR2*基因（*Achn067861*）的表达，并抑制乙烯响应转录因子*ERF5*（*Achn319471*和*Achn063061*）、*ERF016*（*Achn023091*）和*ERF003*（*Achn187281*和*Achn134411*）的基因表达，增加*ERF113*（*Achn364871*）和*ERF4*（*Achn362941*）基因的表达来延迟猕猴桃在贮藏过程中的细胞壁降解[28]。H_2S可能通过抑制乙烯合成途径中关键酶的基因表达来降低乙烯的合成，延缓果蔬的成熟衰老。但是，H_2S在调节乙烯信号转导途径中的作用仍需进一步研究。

2.3 H_2S对果蔬中活性氧体系及其代谢相关酶的调控

活性氧（ROS）等一系列氧化应激反应也是导致果实衰老的重要因素。随着果蔬贮藏时间的延长，机体本身的活性氧平衡体系逐渐失衡，使得大量的超氧阴离子($O_2^{\cdot-}$)、羟自由基($OH\cdot$)和H_2O_2等在细胞内积累，引起细胞膜的过氧化、降解，导致细胞结构的破坏，加速果蔬衰老[9]。植物自身的抗氧化系统通过调控ROS含量水平以达到整个活性氧体系的动态平衡。近些年来，很多研究结果表明低浓度H_2S能有效地提高贮藏中桑葚[6]、荔枝[11]、黄花菜[13]、鲜切梨[16]等果蔬抗氧化酶类的活性，包括超氧化物歧化酶（SOD）、过氧化物酶（POD）、过氧化氢酶（CAT）、抗坏血酸过氧化物酶（APX）和谷胱甘肽还原酶（GR）的活性，降低果实中过量产生的ROS含量，保持细胞内较低的ROS水平，延长果蔬贮藏时间。在对番茄的研究中发现H_2S处理后的抗氧化酶活性与*SlAPX2*、*SlCAT1*、*SlPOD12*和*SlCuZnSOD*的表达呈显著正相关，而与*SlCAT3*和*SlPOD3*的表达呈负相关[29]。抗坏血酸（AsA)和还原型谷胱甘肽（GSH)是非酶类抗氧化物质，在维持植物体内AsA-GSH平衡中起着重要的作用，它们可以通过AsA-GSH循环清除$O_2^{\cdot-}$、H_2O_2等代谢产物[18]。H_2S可能通过上调相关基因的表达来增强抗氧化酶活性，减少非酶抗氧化物质的损失，削弱活性氧分子作用来延缓果蔬衰老。

2.4 H_2S对果蔬细胞壁降解酶基因的调控

作为植物细胞的重要保护结构，细胞壁结构的维持程度与果实的成熟与衰老有关。细胞壁的分解和中间层的一些果胶遭受破坏会导致果实软化，继而影响采后果蔬的品质[30]。结果表明，H_2S处理草莓果实保持了几丁质酶（CHI）和β-1,3-葡聚糖酶（GNS）的活性，降低了果胶甲基酯酶（PME）、聚半乳糖醛酸酶（PG）和β-1,4-内切葡聚糖酶（EGase）的活性，减少细胞壁降解，减缓果实软化程度[31]。根据实验室研究结果可以得出，NO和H_2S协同作用显著影响了乙烯的生物合成和几种细胞壁降解酶（PE，PG和EGase）的活性，抑制了水溶性、CDTA可溶性果胶组分含量的增加和Na_2CO_3可溶性果胶组分含量的减少，这可能有助于优化细胞壁结构，使细胞壁多糖不易被溶解，从而抑制了桃果实的软化[32]。最新研究结果显示H_2S可以通过调控编码细胞壁降解酶*Achn211631*、*Achn155581*、*Achn201381*、*Achn107321*和*Achn330331*基因的表达，并增加果胶酯酶抑制剂（PMEI）*Achn102711*基因的表达来延迟猕猴桃在储存过程中的细胞壁降解，从而延迟了猕猴桃的成熟和衰老[28]。H_2S处理对减缓果实软化的作用可以通过调节细胞壁降解酶基因来实现。

