



Review

The Applications of Molecular Hydrogen in Horticulture

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Abstract: Improvements in the growth, yield, and quality of horticultural crops require the development of simply integrated, cost-efficient, and eco-friendly solutions. Hydrogen gas (H₂) has been observed to have fertilization effects on soils by influencing rhizospheric microorganisms, resulting in improvements in crop yield and quality. Ample studies have shown that H₂ has positive effects on horticultural crops, such as promoting root development, enhancing tolerance against abiotic and biotic stress, prolonging storage life, and improving postharvest quality of fruits, vegetables and cut flowers. In this review, we aim to evaluate the feasibility of molecular hydrogen application in horticulture and the strategies for its application, including H₂ delivery methods, treatment timing, and the concentration of H₂ applied. The discussion will be accompanied by outlining the effects of H₂ and the likely mechanisms of its efficacy. In short, the application of H₂ may provide novel opportunities for simple and cost efficient improvements of horticultural production in terms of increased yield and product quality but with low carbon dioxide emissions.

Keywords: hydrogen gas; hydrogen-rich water; hydrogen nanobubbles; solid H₂-storage material; horticultural crops; metabolism



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1. Introduction

Horticultural crops are grown for food, medical use, and aesthetic enjoyment. They form an important part of agricultural production and contribute to food security as well as nutritional quality. The improvement in the growth, yield, and quality of horticultural crops has attracted widespread attention, especially for developing easy, cheap, and eco-friendly solutions, which is a challenge for a low-carbon society.

Hydrogen is the lightest and most abundant chemical element in the universe. Researchers have proposed that hydrogen gas (H₂) played a critical role in the origin of eukaryotes [1]. Meanwhile, the production and release of H₂ has been observed in algae, animals, and plants [2–4]. Thus, it is not surprising that H₂ has increasingly been attached to various biological functions in animals and plants, which have been observed during the last two decades of studies [5–7].

Despite its low mixing ratio (~530 parts per billion by volume) in current Earth's atmosphere, H₂ contributes to the homeostasis of the oxidation state in the atmosphere [8]. In the context of H₂ biogeochemical cycles, the most important source of H₂ for the atmosphere is methane, while other sources are non-methane hydrocarbons and photochemical oxidation. Conversely, microbial-mediated soil uptake is responsible for ~80% of the tropospheric H₂ losses. H₂ has been shown to maintain microbial viability and activity and, in turn, driven carbon cycling [9]. Since H₂ exposed soil improved plant growth, it has been proposed that H₂ fertilization of soil can be attributed to H₂-oxidizing bacteria in the rhizosphere [10]. Accordingly, the deliberate application of H₂ might have substantial potential in agricultural benefits.

In 2003, Dong et al. [10] observed that H₂-treated soil improved growth in canola (*Brassica napus*) and first proposed the “H₂ fertilization” hypothesis. Since then, a growing number of studies on the application of H₂ in horticulture have been carried out due to its unique properties in stimulating or sustaining plant growth and development, as well as postharvest preservation in particular (Figure 1). So far, there are a total of 62 publications on horticultural H₂ application from China (59), Australia (2), and Canada (1). In 2013, H₂ supplied by hydrogen-rich water (HRW) was observed to enhance plant tolerance with respect to herbicide (paraquat), drought, salinity, and cold stress in alfalfa seedlings [11]. Subsequently, many additional functions of H₂ have been discovered, such as promoting root development in cucumber (*Cucumis sativus*) [12] and tomato (*Lycopersicon esculentum*) [13] and alleviating heavy metal toxicity in pak choi (*Brassica rapa* var. *chinensis*) [14] and alfalfa (*Medicago sativa*) [15]. In addition, H₂ has been shown to improve the yield and quality of daylily (*Hemerocallis fulva* L.) [16], as well as prolonging the shelf life and vase life of fruits and flowers including kiwifruit (*Actinidia chinensis* var. *deliciosa*) [17], lychee (*Litchi chinensis*) [18], rose (*Rosa chinensis*) [19], and carnation (*Dianthus caryophyllus*) [20] (Figure 2). As the mechanism underlying the positive effects of H₂ on horticultural crops is progressively being revealed, the values of the application of H₂ in horticulture are being increasingly realized.

The objective of this review is to evaluate the feasibility of H₂ application in horticulture and the strategies of H₂ application in horticultural crops, including H₂ delivery methods, treatment stages, and H₂ concentration applied. A discussion of the effects of H₂ and its possible mechanisms will also be included. Together, the application of H₂ may provide novel opportunities for improving horticultural production.

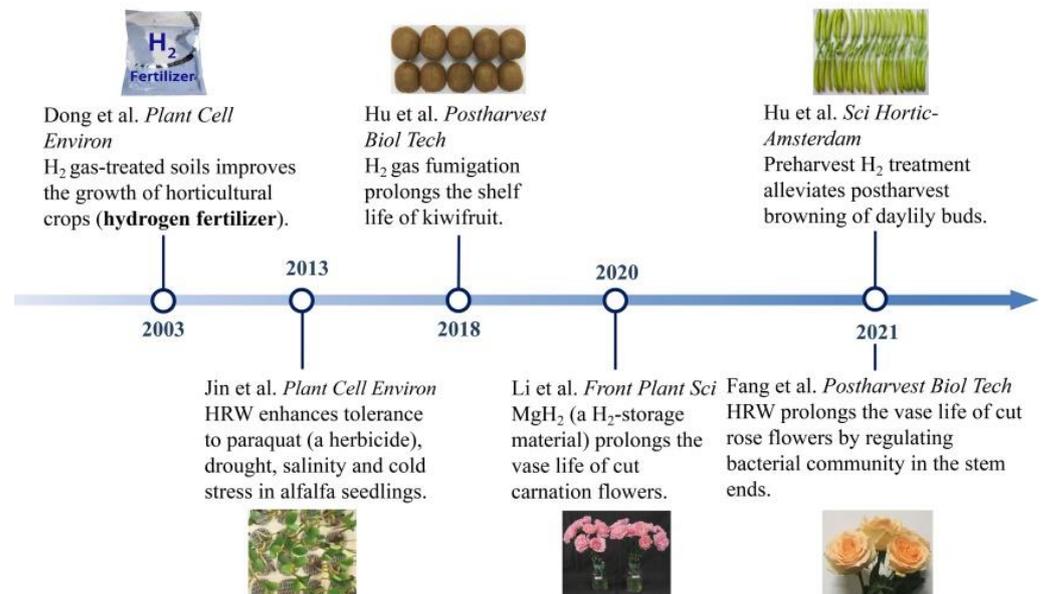


Figure 1. The developing profiles of the application of H₂ in horticulture.

