

## ORGANIC CHEMISTRY

## Highly selective electrochemical hydrogenation of alkynes: Rapid construction of mechanochromic materials

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Electrochemical hydrogenation has emerged as an environmentally benign and operationally simple alternative to traditional catalytic reduction of organic compounds. Here, we have disclosed for the first time the electrochemical hydrogenation of alkynes to a library of synthetically important Z-alkenes under mild conditions with great selectivity and efficiency. The deuterium and control experiments of electrochemical hydrogenation suggest that the hydrogen source comes from the solvent, supporting electrolyte, and base. The scanning electron microscopy and x-ray diffraction experiments demonstrate that palladium nanoparticles generated in the electrochemical reaction act as a chemisorbed hydrogen carrier. Moreover, complete reduction of alkynes to saturated alkanes can be achieved through slightly modified conditions. Furthermore, a series of novel mechanofluorochromic materials have been efficiently constructed with this protocol that showed blue-shifted mechanochromism. This discovery represents the first example of cis-olefins-based organic mechanochromic materials.

## INTRODUCTION

Cis-alkenes are important scaffolds in various natural products, pharmaceuticals, and organic functional materials. They are also key building blocks for developing molecular complexity from their stereospecific transformations (1–8). Thus, considerable efforts have been devoted to the development of straightforward and efficient approaches to access these thermodynamically less stable alkenes (1–7). The transition metal-catalyzed selective semihydrogenation of alkynes is among the most common methods for the synthesis of cis-olefins and is an extremely important process in both industry and academia (1–7). However, this process is often complicated with the use of stoichiometric amounts of reducing reagents (Fig. 1A) (1–7). Moreover, poor chemo- and stereoselectivity and over-reduction of alkenes to alkanes are observed in most cases (1, 3, 9–11). As a result, the development of efficient and environmentally friendly hydrogenation methods is an important subject in organic synthesis (1–8).

Electrochemical synthesis has emerged as a powerful synthetic tool and has gained great interest from both scientific and engineering viewpoints because of its innate advantages, including environmental benignity, operational simplicity, ease of scalability, reaction tenability, and economic efficiency from the use of cheap and/or recyclable electrodes (12–29). Therefore, the electrochemical hydrogenation of alkynes to Z-alkenes with great selectivity and efficiency is doubtless one of the most ideal strategies (Fig. 1B) (12–20, 30–32). In this process, the hydrogen source comes from the solvent or supporting electrolyte rather than the hydrogen gas (30–32), which avoids a series of problems associated with hydrogen gas transportation and storage. As an ideal alternative to traditional catalytic hydrogenation, electrochemical hydrogenation can serve as an environmentally friendly and sustainable synthetic method in organic chemistry (12–14, 30–32). Electrochemical reduction of carbon dioxide, ketones, esters, amides, and alkyl halides has been well established (14). In comparison, reports on reduction of alkynes to Z-olefins are rare. In 1943, Campbell and Young disclosed this process using spongy nickel as the cathode and sulfuric acid as an anolyte under a constant current of 2 A (33). Since then, several groups have attempted this transformation (33, 34).

Unfortunately, these reactions are often associated with various disadvantages such as the use of corrosive sulfuric acid, poor chemo- and stereoselectivity, limited substrate scope, and over-reduction to alkanes (33, 34). Thus, the development of an innovative electrochemical method to overcome these drawbacks is urgently needed. In this study, we report the first example of electrochemical hydrogenation reactions of alkynes to a library of synthetically important Z-alkenes in great selectivity and efficiency (Fig. 1B).

