## ACS APPLIED NANO MATERIALS

# Oxidation Control of 5-Hydroxymethylfurfural to Polymer Building Blocks by Au Clusters and Nanoparticles on Hollow CeO<sub>2</sub> Spheres

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ABSTRACT: Hol lysts were synthe templates and app hydroxymethylfurfu	low and nanoparticulate Au/ esized using hollow microp plied for the controlled oxid ural (HMF) to polymer build	CeO <sub>2</sub> ( orous o ation o ing bloo	(Au/HN-CeO <sub>2</sub> ) cata- organic polymers as of biomass-derived 5- cks, 5-hydroxymethyl-	Controlled Oxidation	Au Clusters	но со

hydroxymethylfurfural (HMF) to polymer building blocks, 5-hydroxymethylfuran-2-carboxylic acid (HMFC) and furan-2,5-dicarboxylic acid (FDC). The optimal amounts of Au in Au/HN-CeO<sub>2</sub> catalysts resulted in the selective formation of HMFC and FDC with excellent yields of up to 93–96%. The Auamount-dependent catalytic performance resulted from the cluster and nanoparticle features of Au species in Au/HN-CeO<sub>2</sub> catalysts. Au/HN-CeO<sub>2</sub> could be recycled in five successive oxidation reactions of HMF to HMFC, maintaining the original catalytic performance.



**KEYWORDS**: nanocatalyst, cerium oxide, gold, biomass, oxidation, 5-hydroxymethylfurfural

Recently, as the social demand to regulate the consumption of petroleum has increased, the exploration of alternative chemical resources has become more and more important.<sup>1</sup> Biomass is the most promising chemical resource to replace petroleum.<sup>1–5</sup> The main chemical components of biomass are lignocellulosic materials.<sup>1–5</sup> In particular, cellulose has attracted considerable attention from scientists as a sustainable chemical resource.<sup>2</sup> Acid hydrolysis of cellulose produces monosaccharides. Successive water abstraction from monosaccharides results in the formation of furan derivatives.<sup>3</sup> As a representative compound, 5-hydroxymethylfurfural (HMF) can be obtained through water abstraction from glucose or fructose.<sup>2–4</sup> While various valuable chemicals can be prepared using HMF through the so-called furanics, HMF-derived polymers are some of the most important materials.<sup>4</sup> In this regard, biomass-derived furan compounds have recently been utilized in the synthesis of polymers.<sup>5</sup>

Recently, biodegradable plastics have attracted great attention from scientists because of increasing environmental concerns.<sup>6</sup> In terms of chemical structure, polyesters are the main class of biodegradable polymers.<sup>6</sup> For example, poly-(caprolactone) (PCL) has been studied as a biodegradable polymer.<sup>7</sup> While PCL is an aliphatic polyester, aromatic rings such as furans can be incorporated into polyesters to induce higher  $T_g$  values. Moreover, the existence of furan rings in polyesters can improve water wettability, which is one of the critical factors for biodegradability. However, poly(5-hydroxymethylfuran-2-carboxylic acid) (PHMFC) has been less explored because of its limited synthetic routes to HMFC (Figure 1).<sup>8</sup>

Another important polyester is poly(ethylene terephthalate) (PET).<sup>9</sup> Because benzene rings in the PET hinder its water



Figure 1. Controlled oxidation of biomass-derived HMF to polymer building blocks (HMFC and FDC). Chemical structures of PEF, PHMFC, and their analogues (PET and PCL).

wettability, alternative polymers of PET, such as poly(ethylene furan-2,5-dicarboxylate) (PEF), have attracted much attention (Figure 1).<sup>9</sup> For the chemistry of PHMFC and PEF, HMFC

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and furan-2,5-dicarboxylic acid (FDC) are required as monomers, respectively.

While oxidation catalysts for the conversion of HMF to FDC have been reported,<sup>10–19</sup> efficient and selective oxidation catalysts for the synthesis of HMFC from HMF are relatively rare in the literature.<sup>20,21</sup> Usually, mixtures of HMFC and FDC were obtained in the oxidation of HMF.<sup>10–21</sup> Moreover, conventional Au/CeO<sub>2</sub> catalysts resulted in poor yields of HMFC and FDC because of the decomposition of HMF. In this work, we report the synthesis of a hollow and nanoparticulate CeO<sub>2</sub> (HN-CeO<sub>2</sub>) support and Au/HN-CeO<sub>2</sub> nanocatalysts and their excellent catalytic performance for the selective oxidation of HMF to HMFC and FDC.