2.5　H_2S对其他信号分子的调控

H_2S不仅与植物体的内源硫代谢途径有关，还能与其他信号分子(Ca^{2+}，NO，CO)和植物激素（SA，JA）相互作用，调控植物的生长发育，有文献对其进行报道和总结[33-34]。但对于H_2S处理采后果蔬的保鲜机制研究来说H_2S与NO的交互作用研究相对较多。NO是一种生物活性分子，内源性NO可能在H_2S介导的信号传递作用中起关键作用，Zhang等[31]对采后草莓的研究中发现，与单独用H_2S或NO处理果实相比，H_2S和NO共同处理有效延长草莓采后保质期，体现了H_2S和NO的协同作用。笔者之前的研究表明，NO和H_2S协同作用对采后桃果实具有保鲜抗软化衰老效果，这与NO和H_2S两种信号分子对细胞壁降解酶的调控有关[32]。在对香蕉采后品质及抗氧化体系影响的研究中，分别用H_2S、NO、c-PTIO(NO抑制剂)和蒸馏水四种方式进行处理，结果显示NO和H_2S处理效果优于蒸馏水和c-PTIO处理，说明NO和H_2S的交互作用有助于维持被处理果实的抗氧化活性，降低氧化胁迫，从而较好地维持低温贮藏条件下果实的品质[35]。目前，H_2S处理对果蔬中其他信号分子与植物激素的交互作用研究大都停留在植物生长阶段，多与生长环境胁迫相关，H_2S对采后果蔬保鲜和抗病害中的作用机制研究还鲜有报道。

2.6　H_2S对果蔬中蛋白质S-巯基化修饰的调控

H_2S的主要信号传导机制与半胱氨酸残基的翻译后修饰（PTM）有关，巯基（R-SH）转化为过硫化物基团（R-SSH）的这一过程就称为蛋白质S-巯基化，会通过提高修饰的半胱氨酸的反应能力来引起蛋白质结构和功能的变化[36]。H_2S可以与特定的半胱氨酸残基相互作用，并通过将其巯基团转移到相关蛋白质的半胱氨酸残基上诱导这些半胱氨酸残基的共价修饰[37]。研究表明H_2S能正向调节拟南芥和豌豆的APX活性，PTM靶向Cys32残基，通过蛋白质组学分析拟南芥的叶片样品发现存在有超过106种蛋白被巯基化修饰，表明蛋白质S-巯基化在细胞信号传导中具有重要作用[38]。蛋白质S-巯基化可能与调控植物叶片衰老、果实成熟、种子萌发和气孔关闭等重要生理功能有关[39]。研究发现，通过生物素转化法检测证明拟南芥中APX等植物蛋白都经历了S-巯基化作用，对经过NaHS进行30 min处理的成熟拟南芥叶蛋白质提取物中APX活性进行测定，结果显示APX活性增加了约40%，APX作为一种抗氧化酶能降低植物中活性氧含量从而调控叶片衰老[40]。苹果酸酶（NADP-ME）是苹果酸代谢中的关键酶，硫化氢处理甜椒果实后可以通过S-巯基化作用对NADP-ME进行调节，从而影响细胞氧化还原状态，调控甜椒果实的成熟[41]。有研究发现H_2S气体递质参与Cys残基的精确调控过程，影响APX和CAT这些抗氧化酶活性并调节H_2O_2含量，目前的证据表明蛋白质巯基化（Cys-SSH）对植物代谢的调控发挥重要作用，笔者推测在对采后果蔬代谢途径的调控上也起着类似作用[42-43]。