## RESULTS

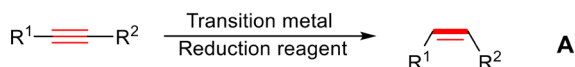
We began our investigation by using 1,2-diphenylethyne (**1a**) as a model substrate to evaluate the feasibility of the electrochemical hydrogenation strategy (table S1). To our delight, **1a** was hydrogenated efficiently to afford (Z)-1,2-diphenylethene (**2a**) in 81% yield with great selectivity (E/Z, 1:99) under a constant current of 0.1 A in a user-friendly undivided three-necked round-bottomed flask at 60°C (table S1, entry 1). Encouraged by these gratifying results, we further optimized the reaction conditions. Among the electrolytes investigated (e.g., <sup>n</sup>Bu<sub>4</sub>Ni, <sup>n</sup>Bu<sub>4</sub>NPF<sub>6</sub>, and <sup>n</sup>Bu<sub>4</sub>NBF<sub>4</sub>), <sup>n</sup>Bu<sub>4</sub>Ni was the most effective one (table S1, entries 1 to 3). After an extensive solvent screening, methanol proved to be the most effective (table S1, entries 4 to 7). It was also found that the selectivity and yield of **2a** were reduced when other bases were used or in the absence of Me<sub>2</sub>NH (table S1, entries 8 to 10). Furthermore, replacement of PdCl<sub>2</sub> with Pd(OAc)<sub>2</sub> led to a slightly decreased reaction yield (table S1, entry 11). Moreover, a substantially lower reaction yield was obtained by decreasing the operating current or temperature (table S1, entries 12 and 13), while no desired product could be obtained in the absence of electric current (table S1, entry 14). It was also found that a very low yield was observed when the same electrode (either Pt/Pt or C/C) was used (table S1, entries 15 and 16). In addition, **2a** was obtained in 18% yield when unwashed and reused Pt electrode was used as the cathode (table S1, entry 17). Delightfully, the desired product was obtained in 76% yield with high selectivity using the recycled palladium nanoparticles (table S1, entry 18), indicating that this protocol has the potential for industrial production. It is worth noting that the potential over-reduced alkane byproduct was not detected in the reaction, making this process unique and extremely valuable (35).

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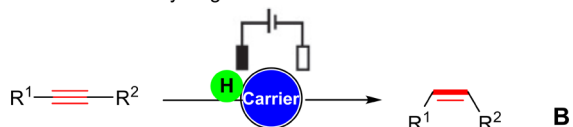
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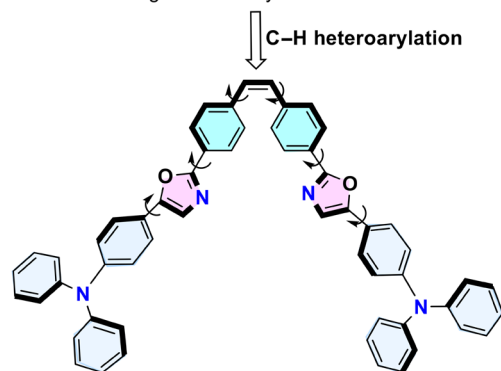
The reported prevailing methods for Z-olefins



This work: Electrochemical hydrogenation



- No extra reducing reagents required
- Excellent selectivity (>99%)
- Hydrogen source comes from the solvent or supporting electrolyte
- Elimination of issues associated with hydrogen storage and transport
- Palladium nanoparticles as the adsorbent carrier
- Great functional group compatibility
- Mild conditions and gram-scale synthesis



- New mechanochromic luminescence materials

**Fig. 1. Hydrogenation of alkynes to Z-alkenes and construction of mechanochromic materials.** (A) The reported prevailing methods for Z-olefins. (B) Electrochemical selective hydrogenation of alkynes to Z-alkenes.

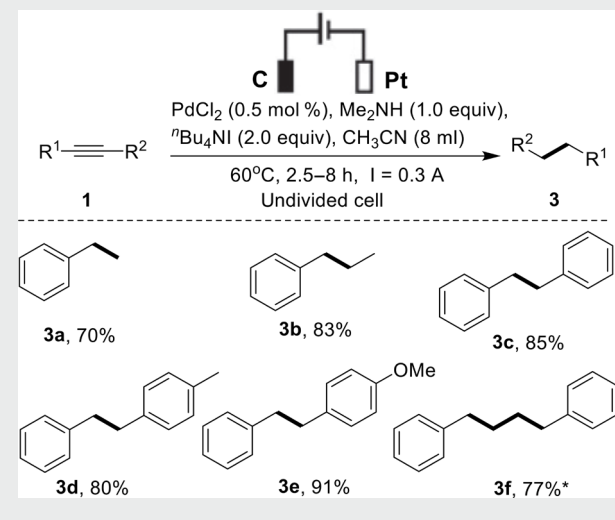
With the optimized conditions in hand, a library of alkynes was subjected to electrochemical hydrogenation, and the corresponding Z-alkenes were obtained in high yields with excellent chemo- and stereoselectivity (Table 1), revealing the general applicability of this method. It is noteworthy that (Z)-1,2-diphenylethene (**2a**) could also be obtained on a gram scale in 78% yield with high Z/E selectivity. In addition, di(hetero)arylethynes with either an electron-donating or electron-withdrawing substituent resulted in good yields of the desired Z-alkenes (**2a** to **2j**). Notably, heteroarylethynes were exclusively reduced to the corresponding Z-alkenes without affecting the heteroaromatic rings (**2e** and **2f**). Furthermore, hydrogenation of unactivated dialkyl acetylenes also proceeded smoothly to provide the corresponding Z-olefins in high yields with excellent selectivity (**2l** to **2n** and **2q** to **2x**). Moreover, terminal alkynes can be easily hydrogenated (**2o** and **2p**). As shown in Table 1, a variety of valuable functionalities such as amino, chloro, cyano, ether, fluoro, methoxy, methyl, silicon, trifluoromethyl, and heterocycle were all well tolerated. It is also worth noting that benzyl and naphthalene were all compatible under the present conditions (**2q** to **2t**), making it a unique process because these two functional groups can be easily hydrogenated by most conventional hydrogenation reactions.