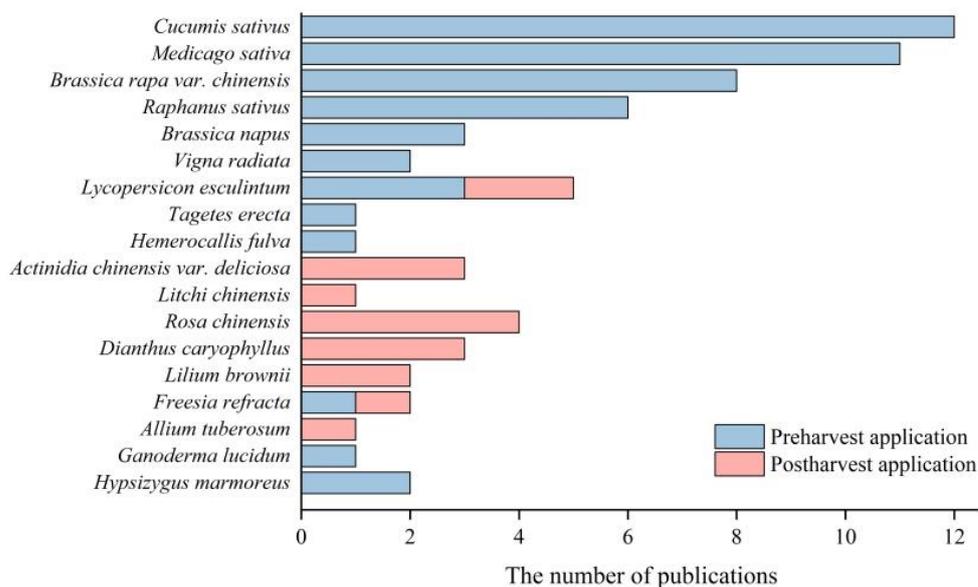


Figure 2. The species of the publications studied on the application of H₂ in horticulture.

2. Strategies of H₂ Application in Horticultural Crops

2.1. The Methods for H₂ Delivery in Horticulture

H₂ is a flammable gas; thus, care needs to be taken with its handling and application. In early studies, the H₂ treatment of soil was complicated, and soils are repeatedly exposed to H₂ gas before planting [10]. Although H₂ applied in gas form is not practical in the field, it is possible to use it under controlled airtight conditions. Previous studies observed that a 3 vol% or lower concentration of H₂ was below the lower flammability limit of H₂ (4 vol%), but the modified atmosphere can prolong the shelf life of Chinese chive (*Allium tuberosum*) [21] or kiwifruit [22] stored at 4 °C or room temperature. Surprisingly, under pure H₂ atmosphere, grapes did not show obvious signs of decay during 90 days of storage [23]. However, it is not practical to apply H₂ in such a high concentration. Safety measures for handling H₂ are necessary and important, but they can be learned from the use of H₂ in the hydrogen energy industry.

The major method of H₂ delivery is dispersion in water. Such a delivery method is very convenient for horticultural crops that are watered and fertilized by micro-irrigation. H₂ produced from water electrolysis or released from a H₂ gas cylinder is infused into water or nutrient solution. Subsequently, H₂ enriched water/nutrient solution is diluted into required concentrations. The saturation concentration of H₂ in water at room temperature and 1 atm was ~800 μM [24]; thus, the use of H₂ in liquid form is relatively safe, easy, and effective for soil and plant treatments, especially in the field. Hydrogen-rich water (HRW) can be used for soaking seeds and fruits, spraying leaves, and irrigating soil, as well as additions to hydroponic solutions.

Since H₂ naturally evolves from liquid, the residence time of H₂ in HRW is ~12 h [25], and HRW is commonly replaced every 12/24 h [14,19]. In order to improve the concentration and residence time of H₂ in liquid, nanobubble technology and solid H₂-storage materials were developed as alternative HRW preparation choices.

H₂ nanobubbles were produced by infusing H₂ into liquid with a nanobubble aerator. The nanobubbles with properties of high internal pressure and negatively charged surface can increase the effective concentration and residence time of H₂ in water [26]. Hydrogen nanobubble water was observed to exhibit improved efficacy compared to conventional HRW for prolonging the vase life of cut carnation flowers [26].

Solid H₂-storage materials dissolved in liquid can supply sustainable H₂. Magnesium hydride (MgH₂) is a promising and widely available H₂-releasing material [27,28]. It has been found that the effect of MgH₂ combined with citrate buffer solution on prolonging

the vase life of cut carnation flowers was better than that of HRW, thus indicating its potential application value in horticulture [25] (Figure 1). Another solid H₂-storage material ammonia borane (AB) also exhibited effects on enhancing rapeseed seedlings tolerance against drought, salinity, or cadmium (Cd) stresses [29]. Additionally, AB@hMSN, a H₂-releasing nanomaterial, not only significantly increased residence time of H₂ in water by more than 3 d but also induced lateral rooting in radish, tomato, rice, Arabidopsis, cucumber, and rapeseed seedlings in various degrees [30]. However, the synthesis of AB@hMSN requires encapsulating AB into hollow mesoporous silica nanoparticles (hMSN), which is a complex and costly process, therefore making its use unpractical for widespread use, such as in horticulture. In addition, the potential environment cost of the release of by-products has to be considered when solid H₂-storage materials are widely used.

2.2. The Timing of Application and/or Growth Stages

H₂ was applied at the preharvest and postharvest stages of horticultural crops. At the preharvest stage, the use of HRW to soak seeds for several hours can promote the growth of mung bean shoots and roots [31] and improve the tolerance to heat [32] or chilling [33] of cucumber seedlings. Seedlings such as cucumber [34], tomato [35], and marigold (*Tagetes erecta*) [36] incubated in HRW for 2–7 d can induce root development (Figure 3). In addition, the H₂ treatment was effective in alleviating abiotic stresses including drought [34], salinity [29], UV-A [37], and osmotic stresses [38] or metal exposure [39–41] either before or under stressors or after the removal of these stressors. HRW added in media for mycelium culture of edible fungus, such as *Ganoderma lucidum* [42] and *Hypsizygus marmoreus* [43], and can also alleviate the toxicities of different stresses (including acetic acid (HAc), salinity, and heavy metals).