Figure 2 shows a synthetic scheme for  $Au/HN-CeO_2$  nanocatalysts (refer to the Experimental section for details).



**Figure 2.** Synthesis of Au/HN-CeO<sub>2</sub> nanocatalysts using H-MOP and a scheme of the Au<sup>3+</sup> reduction to zerovalent Au by the defective  $Ce^{3+}$  species in the nanoscaled CeO<sub>2</sub>.

A hollow microporous organic polymer (H-MOP) was prepared by template synthesis.<sup>22</sup> After silica spheres were coated with MOP by the Sonogashira coupling of tetrakis(4-ethynylphenyl)methane with 1,4-diiodobenzene, they were etched by treatment with a HF solution, resulting in the formation of H-MOP.<sup>22</sup> After CeO<sub>2</sub> precursors were loaded onto H-MOP,<sup>23</sup> successive calcinations in air resulted in the formation of HN-CeO<sub>2</sub>. Then, the reaction of HN-CeO<sub>2</sub> with HAuCl<sub>4</sub> resulted in zerovalent Au on HN-CeO<sub>2</sub> to form Au/HN-CeO<sub>2</sub>. The nanoscaled CeO<sub>2</sub> is known to be rich in oxygen defects and the Ce<sup>3+</sup> species.<sup>23</sup> The Ce<sup>3+</sup> species can be utilized as a reductant in the grafting of zerovalent Au species to CeO<sub>2</sub> (Figure 2).<sup>24</sup> The contents of Au in Au/HN-CeO<sub>2</sub> were controlled by the amounts of HAuCl<sub>4</sub>. With a fixed amount of HN-CeO<sub>2</sub> (0.10 g), the amounts of HAuCl<sub>4</sub>

increased from 1.1 mg to 2.3, 11, and 23 mg to form Au/HN-CeO<sub>2</sub>-1, -2, -3, and -4, respectively.

As control materials, nonhollow  $Au/CeO_2$ -1 and -2 were prepared by the same synthetic procedures of Au/HN-CeO<sub>2</sub>-2 using commercial CeO<sub>2</sub> powder and homemade CeO<sub>2</sub> nanoparticles, respectively, instead of HN-CeO<sub>2</sub> (refer to the Experimental section and Figure S1).

The morphologies of HN-CeO<sub>2</sub>, Au/HN-CeO<sub>2</sub>-1–4, and nonhollow Au/CeO<sub>2</sub>-1 and -2 were investigated by transmission electron microscopy (TEM; Figures 3 and S1 and S2).



Figure 3. TEM images of (a, d, and g) HN-CeO<sub>2</sub>, (b, e, and h) Au/ HN-CeO<sub>2</sub>-2, and (c, f, and i) Au/HN-CeO<sub>2</sub>-4. Refer to Figures S1 and S2 for the TEM images of Au/HN-CeO<sub>2</sub>-1, Au/HN-CeO<sub>2</sub>-3, and nonhollow Au/CeO<sub>2</sub>-1 and -2.

TEM analysis showed the hollow morphologies of HN-CeO<sub>2</sub> and Au/HN-CeO<sub>2</sub> with diameters of 220–240 nm (Figures 3 and S2). Interestingly, the shells of HN-CeO<sub>2</sub> consisted of interconnected CeO<sub>2</sub> nanoparticles with sizes of 4-5 nm (Figure 3a,d,g). As the amounts of Au increased, the sizes of the particles in Au/HN-CeO<sub>2</sub> gradually increased from 6-8 nm (Au/HN-CeO<sub>2</sub>-1) to 7-9 nm (Au/HN-CeO<sub>2</sub>-2), 8-10 nm (Au/HN-CeO<sub>2</sub>-3), and 11-15 nm (Au/HN-CeO<sub>2</sub>-4) (Figures 3b,c,e,f,h,i and S2). In comparison, while TEM analysis of nonhollow Au/CeO<sub>2</sub>-1 revealed irregular granular materials with sizes of 40-60 nm, that of nonhollow Au/CeO<sub>2</sub>-2 showed aggregation of the nanoparticles (Figure S1).