To our delight, complete reduction of alkynes to saturated alkanes was also achieved under slightly modified reaction conditions (Table 2). Compared with the previous studies of electrochemical hydrogenation of alkynes to alkanes, the metal electrode is not sacrificed under the present conditions (36). Moreover, deuterated 1,2-diphenylethane

**Table 1. Electrochemical selective hydrogenation of various alkynes to Z-alkenes.**

<b>2a</b> , 81% (99:1) (Gram-scale, 78%)	<b>2b</b> , 83% (>99:1)	<b>2c</b> , 88% (99:1)
<b>2d</b> , 80% (>99:1)	<b>2e</b> , 82% (99:1)	<b>2f</b> , 92% (>99:1)
<b>2g</b> , 92% (>99:1)	<b>2h</b> , 80%* (98:2)	<b>2i</b> , 70%* (98:2)
<b>2j</b> , 76%* (>99:1)	<b>2k</b> , 80% (>99:1)	<b>2l</b> , 77%† (>99:1)
<b>2m</b> , 83%† (>99:1)	<b>2n</b> , 81%† (>99:1)	<b>2o</b> , 62%
<b>2p</b> , 67%	<b>2q</b> , 88%‡ (>99:1)	<b>2r</b> , 68%‡ (>99:1)
<b>2s</b> , 60%‡ (>99:1)	<b>2t</b> , 80%‡ (>99:1)	<b>2u</b> , 92%‡ (>99:1)
<b>2v</b> , 68%‡ (>99:1)	<b>2w</b> , 69%‡ (>99:1)	<b>2x</b> , 75%‡ (>99:1)

\*Reaction conditions: C anode, Pt cathode, constant current = 0.1 A, **1** (0.80 mmol), PdCl<sub>2</sub> (0.5 mol %), Me<sub>2</sub>NH (0.5 equiv), <sup>t</sup>Bu<sub>4</sub>NI (1.0 equiv), MeOH (8.0 ml), 60°C, 2.5 hours. Isolated yields and Z/E ratios are shown. Selectivity was determined by gas chromatography (GC) or nuclear magnetic resonance (NMR) analysis. †3.5 hours. ‡Constant current = 0.2 A, PdCl<sub>2</sub> (2.0 mol %), 5 hours. #PdCl<sub>2</sub> (1.0 mol %), 3.5 hours.

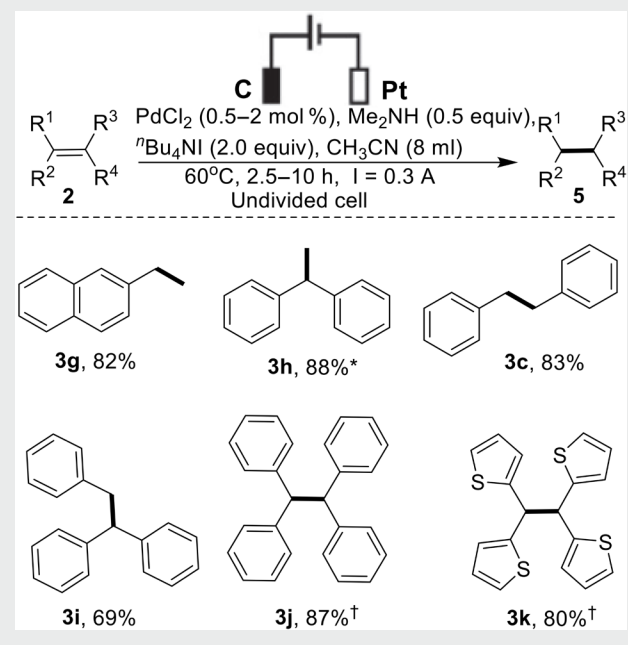
**Table 2. Electrochemical selective hydrogenation of alkynes to alkanes.**