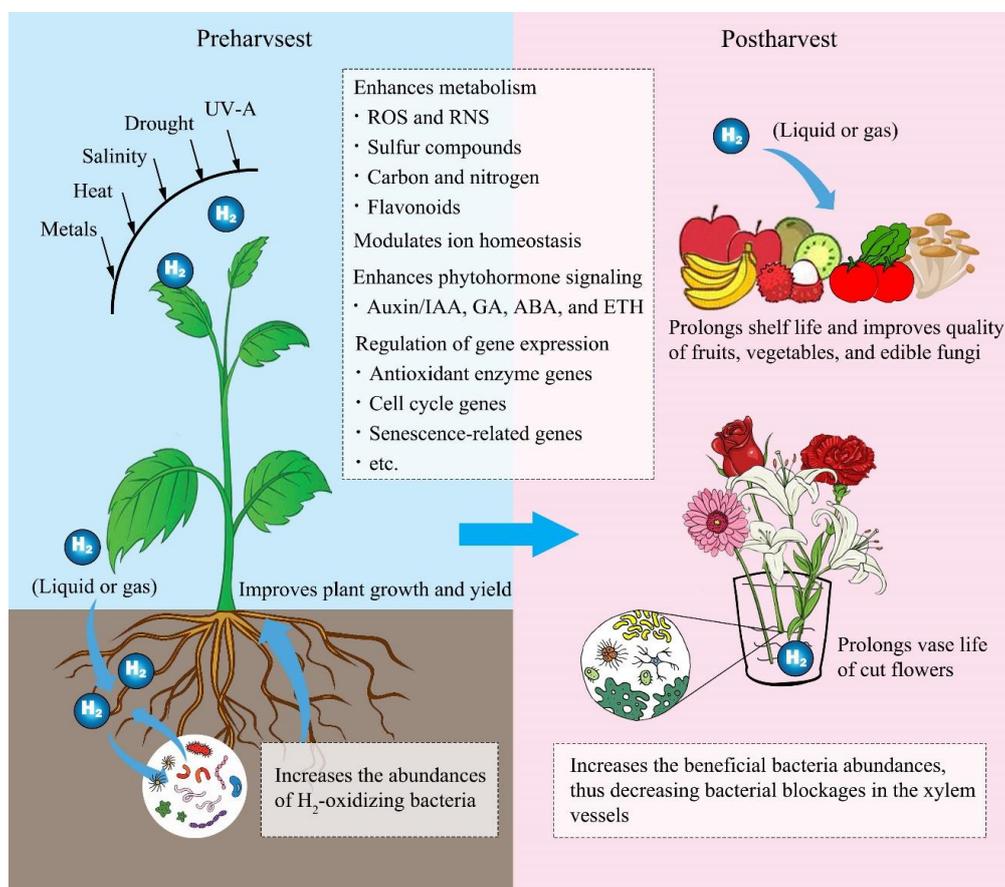


Figure 3. The physiological effects and possible mechanisms of H₂ applied in horticulture. ROS, reactive oxygen species; RNS, reactive nitrogen species; IAA, indolylacetic acid; GA, gibberellin; ABA, abscisic acid; ETH, ethylene.

Soil cultivation, spraying and irrigating with HRW at several growth stages, such as seedling, growing, and blooming period [44,45], or exposure to H₂ gas before planting [10] can improve the growth of plants and promote early flowering. In addition, irrigation of HRW at the stages of bolting, growing, and the day prior to the period of harvest not only increased the yield of daylily buds but also reduced chilling injury and browning at storage, thus maintaining postharvest quality and prolonging shelf life of daylily buds [16]. These findings provide an important practical reference for horticultural production (Figure 1). Similarly, mycelial cultures treated with HRW increased the postharvest quality of *H. marmoreus* [46].

Moreover, postharvest H₂ treatment can be beneficial for the preservation of horticultural products. Pretreatment with HRW by soaking fruits (such as kiwifruit [17], tomato [47], and lychee [18] as well as fresh-cut kiwifruit [48]) for less than 30 min can significantly maintain storage quality and prolong shelf life. H₂ fumigation for pretreatment or throughout storage period can achieve similar effects in kiwifruit [22] (Figure 1) and Chinese chive [21].

HRW as a vase solution also delayed senescence and prolonged the vase life of cut flowers, such as rose [49], lily [50], carnation [25], freesia (*Freesia refracta*) [51], and lisianthus (*Eustoma grandiflorum*) [52]. However, an effective form of H₂ has not yet been investigated for the preservation of cut flowers, which is a key concern due to the typical requirement of cut flower transportation. Perhaps the application of the solid MgH₂ or AB@hMSN H₂ materials may be a solution to this problem.

2.3. The Effective Concentration Range of H₂ Treatment

The range of H₂ concentration is closely associated with the safety and efficacy of H₂. Due to different H₂ production properties of H₂ generators, the concentration of H₂ in fresh HRW (generally regarded as 100% saturation) was commonly around 220–860 µM [34,41,53]. A high concentration of H₂ might show reduced benefits in certain plants [15,26,42,46]. The optimum concentration of HRW is associated with the species and varieties of plants and different treatment periods. For example, the treatment of ~400 µM H₂ in 4-day-old seedlings of pak choi ‘Dongfang 2’ reduced the toxicity of Cd [54] and Ca(NO₃)₂ stresses [44], while in 3-day-old pak choi ‘Wuqing No. 1’, ~78 µM H₂ significantly induced lateral root formation [13]. In addition, lower concentrations of H₂, such as ~4.7 µM H₂ or ~45 µM H₂, can significantly prolong the vase life of the cut rose ‘Movie star’ [55] or lily ‘Manissa’ [19] flowers, respectively, suggesting that cut flowers might be more sensitive to H₂.

Carbon dioxide (CO₂) and nitrogen (N₂) are most often used in modified atmospheres for reducing respiration, thus delaying ripening and senescence of fruits and vegetables during storage [56]. Among horticultural products, the gas atmosphere of package usually consists of a lowered level of oxygen (O₂; 1–10%), a heightened level of CO₂ (0–20%), and N₂ (70–99%) [56]. In addition, 1-methylcyclopropene (1-MCP), an inhibitor of ethylene perception, has been used to extend the commercial life of fruits [57]. However, high levels of CO₂ and low level of O₂ may have a negative influence on the sensorial properties or uniform ripeness of some vegetables and fruits [56]. 1-MCP has also been observed to decrease the contents of sugars and volatiles [57,58].

Recent studies have been observed that H₂-modified atmosphere can also prolong the shelf life of vegetables and fruits. For example, a $\sim 1.2 \times 10^3$ µM H₂ fumigation can maintain the postharvest quality of Chinese chive at 4 °C [21]. In kiwifruit, the positive effect of ~0.2 µM H₂ gas on prolonging shelf life was similar with that of 1-MCP (0.04 µM) [22]. However, high levels of H₂ (~1.8 µM) did not show obvious benefits compared to air control. Moreover, pure H₂ atmosphere can prolong the storage life of grapes up to 90 days while in N₂-atmosphere and air-atmosphere, the grapes have been blackened or are rotten [23]. The effectiveness and the effective concentration of H₂ might vary substantially from species to species, and this needs further investigation.

Accordingly, these observations reflect the complexity of the mechanisms underlying H₂ functions in horticultural crops.

3. H₂ Exhibits Botanical Functions by Influencing Microorganisms

Some of rhizospheric microbes can promote plant growth, such as increasing nutrient uptake and availability, stimulation of root growth, rhizoremediation, and plant stress control, resulting in improving productivity, and they are generally considered as plant-growth promoting rhizobacteria (PGPR) [59]. Naturally H₂ can typically be produced as a byproduct of N₂ fixation by nitrogen-fixing microbes and is consumed by the soil H₂-oxidizing bacteria [60]. Various H₂-oxidizing bacteria are also known PGPR [61]. Previous studies reported that H₂-treated soil promoted the plant's growth [10], attributing to bacteria in rhizosphere rather than fungi [62,63]. The analysis of terminal restriction fragment (TRF) profiles of H₂-exposed soil samples indicated that the metabolism of H₂ by H₂-oxidizing bacteria was responsible for the variation in the microbial community structure of the soil [64]. Among H₂-oxidizing bacteria, *Variovorax paradoxus*, *Flavobacterium johnsoniae*, and *Burkholderia* spp. were found in H₂-treated soil to exert promotion effects on plant root elongation [61]. Thus, plant roots may be greatly benefited from H₂-rich soil.