Analysis of the N<sub>2</sub> adsorption–desorption isotherm curves of HN-CeO<sub>2</sub> based on the Brunauer–Emmett–Teller theory showed a high surface area of 68 m<sup>2</sup>/g due to the hollow and nanoparticulate features. Even after Au loading, the high surface areas of Au/HN-CeO<sub>2</sub>-1, -2, -3, and -4 were retained at 67, 63, 57, and 54 m<sup>2</sup>/g, respectively (Figure 4a and Table S1). In comparison, nonhollow Au/CeO<sub>2</sub>-1 and -2 showed relatively lower surface areas of 27 and 45 m<sup>2</sup>/g, respectively, because of the bigger sizes and aggregation of the particles (Figure S1 and Table S1).

IR absorption spectroscopy of  $HN-CeO_2$  and  $Au/HN-CeO_2$ each showed a unique vibrational peak of Ce–O at 504 cm<sup>-1</sup>



**Figure 4.** (a) N<sub>2</sub> adsorption–desorption isotherm curves at 77 K, (b) IR spectra, and (c) PXRD patterns of HN-CeO<sub>2</sub> and Au/HN-CeO<sub>2</sub>-1-4 (the asterisks in the PXRD patterns of Au/HN-CeO<sub>2</sub>-3 and -4 indicate the (111) diffraction peaks of metallic Au). EDS-based elemental mapping images of (d) Au/HN-CeO<sub>2</sub>-2 and (e) Au/HN-CeO<sub>2</sub>-4.

(Figure 4b).<sup>23</sup> As the amount of Au increased in Au/HN-CeO<sub>2</sub>, the absorption at 500–800 nm by Au materials increased gradually, supporting the increase of the Au contents (Figure S3). Inductively coupled plasma analysis showed that the Au contents in Au/HN-CeO<sub>2</sub>-1, -2, -3, and -4 and nonhollow Au/CeO<sub>2</sub>-1 and -2 are 0.54, 1.1, 4.4, 7.3, 0.98, and 1.1 wt %, respectively.

Powder X-ray diffraction (PXRD) studies indicated the crystalline CeO<sub>2</sub> (JCPDS 81-0792) of HN-CeO<sub>2</sub>, Au/HN-CeO<sub>2</sub>-1-4, and nonhollow Au/CeO<sub>2</sub>-1 and -2 (Figures 4c and S1). While the diffraction peaks of Au were not observed in the PXRD patterns of Au/HN-CeO<sub>2</sub>-1 and -2 and nonhollow Au/CeO<sub>2</sub>-1 and -2, Au/HN-CeO<sub>2</sub>-3 and -4 showed the diffraction peaks of metallic Au (JCPDS 04-0783; Figures 4c and S1). Energy-dispersive X-ray spectroscopy (EDS)-based elemental

mapping studies of Au/HN-CeO<sub>2</sub>-2 and -4 showed that the hollow materials mainly consist of Ce and O. In addition, Au was homogeneously distributed over the HN-CeO<sub>2</sub> materials (Figures  $4d_{e}$ ).

To investigate the chemical surroundings of Au species in  $Au/HN-CeO_2$ , X-ray absorption spectroscopy (XAS) was conducted (Figure 5a,b). While the X-ray absorption near-



Figure 5. (a) XANES and (b) EXAFS spectra of Au/HN-CeO<sub>2</sub>-2–4 and Au foil (the chemical surroundings of Au clusters and Au nanoparticles on CeO<sub>2</sub> are given in the inset). XPS spectra of the (c) Au 4f and (d) Ce 3d orbitals of HN-CeO<sub>2</sub> and Au/HN-CeO<sub>2</sub>-1–4. HR-TEM images of (e) Au/HN-CeO<sub>2</sub>-2 and (f) Au/HN-CeO<sub>2</sub>-4.