3　果蔬内源H_2S的合成

有研究证明内源H_2S与果蔬中的能量状态、抗氧化能力有关，能够延缓叶片变黄，提高贮藏保鲜效果[23]。Aghdam等[9]在对山楂的研究中发现，通过从1.5 $mmol\cdot L^{-1}$ NaHS溶液中释放的H_2S进行熏蒸后，采后果实中内源性H_2S含量增加，这一现象是由于通过增加*D*-半胱氨酸脱硫酶和*L*-半胱氨酸脱硫酶的活性使内源性H_2S含量积累，与较高的SOD、CAT、APX等抗氧化相关酶活性保持一致，从而延缓果实衰老。最新研究结果证明细胞核定位的半胱氨酸脱硫酶是内源H_2S产生所必需的，并参与了番茄果实成熟的调控[44]。研究表明，植物内源H_2S由以下几个途径合成：*L*-半胱氨酸脱巯基酶（*L*-DES）途径、*D*-半胱氨酸脱巯基酶（*D*-DES）途径、亚硫酸还原酶（SIR）途径、*β*-氰基丙氨酸合成酶（CAS）途径和乙酰丝氨酸裂解酶（OASTL）途径[45-46]。Lloyd等[47]首次在拟南芥中发现半胱氨酸脱硫酶，该酶催化降解半胱氨酸转化为丙酮酸、氨和硫化物，*L*-DES途径和*D*-DES途径成为合成内源H_2S的最重要的途径。在植物细胞对硫酸盐（SO_4^{2-}）的同化过程中，植物将根部吸收的硫酸盐首先转化为5-腺苷磷酸硫酸（APS），然后通过APS还原酶（APR）将其还原为亚硫酸盐，后者被亚硫酸盐还原酶（SIR）转化成H_2S，以这种方式形成的H_2S将在质体中生成，因为亚硫酸盐还原酶被认为仅局限在质体中，如果半胱氨酸的形成没有消耗掉亚硫酸盐还原酶合成的所有硫化物，则可能将H_2S排放到植物体外[48]。此外，*β*-氰基丙氨酸合成酶（CAS）也可以催化CYs产生H_2S，*O*-乙酰丝氨酸(硫醇)裂解酶（OASTL）能以H_2S为底物催化合成Cys，防止过多的H_2S积累造成毒性[49]。H_2S是半胱氨酸合成的重要中间产物，能在半胱氨

酸合成酶(CS)的作用下被进一步还原合成含半胱氨酸的蛋白质或多肽如谷胱甘肽(GSH)等，调控植物组织细胞的氧化还原平衡。笔者从采后生理学角度阐述了 H_2S 在果蔬代谢过程中的作用，并从呼吸与能量代谢、乙烯调控、活性氧代谢、细胞壁降解、信号分子互作以及蛋白质翻译后修饰方面探讨了 H_2S 对果蔬采后保鲜的调控机制，如图1所示。