H₂ can increase CO₂ fixation in soil, thus promoting soil carbon deposition [60], which may be associated with bacterial RuBisCo activity of the soil [65]. In addition, it has been observed to increase the contents of soil enzymes (including dehydrogenase, catalase, urease, and invertase) in H₂-treated soil [66]. Thereby, H₂ may improve soil fertility by inducing PGPR metabolic activities.

Harvested fruits and vegetables are readily decayed by spoilage and pathogenic microorganisms. *Botrytis cinerea* causes gray mold disease in tomatoes [67]. It has been found that a 30-minute soak in HRW (125 μM H₂) can reduce gray mold disease injury and lesion areas of inoculated tomato fruit, which might be attributed to H₂-increasing polyphenol oxidase (PPO) activities and nitric oxide (NO) content [68]. Similarly, H₂ fumigation (~0.2 μM H₂) also decreased visible decay symptoms in kiwifruit by inhibiting the progress of *Phomopsis* in vivo rather than in vitro [22]. These results indicated that H₂ can boost natural plant immunity against pathogen infection. Moreover, it has been observed that HRW reduced the total colony number in fresh-cut kiwifruit [48]. The latest study found that HRW can significantly inhibit bacterial colonization and biofilm formation in the xylem vessels of cut rose flowers and increase water uptake by alleviating vascular occlusion [55] (Figure 1). Furthermore, HRW regulated the bacterial community, while the dominant bacteria *Pseudomonas fluorescens* and *Brevundimonas diminuta* promoted the vase life of cut rose flowers. This finding confirms the involvement of H₂ in plant–microbe interactions. However, the identification of a specific mechanism is still lacking.

Notably, the ecological effects of H₂ should be seriously considered, especially the impact for long-term use of H₂ on soil ecosystems due to H₂-modification of the microbial community structure.

4. Possible Mechanisms Underlying H₂ Responses in Horticultural Crops

4.1. Involved in Reactive Oxygen Species (ROS) and Reactive Nitrogen Species (RNS) Metabolism

Reactive oxygen species (ROS) and reactive nitrogen species (RNS) are commonly involved in plants responses to various stresses [69]. For example, chilling [33], osmotic [38,70], paraquat stresses [11], and metal exposure [41,53,71] can induce ROS (including superoxide anions (O₂⁻), hydrogen peroxide (H₂O₂), hydroxyl radical (·OH), etc.) and RNS (nitric oxide (NO), peroxyxynitrite (ONOO⁻), etc.), disturbing the delicate redox homeostasis and causing cellular damage inside the plant cells. In postharvest fruits, vegetables, and cut flowers, ROS overproduction accelerated senescence process [16–18,21,52]. Additionally, ROS and RNS are vital signaling transducers in plant signaling networks for stress and development [72]. Therefore, the metabolic regulation of ROS and RNS is crucial for stress responses, growth, and development in plants.

Endogenous H₂ could be produced under abiotic stresses and senescence conditions in plants [11,32,34,52]. H₂ can increase the activities of antioxidant enzymes such as superoxide dismutase (SOD), catalase (CAT), guaiacol peroxidase (POD), and ascorbate peroxidase (APX) and the transcript levels of corresponding genes, thus resulting in scavenging overproduced ROS and reestablishing redox homeostasis in alfalfa seedlings subjected to osmotic stress [11,70] (Table 1). The similar HRW responses were also observed in cut rose flowers [19] and *H. marmoreus* during storage [46]. Moreover, H₂ was observed to maintain the redox balance by increasing the contents of ascorbic acid (AsA) [40], glutathione (GSH) [15], total phenols [18], and anthocyanin [37]. Therefore, it is possible that H₂ has indirect effects on antioxidant capacity.

Table 1. Role of H₂ involved in reactive oxygen species (ROS) and reactive nitrogen species (RNS) metabolism in horticultural crops.

Materials	Treatment Stage	H ₂ Delivery Methods and Treatment	Effective Concentration of H ₂	Functions of H ₂	Mechanism	Ref. No.
<i>Brassica rapa var. chinensis</i> 'Dongfang 2'	Preharvest	1/4 Hoagland's nutrient solution with H ₂ (830 μM); the seedlings were pretreated for 48 h	~415 μM	Alleviates cadmium toxicity	Regulates NR-dependent NO signaling and enhances antioxidant capacity	[53]
		1/4 Hoagland solution with H ₂ (865 μM); the seedlings were pretreated for 2/3 d (replaced every 12 h)	865 μM	Reduces cadmium uptake in plant roots	Control of NADPH oxidase encoded by <i>RbohD</i> , which operates upstream of IRT1, and regulates root Cd uptake at both the transcriptional and functional levels	[54]
<i>Medicago sativa</i> 'Biaogan'	Preharvest	HRW (220 μM); the seedlings were pretreated for 12 h	~110 μM	Enhances tolerance to paraquat Alleviates aluminum toxicity	Modulates HO-1 signaling Decreases NO production	[11] [41]
		HRW (780 μM); the seedlings were pretreated for 12 h	~390 μM	Induces osmotic stress tolerance	Regulates H ₂ O ₂ and HO-1 signaling NO-mediated proline accumulation and reestablishment of redox balance	[38] [70]
		HRW (450 μM); the seedlings were incubated for 2/5 d (changed daily)	~225 μM	Promotes adventitious rooting Induces adventitious rooting under cadmium stress	Regulates CO signaling and activates antioxidant system Regulates NO signaling Decreases oxidative damage, increases osmotic adjustment substance content, and regulates rooting-related enzyme activity	[34] [73,74] [71]
<i>Cucumis sativus</i> 'Jinyou 35'	Preharvest	HRW (450 μM); the seeds were soaked for 8 h	450 μM	Enhances cold tolerance	Enhances antioxidant capacity and slows dehydration rate by improving osmotic adjustment ability	[33]
<i>Solanum lycopersicum</i> 'Baiguo-qiangfeng'	Preharvest	AB@hMSN (10 mg/L); the seedlings were incubated for 2/5 d	~400 μM	Induces lateral root formation	Modulates NR-dependent NO synthesis, cell cycle regulatory genes, and miRNAs expression	[30]
<i>Hypsizygus marmoreus</i>	Preharvest	HRW (1000 μM); the mycelia were cultivated until harvesting HRW (1.6 μM); irrigation at the stages of bolting, growing and the day prior to the period of harvest	~250 μM	Increases postharvest quality	Enhances antioxidant defense	[46]
<i>Hemerocallis fulva</i> 'Dawuzui'	Preharvest	HRW (1.6 μM); irrigation at the stages of bolting, growing and the day prior to the period of harvest	~0.8 μM	Promotes daylily bud yield and alleviation of bud browning	Decreases ROS level, increases the unsaturated:saturated fatty acid ratio, endogenous H ₂ and total phenol content, and reduces PAL and PPO activity	[16]
<i>Actinidia chinensis</i> 'Huayou'	Postharvest	HRW (660 μM); the fruits were soaked for 5 min	~528 μM	Delays postharvest ripening and senescence	Enhances antioxidant defense	[17]
<i>Litchi chinensis</i> 'Huaizhi'	Postharvest	HRW (500 μM); the fruits were soaked for 3 min	~350 μM	Delays the pericarp browning	Induces antioxidant system-related characters	[18]

Table 1. Cont.