edge structure (XANES) spectrum could not be obtained for the Au species in Au/HN-CeO<sub>2</sub>-1, because of its minor amount, those of Au/HN-CeO<sub>2</sub>-2–4 indicated that the main Au species have zerovalent states (Figure 5a).<sup>24</sup> The extended X-ray absorption fine structure (EXAFS) spectrum of Au/HN-CeO<sub>2</sub>-2 showed significant signals at 1.1–2.2 Å (Au–O), in addition to those at 2.2–3.6 Å (Au–Au), indicating *the cluster feature* of Au species (Figure 5b and the inset of Figure 5a).<sup>24</sup> In comparison, the EXAFS spectra of Au/HN-CeO<sub>2</sub>-3 and -4 showed the main signals of the Au–Au bonds at 2.2–3.6 Å, indicating *the nanoparticle feature* of Au species (Figure 5b and the inset of Figure 5a).<sup>24</sup>

The X-ray photoelectron spectroscopy (XPS) spectra of Au/ HN-CeO<sub>2</sub>-1-4 and nonhollow Au/CeO<sub>2</sub>-1 and -2 showed the Au  $4f_{7/2}$  and  $4f_{5/2}$  orbital peaks at 83.5 and 87.2 eV, respectively, indicating that the main Au species in the catalysts have zerovalent states (Figures 5c and S1 and S4).<sup>24</sup> The XPS spectra of HN-CeO<sub>2</sub> and Au/HN-CeO<sub>2</sub> showed the  $3d_{5/2}$  and  $3d_{3/2}$  orbital peaks of defective Ce<sup>3+</sup> at 885.3 and 903.4 eV, respectively, confirming the nanoregime-enhanced defective feature of CeO<sub>2</sub> (Figure 5d).<sup>23</sup> To further confirm the different chemical situations of Au species in Au/HN-CeO<sub>2</sub>-2 and Au/HN-CeO<sub>2</sub>-4, high-resolution TEM (HR-TEM) analysis was conducted. As shown in Figure 5e, Au nanoparticles were not detected in the HR-TEM analysis of Au/HN-CeO<sub>2</sub>-2. Instead, the (111) and (200) crystalline planes of CeO<sub>2</sub> nanoparticles were mainly observed. In comparison, Au nanoparticles were directly detected with diameters of 10-15 nm in the HR-TEM analysis of Au/HN- $CeO_2$ -4 (Figure 5f), matching the results of XAS studies (Figure 5a,b).

During the past decade, Au/CeO<sub>2</sub> materials have been applied as heterogeneous catalysts in various organic transformations including oxidation.<sup>25–28</sup> In addition, it has been reported that the hollow structural engineering of nanocatalysts provides benefits in their catalytic performance because of the facilitated mass transfer of substrates.<sup>29</sup> Considering the nanoparticulate and hollow features of Au/HN-CeO<sub>2</sub> materials, we studied their catalytic performance in the selective oxidation of HMF to HMFC and FDC. Table 1 and Figures 6 and S5–S7 summarize the results.

When no catalysts or HN-CeO<sub>2</sub> was used, the oxidation products of HMF were not detected or poorly obtained (entries 1-3 in Table 1). In comparison, when Au/HN-CeO<sub>2</sub>-1 (0.50 mol % Au) was used as an oxidation catalyst at 100 °C in the presence of 0.5 MPa O2 and NaOH, HMFC was obtained from HMF with a promising yield of 82% after 5 h (entry 4 in Table 1). Moreover, when Au/HN-CeO<sub>2</sub>-2 (0.50) mol % Au) was used as a catalyst, the yield of HMFC increased to 93% (an isolated yield of 89%) without the formation of FDC (entry 5 in Table 1 and Figure 6a). Without  $O_2$  or NaOH, Au/HN-CeO<sub>2</sub>-2 did not produce HMFC (entries 6 and 7 in Table 1). When nonhollow Au/CeO<sub>2</sub>-1 and -2 (0.50 mol % Au) were used as control catalysts of Au/HN-CeO<sub>2</sub>-2, HMFCs were obtained with poor yields of 13-19% because of the significant decomposition of HMF (entries 8 and 9 in Table 1). These results indicate that the hollow and nanoparticulate feature of Au/HN-CeO<sub>2</sub>-2 is critical for the efficient oxidation of HMF to HMFC.