\*Reaction conditions: C anode, Pt cathode, constant current = 0.3 A, **1** (0.80 mmol), PdCl<sub>2</sub> (0.5 mol %), Me<sub>2</sub>NH (1.0 equiv), <sup>n</sup>Bu<sub>4</sub>NI (2.0 equiv), MeCN (8.0 ml), 60°C, 2.5 hours. †PdCl<sub>2</sub> (1.0 mol %), Me<sub>2</sub>NH (2.0 equiv), <sup>n</sup>Bu<sub>4</sub>NI (3.0 equiv), 8 hours.

was obtained with 100% of deuterium incorporation in 83% yield with CD<sub>3</sub>CN as the solvent under the standard reaction conditions (scheme S2). Alkenes were also reduced cleanly to alkanes with this protocol. This process also showed a good catalytic activity toward mono-, di-, tri-, and tetra-substituted alkenes (Table 3). It should be mentioned that traditional catalytic hydrogenation of tri- or tetra-substituted alkenes often requires harsh reaction conditions such as high temperatures and high H<sub>2</sub> pressures (37).

In recent years, the development of mechanochromic materials has attracted considerable attention in view of their great potential for various applications such as chemosensors, security systems, optical displays, and rewritable optical media (38–43). However, the design strategy for organic small-molecule mechanochromic materials still remains obscure (38, 41–43). Mechanochromism of organic materials mainly depends on efficient molecular packing from intermolecular interactions such as hydrogen bond and  $\pi$ - $\pi$  and dipole-dipole interactions (38, 41–43). The weak intermolecular interactions and relatively loose packing usually exist in highly twisted molecules. The highly twisted conformation is susceptible to external perturbation to endow a chromic response. The triphenylamine (TPA) group has been well recognized for its efficient hole-transporting capability, good electron-donating property, and propeller-like nonplanar characteristic (44–46). As a result, we designed and synthesized a series of novel TPA-bearing (z)-2-(4-styrylphenyl)oxazole scaffolds (**4a** to **4d**) (Fig. 1 and Table 4). It was envisaged that the propeller-like geometry of TPA and the  $\pi$ -conjugated nonplanar geometry of (Z)-1,2-diphenylethenes may endow them with a strong emission and highly twisted conformation.

Given that the highly selective electrochemical hydrogenation protocol developed here can tolerate the reactive chloride, (z)-1-chloro-4-styrylbenzene and (z)-1,2-bis(4-chlorophenyl)ethane were used as starting materials to avoid tedious multiple-step synthesis and thus greatly streamline synthetic routes. The palladium-catalyzed C–H/C–Cl