Materials	Treatment Stage	H ₂ Delivery Methods and Treatment	Effective Concentration of H ₂	Functions of H ₂	Mechanism	Ref. No.
<i>Rosa chinensis</i> 'Kardinal'; <i>Lilium brownii</i> 'Manissa'	Postharvest	HRW (450 μM); cut flowers were incubated for vase period (changed daily)	~225 μM (Rose); ~45 μM (Lily)	Improves the vase life and quality	Maintains water balance and membrane stability by reducing stomatal size and oxidative damage	[19]
<i>Allium tuberosum</i>	Postharvest	Gas; the leaves were fumigated for storage period (renewed daily)	~1.2 × 10 ³ μM	Prolongs the shelf life and maintain storage quality	Increases antioxidant capacity	[21]
<i>Dianthus caryophyllus</i> 'Pink Diamond'	Postharvest	HNW (~500 μM); cut flowers were incubated for 3 d (changed daily)	~50 μM	Prolongs the vase life	Reduces ROS accumulation and senescence-associated enzyme activities	[26]
<i>Rosa chinensis</i> 'Carola'	Postharvest	MgH ₂ (0.001 g/L); cut flowers were incubated for vase periods (changed daily)	Not shown	Prolongs the vase life	Maintains ROS balance by modulating NO synthesis	[28]
<i>Lilium brownii</i> 'Manissa'	Postharvest	HRW; cut flowers were incubated for vase period (changed daily)	Not shown (1% saturation HRW)	Prolongs the vase life	Regulates NO signaling and regulates the expression of the photosynthesis-related AtpA	[50]
<i>Freesia refracta</i> 'Red passion'	Postharvest	HRW (75 μM); cut flowers were pretreated for 12 h	~0.75 μM	Prolongs the vase life	Improves antioxidant capacity	[51]
<i>Eustoma grandiflorum</i>	Postharvest	HRW (780 μM); cut flowers were incubated for vase period (changed daily)	~78 μM	Prolongs the vase life	Maintains redox homeostasis	[52]

Moreover, H₂ can modulate H₂O₂ signaling by respiratory burst oxidase homolog D (RbohD), mediated by Ca²⁺ signaling, which resulted in a decrease in Cd uptake in the roots of pak choi seedlings [57]. H₂O₂ also plays a vital role in H₂-triggered osmotic tolerance via heme oxygenase-1 (HO-1) signaling in alfalfa [38].

NO as a downstream signal molecule was involved in H₂-enhanced tolerance to osmosis [70], the fungal pathogen [68], and H₂-promoted root development [73,74], as well as prolonging the vase life of cut flowers [28,50] (Table 1). H₂ can induce NO synthesis mainly by nitrate reductase (NR), thus activating the antioxidant enzymatic system [28,53]. AB@hMSN-mediated H₂ supply also induced lateral root formation in tomato by regulating the transcription levels of cell cycle regulatory genes, *miR160*, and *miR390a* via NR-dependent NO [30]. However, there is no evidence of direct interactions among H₂, ROS, and RNS in plants. The role of H₂ in ROS and RNS signaling networks needs to be a focus for further research.

4.2. Modulation in Sulfur Compounds' Metabolism

Sulfur assimilation, cysteine and methionine metabolism, and GSH metabolism eventually influence plant growth, development, and stress responses [75]. For example, under Cd stress, HRW upregulated the genes involved in sulfate absorption, transport, and sulfur assimilation (including *ATP sulfurylases*, *5'-adenylylsulfate reductases*, *O-acetylserine(thiol)lyase*, *glutathione S-transferase* (GST), *cysteine desulfurases*, etc.), thus increasing sulfur contents of both leaves and roots in alfalfa [76,77] (Table 2). GSH content and GSH/GSSG ratio increased after HRW pretreatment by increasing the transcripts of *glutathione synthase* (GS) and *glutathione reductase* (GR) [15,39,40], as well as phytochelatin (PCs) content [76], thus associating with Cd chelation and antioxidant capacity in pak choi. Subsequently, H₂ was observed to increase transcript levels of *SIGSH1* and *SIGSH2* that encode γ-glutamylcysteine synthetase (γ-ECS) and GS, confirming the stimulation of GSH synthesis and, thus, resulting in inducing lateral root branching of tomato [35].

Table 2. Role of H₂ involved in sulfur compounds metabolism in horticultural crops.

Materials	Treatment Stage	H ₂ Delivery Methods and Treatment	Effective Concentration of H ₂	Functions of H ₂	Mechanism	Ref. No.
<i>Brassica rapa</i> var. <i>chinensis</i> 'Dongfang 2'	Preharvest	1/4 Hoagland's nutrient solution with H ₂ ; the seedlings were incubated for 48 h (replaced every 12 h) after removing cadmium stress	Not shown (50% saturation HRW)	Enhances cadmium tolerance	Reestablishes reduced GSH homeostasis	[39]
<i>Medicago sativa</i> 'Victoria'	Preharvest	HRW (220 μM); the seedlings were pretreated for 12 h	~22 μM	Alleviates cadmium toxicity	Reduces cadmium accumulation and reestablishes GSH homeostasis	[15]
					Expression regulation of genes relevant to sulfur and glutathione metabolism, resulting in enhanced glutathione metabolism and activating antioxidant defense and cadmium chelation	[76]
					Decreases oxidative damage, enhances sulfur compound metabolic process, and reestablishes nutrient element homeostasis	[77]
<i>Solanum lycopersicum</i> 'Baiguo-qiangfeng'	Preharvest	HRW (780 μM); the seedlings were incubated for 4 d (changed daily)	~390 μM	Influences lateral root branching	Alleviates mercury toxicity	[40]
					Promotes γ-ECS-dependent GSH production	[35]
<i>Ganoderma lucidum</i> strain HG	Preharvest	HRW (220 μM); added to the medium after 4 days of mycelium culture.	~11 μM	Regulates morphology, growth, and secondary metabolism	Increases glutathione peroxidase activity under HAc stress	[42]
<i>Dianthus caryophyllus</i> 'Pink Diamond'	Postharvest	MgH ₂ (0.1 g/L MgH ₂ and 0.1 M PBS (pH 3.4); cut flowers were incubated for vase period (changed daily)	~400 μM	Prolongs the vase life	H ₂ S-mediated reestablishment of redox homeostasis and increased transcript levels of <i>DcbGal</i> and <i>DcGST1</i>	[25]

Glutathione peroxidase (GPx) is an essential component of glutathione antioxidant system [78]. In *G. lucidum*, HAc caused ROS production and inhibited GPX activity [42]. However, HRW application could restore GPX activity and reestablish GSH homeostasis, thus reestablishing redox balance. It has been further found that HRW was unable to alleviate HAc-induced ROS overproduction and decreased biomass in GPX defective strain, while *gpx* overexpression strains exerted tolerance to oxidative stress. Thus, it suggested that *GPX* might be a target gene of H₂ signaling.