As the reaction temperature decreased from 100 °C to 80, 60, 40, and 25 °C, the yields of HMFC obtained by Au/HN-CeO<sub>2</sub>-2 gradually decreased from 90% to 72, 54, 30, and 20%, respectively (entries 5 and 10–13 in Table 1). When Au/HN-CeO<sub>2</sub>-3 (0.50 mol % Au) or Au/HN-CeO<sub>2</sub>-4 (0.50 mol % Au) was used as an oxidation catalyst, FDC was obtained with good yields of 83 and 96%, respectively, without the formation of HMFC (entries 14 and 15 in Table 1 and Figure 6a). While various catalysts have been reported for the full oxidation of HMF to FDC, the controlled oxidation of HMF to HMFC has been explored relatively less.<sup>10–21</sup> Our results indicate that both HMFC and FDC can be obtained through the amount of

Table 1. Oxidation of HMF to HMFC and FDC by Au/HN-CeO<sub>2</sub> Catalysts<sup>a</sup>

	0	Cat., O <sub>2</sub>			ິ່ງ	<b>o</b> //
OHC	√ ∕∕он	NaOH HO	$\sim$	^он⁺ н	io ()	ОН
	HMF	H₂O	HMFC		FDC	;
					vield	(%) <sup>b</sup>
			0	tomn		
entry	catalyst <sup>c</sup>	base	(MPa)	(°C)	HMFC	FDC
1				100		
2		NaOH	0.5	100	5	
3 <sup>d</sup>	$HN-CeO_2$	NaOH	0.5	100		
4	1	NaOH	0.5	100	82	
5	2	NaOH	0.5	100	93 (89)	
6	2	NaOH		100		
7	2		0.5	100		
8	$Au/CeO_2$ -1 <sup>e</sup>	NaOH	0.5	100	13	
9	$Au/CeO_2$ - $2^f$	NaOH	0.5	100	19	
10	2	NaOH	0.5	80	72	
11	2	NaOH	0.5	60	54	
12	2	NaOH	0.5	40	30	
13	2	NaOH	0.5	25	20	
14	3	NaOH	0.5	100		83
15	4	NaOH	0.5	100		96 (93)
16 <sup>g</sup>	2	NaOH	0.5	100	93	
17 <sup>h</sup>	2	NaOH	0.5	100	91	
18 <sup>i</sup>	2	NaOH	0.5	100	92	
19 <sup>i</sup>	2	NaOH	0.5	100	91	
20 <sup>k</sup>	4	NaOH	0.5	100		94
21 <sup>1</sup>	4	NaOH	0.5	100		95
22 <sup>m</sup>	4	NaOH	0.5	100		94
23 <sup>n</sup>	4	NaOH	0.5	100		93

<sup>a</sup>Reaction conditions: Au/HN-CeO<sub>2</sub> (0.50 mol % Au), HMF (0.32 mmol), NaOH (4 equiv, 1.28 mmol), H<sub>2</sub>O (4 mL), 5 h. <sup>b</sup>NMR yields using maleic acid as an internal standard. The isolated yields are indicated in parentheses. <sup>c</sup>Au/HN-CeO<sub>2</sub>-1 (1), Au/HN-CeO<sub>2</sub>-2 (2), Au/HN-CeO<sub>2</sub>-3 (3), and Au/HN-CeO<sub>2</sub>-4 (4). <sup>d</sup>28.8 mg of HN-CeO<sub>2</sub> was used as a catalyst. <sup>e</sup>Nonhollow Au/CeO<sub>2</sub>-1 (0.50 mol % Au) was used as a catalyst (refer to Figure S1). <sup>J</sup>Nonhollow Au/CeO<sub>2</sub>-2 (0.50 mol % Au) was used as a catalyst recovered from entry 5 was used. <sup>h</sup>The catalyst recovered from entry 16 was used. <sup>l</sup>The catalyst recovered from entry 18 was used. <sup>k</sup>The catalyst recovered from entry 15 was used. <sup>l</sup>The catalyst recovered from entry 20 was used. <sup>m</sup>The catalyst recovered from entry 21 was used. <sup>n</sup>The catalyst recovered from entry 22 was used.

optimization of Au species in the  $Au/HN-CeO_2$  catalysts (entries 5 and 15 in Table 1 and Figures 6a and S5).