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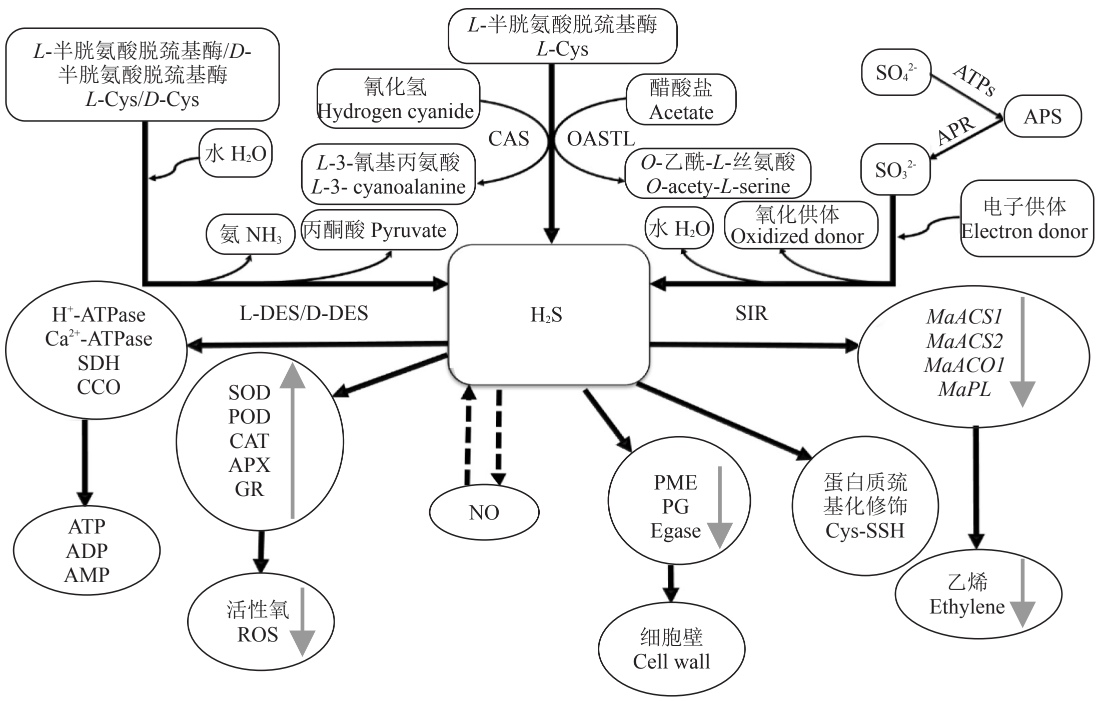
随着越来越多的研究人员对 H_2S 在果蔬保鲜领域中的关注，需要更加明确外源 H_2S 对采后果蔬的保鲜机制，为更好地应用于采后果蔬的保鲜与病害防治，现如今表现出来的一些问题有待于解决。(1) H_2S 处理对果蔬中其他信号分子与植物激素的交互作用研究还停留在植物生长阶段，多与生长环境胁迫有关，笔者课题组通过转录组分析证明硫化氢与乙烯的关系，推测在采后果蔬中 H_2S 可能与NO、SA、JA等体内其它信号分子相互串扰调控果蔬的保鲜性能和抗病性。(2)半胱氨酸蛋白质巯基化修饰(Cys-SSH)是 H_2S 信号传导的主要机制，目前的证据表明蛋白质巯基化(Cys-SSH)对植物代谢的调控发挥重要作用，推测在对采后果蔬代谢途径的调控上也起着类似作用，如何对采后果蔬贮藏保鲜起到积极作用还需要进一步探索，也是未来研究的重点。



实线箭头表示调控阶段，虚线箭头表示可能调控过程。*L*-DES. *L*-半胱氨酸脱巯基酶；*D*-DES. *D*-半胱氨酸脱巯基酶; SIR. 亚硫酸盐还原酶; CAS. *β*-氰基丙氨酸合成酶; OASTL. *O*-乙酰丝氨酸(硫醇)裂解酶; H^+-ATPase. 氢离子 ATP 酶; Ca^{2+}-ATPase. 钙离子 ATP 酶; SDH. 琥珀酸脱氢酶; CCO. 细胞色素氧化酶; SOD. 超氧化物歧化酶; POD. 过氧化物酶; CAT. 过氧化氢酶; APX. 抗坏血酸过氧化物酶; GR. 谷胱甘肽还原酶; PME. 果胶酯酶; PG. 聚半乳糖醛酸酶; EGase. *β*-1,4-内切葡聚糖酶。

Response stage of regulation are shown by solid arrows, possible progress of regulation by dotted arrows. *L*-DES. *L*-cysteine desulfhydrase; *D*-Cys. *D*-cysteine desulfhydrase; SIR. Sulfite reductase; CAS. *β*-cyanoalanine synthase; OASTL. *O*-acetylserine (thiol) lyase; H^+-ATPase. Hydrogen ion ATPase; Ca^{2+}-ATPase. Calcium ion ATPase; SDH. Succinate dehydrogenase; CCO. Cytochrome c oxidase; SOD. Superoxide dismutase; POD. Peroxidase; CAT. Catalase; APX. Ascorbic acid peroxidase; GR. Glutathione reductase; PME. Pectinesterase; PG. Polygalacturonase; Egase. *β*-1,4-endoglucanase.

图1 内源 H_2S 合成途径及采后果蔬保鲜机理

Fig. 1 Source and mechanism of endogenous H_2S

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