Hydrogen sulfide (H₂S), a component of cysteine metabolism, can act as a signal molecule involved in various physiological processes in plants, including the responses to abiotic stresses, seed germination, root organogenesis, fruit ripening, etc. [79]. The regulatory function of H₂S partly acts through protein post-translational modification and persulfidation [80]. Therefore, H₂ and H₂S may share roles in the signaling pathway of plants, while the interaction between H₂ and H₂S was also observed [25,81]. For example, H₂ could enhance L-Cys desulfhydrase (DES)-dependent H₂S synthesis [81]. Genetic evidence further showed that H₂S acted as a downstream molecule of endogenous H₂ control of stomatal closure and resulted in enhanced osmotic tolerance. A recent study also found that H₂S was involved in MgH₂-prolonged vase life of cut carnation flowers via

increasing *GST* expression [25]. However, whether or how H_2 influences H_2S -dependent persulfidation requires further investigation.

4.3. Involvement in Flavonoids Metabolism

In plants, flavonoids and their glycoconjugates (glycosides) have evolved to protect against ultraviolet radiation (UV)-triggered oxidative damage [82]. Xie et al. [83] found that under UV-B irradiation, HRW promoted alfalfa tolerance to UV-B stress, accompanied by enhancement of flavonoids profiles (included isoflavone, flavanone, flavonol, chalcone, and pterocarpan). HRW can increase transcript levels of flavonoids biosynthetic-related genes, including *L-phenylalanin ammonialyase (PAL)*, *chalcone synthase (CHS)*, *chalcone isomerase (CHI)*, *flavonol synthase (FLS)*, *isoflavone synthase (IFS)*, and *isoflavone 6-O-methyl transferase (6IOMT)* (Table 3).

Anthocyanins, one of the important flavonoids, are the main pigments responsible for the red and blue colors of fruits and flowers, playing a vital role in attracting pollinators and protecting plants from UV irradiation [84]. Moreover, anthocyanin-rich foods attract consumers due to their desirable colors and health-promoting value [85]. Under UV-A irradiation, cyanidin, the main anthocyanidin in the hypocotyls of radish sprouts, was strongly accumulated by HRW treatment [37]. However, the positive effect of H_2 on anthocyanidins accumulation varied according to cultivars of radish. HRW intensified the transcript levels for anthocyanin biosynthesis-related genes, including *PAL*, *CHS*, *flavanone 3-hydroxylase (F3H)*, *dihydroflavonol 4-reductase (DFR)*, and *anthocyanidin synthase (ANS)*. Moreover, inositol 1,4,5-trisphosphate ($InsP_3$)-dependent calcium signaling pathways might play an important role in HRW-regulated anthocyanin biosynthesis under UV-A irradiation [86]. Transcriptome analysis further revealed that the MYB-bHLH-WD40 complex accounting for major transcription factors was involved in HRW-regulated anthocyanin biosynthesis in radish sprouts under UV-A irradiation [87]. In addition to UVA, HRW could also increase anthocyanidins contents under blue light [88].

Flavonoids are well known for their benefits in human health and are used in nutrition, pharmaceuticals, medicine, and cosmetics [89]. Therefore, HRW may provide a method to improve the quality of horticultural crops.

Table 3. Role of H_2 involved in flavonoids metabolism in horticultural crops.

Materials	Treatment Stage	H_2 Delivery Methods and Treatment	Effective Concentration of H_2	Functions of H_2	Mechanism	Ref. No.
<i>Raphanus sativus</i> 'Qingtou'; <i>R. sativus</i> 'Yanghua'	Preharvest	HRW (220 μ M); 1/4 Hoagland's nutrient solution with H_2 (220 μ M H_2); the seeds were soaked in HRW for 12 h; sprouts were incubated in nutrient solution with H_2 for 3 d (replaced every 12 h) under UV-A	~220 μ M	Regulates anthocyanin synthesis under UV-A	Reestablishes ROS homeostasis and regulates anthocyanin biosynthesis-related gene expression	[37]
<i>Raphanus sativus</i> 'Yanghua'	Preharvest	HRW (781 μ M); the seedlings were incubated for 48/60 h (replaced every 12 h) under UV-A	~781 μ M	Promotes the biosynthesis of anthocyanin under UV-A	Regulates $InsP_3$ -dependent calcium signaling Involved in phytohormones, MAPKs and Ca^{2+} signaling	[86] [87]
<i>Medicago sativa</i> 'Victoria'	Preharvest	HRW (220 μ M); the seedlings were incubated for 72 h (replaced every 12 h) under short wavelength light	~220 μ M	Promotes anthocyanin accumulation under short wavelength light	Promotes activities and transcription of anthocyanin biosynthesis-related enzyme (including CHS and UFGT)	[88]
<i>Medicago sativa</i> 'Victoria'	Preharvest	HRW (781 μ M); the seedlings were pretreated for 12 h	~390 μ M	Alleviates UV-B-triggered oxidative damage	Regulates (iso)flavonoids metabolism and antioxidant defense	[83]

4.4. H₂ Is Involved in Carbon and Nitrogen Metabolism

A previous study has observed that endogenous H₂ production can be inhibited by an inhibitor of photosynthetic electron flow, indicating that, in plants, endogenous H₂ production may be associated with photosynthesis [52], and H₂ could, in turn, have an impact on photosynthesis [32] (Table 4). It has been observed that H₂ increased chlorophyll content, alleviated heat-induced damage to PSII, and effectively maintained higher photosynthetic capacity for cucumber seedlings subjected to heat stress [32]. H₂ also mitigated photoinhibition caused by chilling stress [90]. The activities of the carbon metabolism-related enzymes, such as sucrose synthetase (SS) and sucrose phosphate synthetase (SPS), and nitrogen metabolism-related enzymes, such as reduced nitrate reductase (NR), glutamine synthetase (GS), glutamate synthase (GOGAT), and glutamate dehydrogenase (GDH), were obviously increased by HRW application, resulting in enhancements in the contents of total sugar, sucrose, total nitrogen, ammonia, and nitrate nitrogen in cucumber seedlings [90]. These results indicated that H₂ can enhance plant tolerance relative to extreme temperature stress by increasing the accumulation of carbon and nitrogen compounds. Additionally, in *H. marmoreus* mycelia, HRW activated pyruvate kinase, in combination with its induced gene expression, suggesting that HRW might enhance glucose metabolism [43].