Next, the recyclability of Au/HN-CeO<sub>2</sub>-2 was studied in the selective oxidation of HMF to HMFC or FDC (Figures 6 and S6). As shown in entries 5, 15, and 16–23 in Table 1 and Figures 6b and S6, Au/H-CeO<sub>2</sub>-2 maintained its catalytic performance in five successive oxidation reactions of HMF to HMFC or FDC with yields in the ranges of 91–93% and 93–96%, respectively. The TEM studies on Au/H-CeO<sub>2</sub>-2 that were recovered after five oxidation reactions of HMF to HMFC indicated that the original hollow and nanoparticulate morphologies were completely retained after reactions (Figure 6c). In addition, the XPS studies indicated that the original zerovalent Au state in Au/H-CeO<sub>2</sub>-2 was completely retained during the oxidation reactions (Figure 6d and S7).



**Figure 6.** (a) <sup>1</sup>H NMR spectra (DMSO- $d^6$ ) of HMF and isolated HMFC and FDC (refer to Figure S5 for <sup>13</sup>C NMR spectra). (b) Recyclability tests of Au/HN-CeO<sub>2</sub>-2 in the oxidation of HMF to HMFC (reaction conditions: 0.50 mol % Au, 0.32 mmol of HMF, 1.28 mmol of NaOH, 4 mL of H<sub>2</sub>O, 0.5 MPa O<sub>2</sub>, 100 °C, 5 h). (c) TEM image of Au/HN-CeO<sub>2</sub>-2 recovered after five successive catalytic reactions. (d) XPS spectra (Au 4f orbitals) of Au/HN-CeO<sub>2</sub>-2 before and after five successive catalytic reactions.

The catalytic performance of 0.50 mol % Au/HN-CeO<sub>2</sub>-2 for the selective oxidation of HMF to HMFC (93%) with a turnover number (TON) of 186 and a turnover frequency (TOF) of 37 h<sup>-1</sup> is superior to that of a 0.625 mol % Au-based catalytic system with a TON of 149 and a TOF of 12 h<sup>-1</sup> in the literature (Table S2).<sup>20</sup> In addition, the catalytic performance of 0.50 mol % Au/HN-CeO<sub>2</sub>-4 for the oxidation of HMF to FDC (96%) with a TON of 192 and a TOF of 38 h<sup>-1</sup> is superior to those of 0.625–1 mol % Au-based catalytic systems with TONs of 93–150 and TOFs of 7–20 h<sup>-1</sup> in the literature (Table S2).<sup>10–21</sup>

The excellent catalytic performances of Au/HN-CeO<sub>2</sub>-2 and -4 are attributable to their hollow morphology-induced facile mass transfer<sup>29</sup> and nanoparticulate feature-induced high surface areas (entries 5, 8, 9, and 15 in Table 1). In addition, the distinctly different catalytic performances of Au/HN-CeO<sub>2</sub>-2 and -4 are attributable to the cluster and nanoparticle features of Au species in catalysts, respectively (Figure 5b). The controlled reactivities of Au clusters and Au nanoparticles on CeO<sub>2</sub> supports and the Au–support interactions have been reported in the literature.<sup>24,30</sup>

In conclusion, hollow and nanoparticulate Au/HN-CeO<sub>2</sub> catalysts were developed using H-MOP as the structural platform. It was found that the oxidation of HMF to HMFC and FDC can be selectively controlled with high isolated yields through the systematic control of Au species in the Au/HN-CeO<sub>2</sub> catalysts. We believe that the Au/HN-CeO<sub>2</sub> nano-catalysts of this work can be applied to more various oxidative transformations of biomass.<sup>25–28</sup>

#### ASSOCIATED CONTENT

#### **1** Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsanm.2c00120.

Synthetic procedures of HN-CeO<sub>2</sub>, Au/HN-CeO<sub>2</sub>, and nonhollow Au/CeO<sub>2</sub>, experimental procedures of catalytic reactions, characterization data of nonhollow Au/CeO<sub>2</sub>, additional TEM images of Au/HN-CeO<sub>2</sub>, UV/vis absorption spectra of HN-CeO<sub>2</sub> and Au/HN-CeO<sub>2</sub>, XPS analysis, <sup>13</sup>C NMR spectra, recyclability tests, and comparison tables of the catalytic performance (PDF)

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#### Notes

The authors declare no competing financial interest.

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