**Table 3. Electrochemical selective hydrogenation of alkenes to alkanes.**

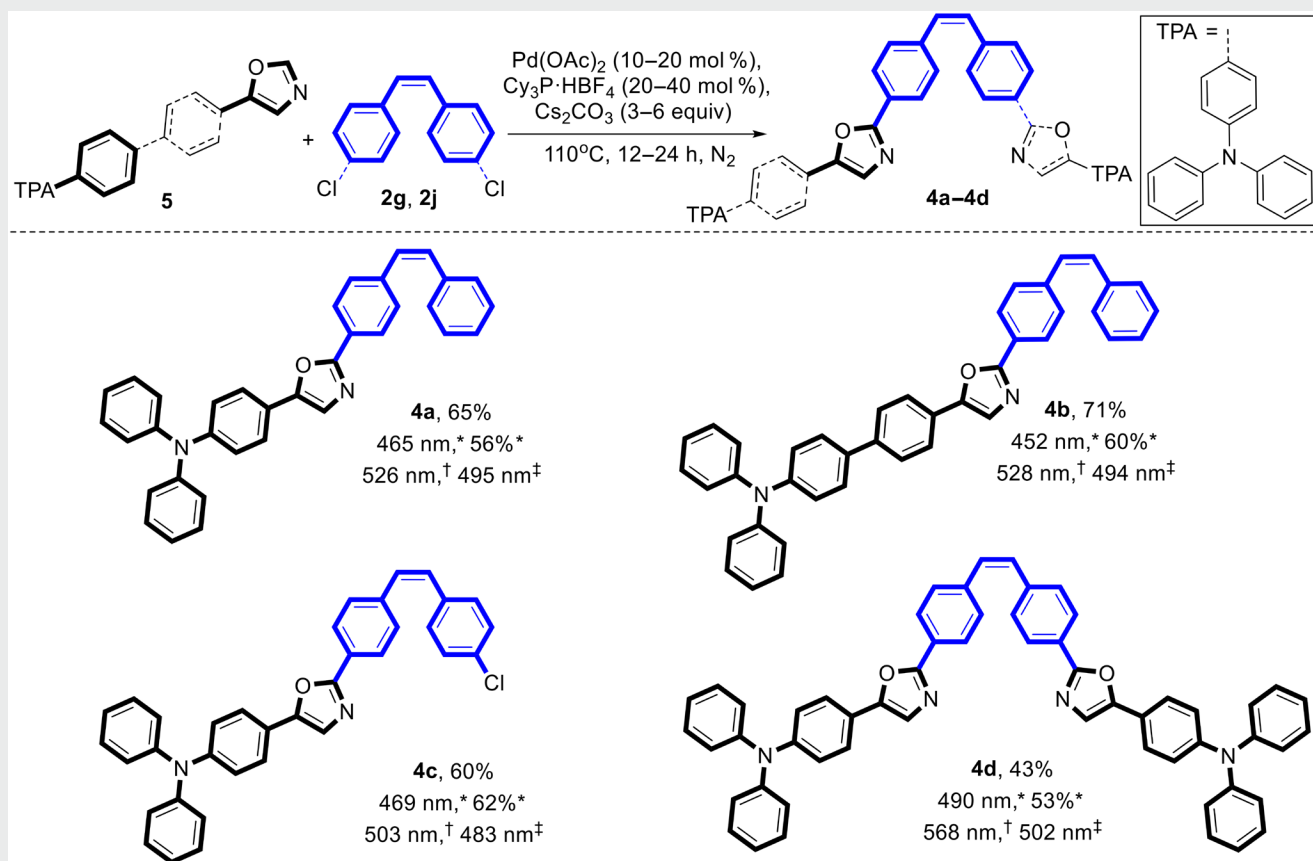
\*Reaction conditions: C anode, Pt cathode, constant current = 0.3 A, **2** (0.80 mmol), PdCl<sub>2</sub> (0.5 mol %), Me<sub>2</sub>NH (1.0 equiv), <sup>n</sup>Bu<sub>4</sub>NI (2.0 equiv), MeCN (8.0 ml), 60°C, 2.5 hours. †PdCl<sub>2</sub> (1.0 mol %). ‡PdCl<sub>2</sub> (2.0 mol %), 10 hours.

cross-coupling of TPA-bearing oxazoles (**5**) with **2g** or **2j** was performed to obtain the corresponding TPA-bearing (z)-2-(4-styrylphenyl)oxazole scaffolds **4a** to **4d** (Table 4).

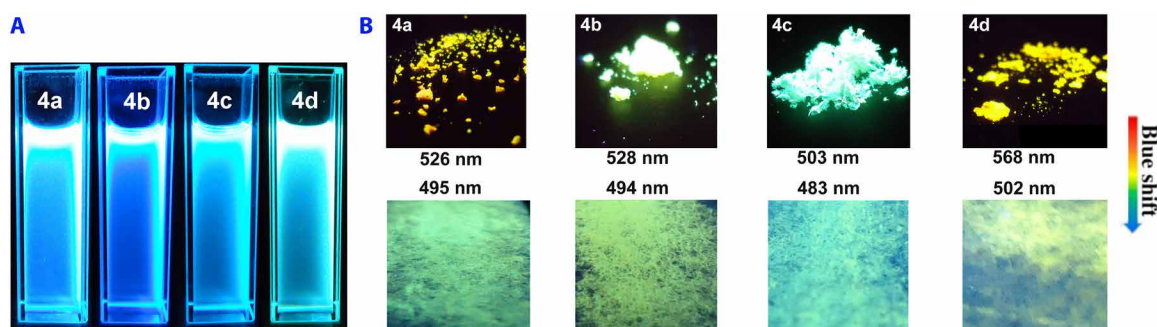
The photophysical properties of these scaffolds (**4a** to **4d**) were measured with respect to the emission maximum, along with quantum yields in toluene solution ( $2.0 \times 10^{-5}$  M) and emission maxima before and after grinding (Table 4 and Fig. 2). As shown in Fig. 2A and fig. S1B, their emission wavelengths in toluene are located in the blue region (452 to 490 nm), and high fluorescence quantum yields in toluene (53 to 62%) have been determined. Importantly, **4b** displayed deep-blue emission with International Commission on Illumination 1931 (CIE<sub>1931</sub>) of (0.15, 0.08), which is very close to European Broadcasting Union (EBU) coordinates of (0.15, 0.06) (fig. S2). The absorption and emission spectra of **4a** to **4d** in toluene are shown in fig. S1.