Table 4. Roles of H₂ involved in carbon and nitrogen metabolism in horticultural crops.

Materials	Treatment Stage	H ₂ Delivery Methods and Treatment	Effective Concentration of H ₂	Functions of H ₂	Mechanism	Ref. No.
<i>Cucumis sativus</i> 'XinJinchun No. 4'	Preharvest	Hoagland's nutrient solution with H ₂ (220 μM H ₂); the seedlings were pretreated for 7 d (replaced daily) HRW; 1/4 Hoagland's nutrient solution with H ₂ (835.1 μM H ₂); regarding soil cultivation, sprays with HRW (50 mL) at every 12 h for 17 d; for hydroponic solutions, the seedlings were incubated in 1/4 Hoagland solution with H ₂ for 4 d (replaced every 12 h) with Ca(NO ₃) ₂	~110 μM	Improves heat tolerance	Improves photosynthetic and antioxidant and increases HSP70 content	[32]
<i>Brassica rapa</i> var. <i>chinensis</i> 'Dongfang 2'	Preharvest	HRW (450 μM); the seeds were soaked for 8 h	~417 μM	Reduces Ca(NO ₃) ₂ toxicity and improves the growth of seedlings	Enhances antioxidant capacities and reestablishes nitrate homeostasis	[44]
<i>Cucumis sativus</i> 'Jinyou 35'	Preharvest	HRW (800 μM); mycelia were incubated for 5 d (replaced every 12 h) after removal of cadmium stress	~450 μM	Enhances lower temperature tolerance	Increases the activities of key photosynthetic enzymes and maintains a high level of carbon and nitrogen metabolism	[90]
<i>Hypsizygos marmoreus</i>	Preharvest	HRW (780 μM); the fruits were soaked for 20 min	~800 μM	Alleviates salinity and heavy metal toxicity	Activates pyruvate kinase, along with its induced gene expression	[43]
<i>Solanum lycopersicum</i> 'Jiafen No. 2'	Postharvest		~585 μM	Reduces nitrite accumulation during storage	Inhibits/increases the activity and transcript level of NR/NiR	[47]

The overuse of nitrogen fertilizer can cause severe secondary salinization and decrease yield in horticultural crops [91]. Vegetables are the main source of nitrate intake into the human body. With bacterial activity, excessive nitrate is converted to nitrite, which is considered as an important human dietary carcinogenic factor [92]. Thus, the accumulations of nitrate and nitrite are increasingly closely monitored. A recent study has shown that nitrate content in pak choi could be reduced by HRW treatment through enhancing the activities of NR and GS [44]. Moreover, HRW regulated the transcripts of long-distance transporters (*BcNRT1.5* and *BcNRT1.8*) to reduce nitrate transport to shoots, resulting in decreased nitrate content in edible parts of seedlings. During postharvest storage of tomatoes, HRW

can also decrease nitrite accumulation by either inhibiting or enhancing the activities and transcripts of NR and nitrite reductase (NiR), respectively [47].

4.5. Modulation of Ion Homeostasis

Ion homeostasis plays an important role in plant tolerance to drought, salinity, and heavy metal stress [93]. It has been observed that $\text{NH}_3 \cdot \text{BH}_3$ can decrease Na content and increase K content, resulting in a decreased Na/K ratio in rapeseed seedling roots subjected to NaCl stress [29] (Table 5). Moreover, NaCl-induced transcript levels of Na^+ transporter (*BnSOS1* and *BnNHX1*) and K^+ transporter (*BnKT1*) were strengthened by $\text{NH}_3 \cdot \text{BH}_3$. High levels of net Na^+ efflux and H^+ influx and lower net K^+ efflux were observed in $\text{NH}_3 \cdot \text{BH}_3$ -treated seedling roots. This $\text{NH}_3 \cdot \text{BH}_3$ -rebuilt ion homeostasis was closely associated with NO signaling.

Table 5. Roles of H_2 involved in modulation of ion homeostasis in horticultural crops.

Materials	Treatment Stage	H_2 Delivery Methods and Treatment	Effective Concentration of H_2	Functions of H_2	Mechanism	Ref. No.
<i>Brassica rapa</i> var. <i>chinensis</i> 'Dongfang 2'	Preharvest	1/4 Hoagland's nutrient solution with H_2 ; the seedlings were pretreated for 1 d (replaced every 12 h)	Not shown (50% saturation HRW)	Reduces cadmium accumulation	Inhibits the expression of <i>BcIRT1</i> and <i>BcZIP2</i> , and reduces cadmium absorption	[94,95]
<i>Brassica napus</i> 'Zhongshuang 11'	Preharvest	Ammonia borane ($\text{NH}_3 \cdot \text{BH}_3$; 2 mg/L); the seedlings were incubated for 3 d (changed daily) under NaCl, PEG, or Cd stress	~300 μM	Enhances the tolerance against salinity, drought, or cadmium	Decreases cell death rebuilds redox and ion homeostasis, increases proline content, thus reducing cadmium absorption and accumulation	[29]
<i>Cucumis sativus</i> 'Xinchun 4'	Preharvest	HRW (450 μM); the seedlings incubated for 2/5 d (changed daily)	~450 μM	Induces adventitious rooting	Regulates the protein and gene expressions of PM H^+ -ATPase and 14-3-3 mediated by NO.	[96]

HRW can also reduce Cd absorption by regulating the metal ion transporters in pak choi seedlings. *BcIRT1* (iron-regulated transporter 1) and *BcZIP2* (zinc-regulated transporter protein 2) are the main Cd transporters selected in pak choi, which have the ability to transport Cd^{2+} , Mn^{2+} , Zn^{2+} , and Fe^{2+} [94]. In pak choi and wild-type (*Col-0*) and transgenic Arabidopsis of *IRT1* and *ZIP2*, Cd concentrations were significantly reduced by HRW, except for the *irt1*-mutant and *zip2*-mutant. Meanwhile, HRW decreased Cd^{2+} influx in roots of WT and transgenic lines, along with enhancing the competition between Zn and Cd [95].

In addition, H_2 can regulate the interaction of PM H^+ -ATPase and 14-3-3 proteins [96]. However, whether there are H_2 targets on the cell membrane is worthy of further investigation.

4.6. H_2 Is Involved in Phytohormones Signaling

Abscisic acid (ABA), ethylene (ETH), and jasmonate acid (JA) can induce H_2 , but the specific biosynthesis pathway has yet to be elucidated [31,97]. For alfalfa drought response, H_2 acted as a positive regulator in the ABA signaling cascade to regulate stomatal movement [97] (Table 6). H_2 -modified apoplasmic pH by H^+ -ATPase might be involved in this signaling process. Moreover, H_2 differentially increased the transcriptional factor genes involved in ABA signaling, including *MYB102*, *MYC2*, and *ABF/AREB2* [98].

HRW also increased gibberellin (GA) and indolylacetic acid (IAA) contents in the hypocotyl and roots of mung beans, respectively, thus promoting the growth of seedlings [99]. These changes in phytohormones induced by HRW indicated tissue specificity. Similarly, Zeng et al. [31] reported that HRW-induced changes in the transcription of phytohormones were greater in shoots than in roots, suggesting that the interaction of H_2 and GA and IAA might be in a tissue-dependent manner. Moreover, HRW regulated auxin signaling-

related and adventitious rooting-related genes, such as *CsDNAJ-1*, *CsCDPK1/5*, *CsCDC6*, *CsAUX22B-like*, and *CsAUX22D-like*, via the modulation of HO-1 in cucumber explants [12]. It has also been observed that soaking freesia bulbs and/or irrigating with HRW can increase IAA, zeatin nucleoside, and GA contents, with reduced ABA content in the flower stalks resulting in early flowering, increased length, and diameter of flower stalks, as well as increased diameter and number of florets [45].

ETH is a pleiotropic phytohormone, involving in a variety of developmental processes, such as rooting, ripening, and senescence in plants. A previous study reported that ETH may be another downstream signaling molecule in H₂-promoted cucumber adventitious root formation [100]. Meanwhile, RuBisCO, SBPase, and OEE1 (photosynthesis-related proteins); TDH (amino acid metabolism-related protein); CAPX (stress response-related protein); and PDI (folding, modification, and degradation-related protein) might play important roles during these processes. In addition, both H₂ gas and HRW can inhibit ETH biosynthesis by decreasing 1-aminocyclopropane-1-carboxylate (ACC) concentration; ACC synthase and ACC oxidase (ACO) activities; and corresponding genes and ETH receptor gene (*ETR1* and *ETR3*) transcriptions, resulting in delayed kiwifruit ripening [22] and cut rose flower senescence [49].

Therefore, the interactions between H₂ and phytohormones are very complex, showing temporal and tissue specificity.

Table 6. Roles of H₂ involved in phytohormones signaling in horticultural crops.

Materials	Treatment Stage	H ₂ Delivery Methods and Treatment	Effective Concentration of H ₂	Functions of H ₂	Mechanism	Ref. No.
<i>Medicago sativa</i> 'Victoria'	Preharvest	HRW; the seedlings were irrigated for 7 d before 15-d drought treatment	Not shown (50% saturation HRW)	Induces drought tolerance	Modulates stomatal sensitivity to ABA and Apoplastic pH	[97]
<i>Medicago sativa</i> 'Victoria'	Preharvest	1/4 Hoagland's nutrient solution with H ₂ (780 μM H ₂); the seedlings were pretreated for 12 h	~390 μM	Induces tolerance against osmotic stress	Involved in phytohormone signaling	[98]
<i>Cucumis sativus</i> 'Xinchun 4'	Preharvest	HRW (680 μM); the seedlings were incubated for 7 d (changed daily)	~350 μM	Induces adventitious rooting	Ethylene may be the downstream signaling molecule during H ₂ -induced adventitious rooting, and proteins RuBisCo, SBPase, OEE1, TDH, CAPX, and PDI may play important roles	[100]
<i>Cucumis sativus</i> 'Lufeng'	Preharvest	HRW (220 μM); incubated for 4 d	~110 μM	Regulates adventitious root development	Regulates HO-1 signaling	[12]
<i>Vigna radiata</i> ; <i>Cucumis sativus</i> 'Jinchun 4'; <i>Raphanus sativus</i> 'Yanghua'	Preharvest	1/8 strength Hoagland nutrition solution with H ₂ (800 μM); the seedlings were incubated for 5 d (replaced every 12 h)	~480 μM	Promotes elongation of hypocotyls and roots	Increases GA and IAA contents in the hypocotyl and the root	[99]
<i>Vigna radiata</i>	Preharvest	HRW; seeds were soaked for 3 d	100/250 μM	Promotes the growth of shoots and roots	Involved in phytohormone signaling	[31]
<i>Freesia refracta</i>	Preharvest	HRW (75 μM); the bulbs were soaked for 6 h; irrigated HRW at every 7–10 d and total 3 times after scape sticking out	~37.5 μM	Promotes early flowering; increases the number and diameters of florets	Regulates phytohormone and soluble sugar content	[45]
<i>Actinidia deliciosa</i> 'Xuxiang'	Postharvest	Gas; the fruits were fumigated for 24 h/12 h + 12 h	~0.2 μM	Prolongs the shelf life	Decreases ethylene biosynthesis	[22]
<i>Rosa chinensis</i> 'Movie star'	Postharvest	HRW (235 μM); cut flowers were incubated for vase periods (changed daily)	~2.35 μM	Alleviates postharvest senescence	Inhibits ethylene production and alleviates ethylene signal transduction	[49]

5. Conclusions and Prospects

Maintaining or increasing horticultural yield requires NPK fertilizers, manure, hazardous preservatives, or other polluting methods, which could be offset via cleaner or healthier alternatives. H₂ is a carbon-free energy carrier that may be an attractive plant growth regulator for horticultural sustainability. Currently, over 95% of H₂ is made by using fossil fuels, with the most common process of H₂ production being steam methane reformation, which may produce H₂ for ~USD 1.15/kg H₂ in the US [101]. Other H₂ production technologies, such as water electrolysis, are estimated to produce H₂ for ~USD 5.50 per kilogram of H₂. Although renewable H₂ is relatively expensive, its production costs are reducing. According to the BloombergNEF's report of "Hydrogen Economy Outlook" [102], between 2014 and 2019, the cost of alkaline electrolyzers fell 40% in North America and Europe, and systems made in China are already up to 80% cheaper than those made elsewhere. They forecast that renewable H₂ could be produced for USD 0.7 to USD 1.6/kg H₂ in most parts of the world before 2050. Thus, the cost for applying H₂ in horticulture is primarily dependent on the cost of labor, which is both feasible and affordable, at least under current economic conditions.

H₂ has been applied in the above-mentioned important horticultural crops, confirming its positive effects both on plant growth, development, stress tolerance, and postharvest storage (Figure 3). A recent field trial has observed that H₂ infusion increased H₂-oxidizing bacteria activities, accompanied with an alteration of composition and structure of the microbial community [103]. However, the above effects of H₂ on soil microbe were significantly influenced by environmental conditions, which would be taken into account in further H₂ field trials. The potential negative effect of H₂ on soil ecosystems should also be concerning. For example, H₂ exposure may stimulate methane oxidation and the activities of pathogens that use H₂ as an energy source [9]. Therefore, long-term and large-scale commercial field trials of H₂ require further investigation, especially in the evaluation of resistance to pests and diseases, yield, and quality, as well as environmental impact. In addition, enhanced understanding is required with respect to the causal mechanisms underlying plant H₂ production and action.

Overall, H₂ has a substantial potential in horticultural applications to reduce fertilizer and pesticide use, providing higher-value and nutrient-rich horticultural crops. Since making technology cheap requires technological advance, we urge the cooperation of the industrial community. The next step may focus on practical application of H₂ in horticulture.

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