Molecules **4a** to **4d** displayed blue-shifted mechanochromic luminescence properties (Fig. 2B). Grinding of pristine powders **4a** to **4d** induced a blue shift with emission color change from yellow ( $\lambda_{em} = 503$  to 568 nm) to blue-green ( $\lambda_{em} = 483$  to 502 nm), approximately 31, 34, 20, and 66 nm, respectively (Table 4, Fig. 2, and fig. S3). The fluorescence blue shift, after grinding powders **4a** to **4d**, could be ascribed to weakened intermolecular  $\pi$ - $\pi$  interactions. To the best of our knowledge, this is the first example of cis-olefin-based organic mechanochromic materials (38–43).

To explore the mechanochromic mechanism, **4b** was further investigated as a representative sample, and its powder phase characteristics were studied by differential scanning calorimetry (DSC) and powder x-ray diffraction (PXRD) analysis. The DSC experiment of unground **4b** did not present endothermic or exothermic peaks. In

**Table 4. Synthesis of TPA-containing (z)-2-(4-styrylphenyl)oxazoles.**

\*For detailed reaction conditions, see the Supplementary Materials. †Emission maximum and quantum yields in toluene ( $2 \times 10^{-5}$  M). ‡Emission maximum in pristine powder. §Emission maximum in ground powder.



**Fig. 2. Fluorescence images.** (A) Fluorescence images of **4a** to **4d** in toluene ( $2.0 \times 10^{-5}$  M) under ultraviolet (UV) light (365 nm). (B) Fluorescence images of **4a** to **4d** before and after grinding.

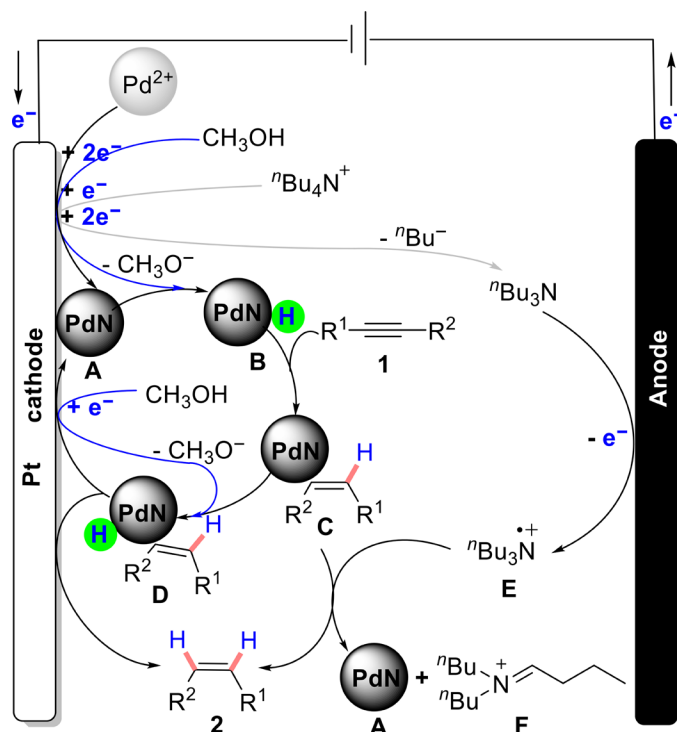
contrast, ground **4b** exhibited an obvious endothermic peak, indicating a transition from the metastable state to the stable state (fig. S4). The PXRD patterns of the pristine solid of **4b** exhibited sharp and intense reflections, whereas the sharp peaks disappeared after grinding (fig. S5). These observations demonstrated a morphological transition from the crystalline to amorphous phase (38–43). Furthermore, its thermal stability was also evaluated by thermal gravimetric analysis (fig. S6).

The thermal decomposition temperature ( $T_d$ ) of **4b** is 343°C, which indicates that it is thermally stable.

## DISCUSSION

To get some insights into the mechanism of the selective electrochemical hydrogenation reaction, a series of deuterium-labeling

experiments were performed to verify the hydrogen source of *Z*-alkenes (scheme S1 and section S9). With CD<sub>3</sub>OD as the solvent, (*Z*)-1,2-diphenylethene ([D]-**2a**) was obtained with 83% of deuterium incorporation in the absence of a base (scheme S1A), indicating that the hydrogen comes from both CD<sub>3</sub>OD and the electrolyte <sup>n</sup>Bu<sub>4</sub>NI. Furthermore, a slightly smaller proportion of deuterated product was observed with the addition of diisopropylamine instead of diisopropylamine-*d* (scheme S1, B and C). This observation implied that diisopropylamine may also provide hydrogen in the reaction. In addition, with CH<sub>3</sub>OD as the solvent, the corresponding [D]-**2a** (D incorporation: ca. 82%) was observed (scheme S1D). This result suggests that hydrogen was not provided by the methyl group in

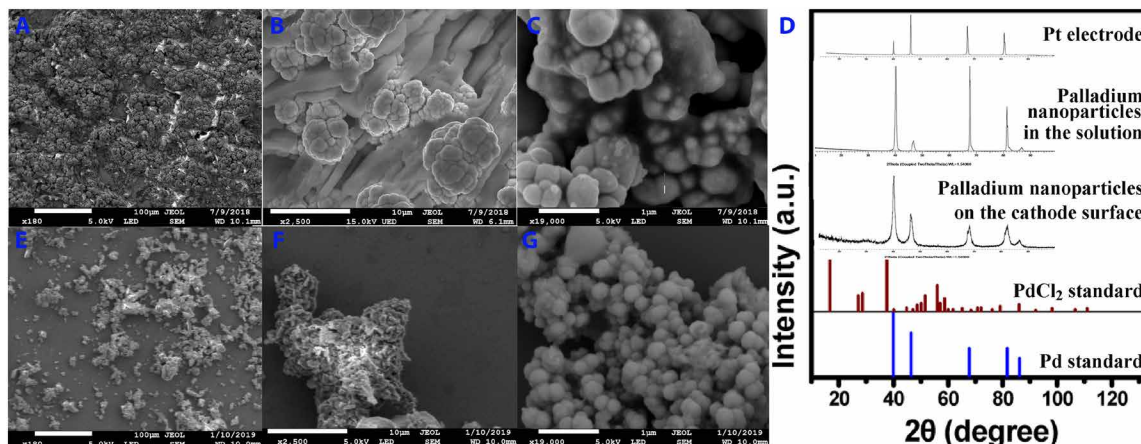


**Fig. 3. A plausible mechanism of electrochemical selective hydrogenation of alkynes.**

methanol in the reaction. As a result, the hydrogen sources are believed to be the hydroxyl group in methanol, electrolyte <sup>n</sup>Bu<sub>4</sub>NI, and dimethylamine under the standard reaction conditions (Fig. 3). Next, a series of control experiments were conducted to probe the reaction pathway. The reaction either failed or proceeded with low efficiency when the solvent methanol was changed to formaldehyde or formic acid (see scheme S1, F and I). These results indicate that a potential pathway involving the combination of carboxylic acid and zerovalent palladium catalyst could be excluded. In addition, when the reaction was performed with PdCl<sub>2</sub> or Pd(PPh<sub>3</sub>)<sub>4</sub> as a catalyst under 1 atm H<sub>2</sub>, only 2 to 6% of (*Z*)-1,2-diphenylethene was observed (see scheme S1, J to L), which excludes the possibility of the mechanism of hydrogenation with molecular hydrogen (H<sub>2</sub>). Furthermore, cyclic voltammetry (CV) of 1,2-diphenylethyne (**1a**) in CH<sub>3</sub>OH was measured (fig. S7). **1a** showed a single irreversible reduction peak at -0.67 V (versus Ag/Ag<sup>+</sup>), indicating that **1a** can be reduced in CH<sub>3</sub>OH. Moreover, the morphologic analyses of all palladium particles including those from the cathode surface and the solution were carried out with scanning electron microscopy (SEM) (Fig. 4). SEM micrographs revealed irregular palladium deposits of nanometric dimensions. X-ray diffraction (XRD) of these palladium particles showed that they are completely the Pd<sup>0</sup> (Fig. 4D). On the basis of the above observed results and previous reports, a plausible mechanism for the selective electrochemical hydrogenation reaction of alkynes to *Z*-alkenes was proposed (Fig. 3) (12–20, 30–36, 47, 48). Initially, methanol is used as a hydrogen source to generate chemisorbed hydrogen at the cathode. Palladium(0) nanoparticles are generated on the cathode and adsorb hydrogen. Next, a hydrogen transfer process occurs with alkynes to give intermediate C. Subsequently, intermediate C adsorbs another hydrogen atom to generate intermediate D. Finally, *Z*-alkene products are generated and desorbed, and adsorption sites are regenerated. In the reaction, the tetrabutylammonium ion is reduced by the cathode to generate tributylamine, which then loses an electron on the anode to form amine radical cation E (14, 15). This radical cation species could also transfer a hydrogen atom to intermediate C to afford the product **2** (48).

## CONCLUSION

In summary, we have developed the first example of electrochemical hydrogenation reactions of alkynes to a library of *Z*-alkenes in high



**Fig. 4. SEM micrographs and XRD diffractograms. (A to C)** SEM micrographs of palladium nanoparticles formed on the cathode surface. **(D)** XRD of the palladium nanoparticles. **(E to G)** SEM micrographs of the Pd nanoparticles from the solution. a.u., arbitrary units.

yields with excellent chemo- and stereoselectivity. Detailed mechanistic studies of electrochemical hydrogenation were also conducted. In the electrochemical selective hydrogenation process, deuterium-labeling experiments showed that hydrogen comes from the solvent, supporting electrolyte, and base. As demonstrated by SEM and XRD, palladium nanoparticles generated in the electrochemical reaction act as a chemisorbed hydrogen carrier in the process. A library of alkynes readily underwent electrochemical hydrogenation to provide the corresponding Z-alkenes in high yields with excellent chemo- and stereoselectivity. As a green synthetic method, this approach provides a great opportunity for synthetic application. As shown in this study, this newly developed method provided a straightforward access to TPA-bearing (z)-2-(4-styrylphenyl)oxazoles, which opens up a new avenue for a rapid buildup of new mechanofluorochromic materials. Furthermore, complete reduction of alkynes to saturated alkanes was also achieved by slightly tuning the conditions.

## MATERIALS AND METHODS

### General procedure

The electrochemical hydrogenation was carried out in a three-necked round-bottomed flask (10 ml), with a graphite rod anode and a platinum disc cathode. **1** (0.80 mmol), PdCl<sub>2</sub> [0.5 mole percent (mol %), 0.7 mg], Me<sub>2</sub>NH (0.5 equiv, 0.2 ml, 2.0 M in the methanol), <sup>119</sup>Bu<sub>4</sub>NI (1.0 equiv, 295.5 mg), and MeOH (8.0 ml) were placed in a three-necked round-bottomed flask at 60°C, with a constant current of 0.1 A maintained for 2.5 to 5 hours. The mixture was cooled to room temperature and diluted with 20 ml of EtOAc. The organic mixture was then washed with brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and evaporated under vacuum. The residue was purified by flash column chromatography (*n*-hexane) on silica gel to provide the desired product **2**.

## SUPPLEMENTARY MATERIALS

Supplementary material for this article is available at <http://advances.sciencemag.org/cgi/content/full/5/5/eaaw2774/DC1>

Section S1. General remarks

Section S2. Optimization of the electrochemical hydrogenation reaction conditions

Section S3. General procedure for the electrochemical hydrogenation of alkynes to Z-alkenes

Section S4. General procedure for Pd-catalyzed hydrogenation of alkynes to alkanes via electroreduction

Section S5. General procedure for Pd-catalyzed hydrogenation of alkenes to alkanes via electroreduction

Section S6. The photophysical and mechanochromic luminescence properties of **4a** to **4d**

Section S7. TGA curves of **4b**

Section S8. Cyclic voltammetry

Section S9. Mechanism study

Section S10. Experimental data for the described substances

Section S11. Copies of <sup>1</sup>H and <sup>13</sup>C NMR spectra

Table S1. Optimization of the electrochemical hydrogenation reaction conditions.

Scheme S1. Deuterium-labeling experiments and control experiments of selective hydrogenation of alkynes.

Scheme S2. Deuterium-labeling experiments of hydrogenation of alkynes to alkanes.

Fig. S1. The UV absorption and fluorescence emission spectra.

Fig. S2. Emission color coordinates of **4b** in the CIE<sub>1931</sub> chromaticity diagram.

Fig. S3. The fluorescence emission spectra of unground and ground **4a** to **4d**.

Fig. S4. DSC trace of **4b** in different states.

Fig. S5. Powder XRD patterns of **4b** in different states.

Fig. S6. TGA curves of **4b**.

Fig. S7. CV of 1,2-diphenylethyne.

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