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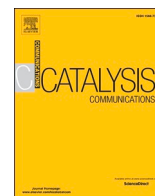
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Short communication

## Ultrasound-assisted synthesis of NiO nanoparticles and their catalytic application for the synthesis of trisubstituted imidazoles under solvent free conditions

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## ABSTRACT

The present protocol reports the ultrasound assisted synthesis of NiO nanoparticles (NPs) using benzylamine as a base and different types of cyclodextrins (CDs) as capping agents. The use of  $\alpha$ -CD,  $\beta$ -CD or  $\gamma$ -CD leads to different morphologies of NiO NPs. In particular, NiO nanosheets obtained using  $\beta$ -CD as the capping agent. The synthesized NPs were characterized by FEG-SEM, TEM, XRD and EDS analysis. They showed high catalytic activity towards synthesis of different trisubstituted imidazoles under solvent free conditions. In addition, NiO NPs could be recycled and reused consecutively up to four recycle runs without much loss of their catalytic activity.

### 1. Introduction

Metals and metal oxide nanomaterials has played an important role in the different fields because of their size, shape and higher surface to volume ratio [1]. Various methods are available for the synthesis of metal and metal oxide nanomaterials based on the microwave, solvothermal, solar assisted, electro deposition, thermal decomposition based techniques [2–5]. The synthesis and application of NiO nanoparticles (NPs) are in demand for its applications in various fields such as catalysts in the organic synthesis [2], sensors [3], photo catalysts [6] etc.

Multicomponent reactions (MCRs) are the reactions in which two or more molecules react together in a one-pot fashion to give the desired products. MCRs showed high atom economy as most of the atoms of reactant will present in the desired product. They avoid the handling loss of compounds as compared with the convergent methods of the synthesis and the methodology is important for the synthesis of biological active and complex compounds [7]. Synthesis of imidazoles is achieved by one-pot synthesis, which containing nitrogen atom at 1,3 positions of the five member ring. Substituted imidazoles are useful in biological and therapeutic applications such as antimicrobial activity, anticancer, inhibitors such as P38 MAP kinase, B-Raf Kinase, calcium antagonist and inhibitors of thromboxane A2 synthetase anti-retro viral [8–11]. A part from these biological and therapeutic actions, they are

also used in the photographic sensitizers [12]. Some important moieties of imidazoles derivatives such trifenagrel is a potent arachidonate cyclooxygenase inhibitor that reduces platelet aggregation, Lophine which is used chemiluminescent molecules, P38 map inhibitor [13] as shown in the Fig. 1.

The imidazoles and its derivatives can be synthesized by condensation of benzil, aldehyde and ammonium acetate in the presence of suitable catalyst. The different catalysts are used for the synthesis of substituted pyrroles such as ionic liquids [14], supported Fe<sub>3</sub>O<sub>4</sub> [15], K<sub>5</sub>CoW<sub>12</sub>O<sub>40</sub>·3H<sub>2</sub>O [16], Zeolite [17], MOFs [18] Ni<sub>0.5</sub>Zn<sub>0.5</sub>Fe<sub>2</sub>O<sub>4</sub> [19], Modified SBA-15 [20], MoO<sub>3</sub>/SiO<sub>2</sub> [21], ZrO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> [22], NiCl<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> [23,26], heteropolyacids [24] nano-SnCl<sub>4</sub>•SiO<sub>2</sub> [25] etc. These systems have their own advantages as well as they also suffer from one or more limitations such as difficulty in the preparation of the catalyst, recovery of the catalyst, long reaction times, moisture sensitive catalyst, facing problems during the work up of the reaction etc. Hence, there is a need to develop a greener protocol which can avoid such disadvantages.

In the present protocol, we have utilized the ultrasound for the synthesis of NiO NPs by using benzylamine as a base and various CDs as capping agents. The synthesis protocol is schematically depicted and described in the following experimental section. CDs are a class of naturally occurring receptors, which are cyclic oligosaccharides, constituted of  $n$  D-glucopyranose units ( $n = 6, 7$  and  $8$  for  $\alpha$ -,  $\beta$ - and  $\gamma$ -CD

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multiple conformations of the nickel-based adduct. Beyond this, it should be noted that the effects observed between cyclodextrin, Ni acetate and benzylamine in solution are not limited to  $\beta$ -CD but have also been observed using  $\alpha$ -CD (Fig. S4) and  $\gamma$ -CD (Fig. S5). In light of these results showing that the coordination ability of benzylamine to nickel cations can be preserved within the CD cavity, it appears interesting to exploit these supramolecular assemblies as potential templates in the synthesis of NiO materials assisted by ultrasound.

### 3.2. Synthesis of NiO NPs

In a 100 mL beaker Ni(OAc)<sub>2</sub> (500 mg),  $\alpha$ -CD (100 mg) were dissolved in 10 mL of distilled water. Then drop wise addition of 10 mL of benzylamine gave formation of a light green coloured precipitate. Then the solution was irradiated under ultrasound using an ultrasonic probe for 90 pulses at 30 amplitude ((PCI Analytics Pvt. Ltd., India). Green coloured Ni(OH)<sub>2</sub> was formed and thereafter it was separated by centrifugation, washed twice with distilled water (2 × 10 mL) followed by ethanol (1 × 10 mL). The product was dried at 80 °C for 2 h. The Ni(OH)<sub>2</sub> prepared by using  $\alpha$ -CD as a capping was designated as Ni(OH)<sub>2</sub>- $\alpha$ . The latter gave nickel oxide NPs, which was designated as NiO- $\alpha$ , after calcination at 500 °C for 5 h. The same procedure was followed with  $\beta$ -CD and  $\gamma$ -CD. Ni(OH)<sub>2</sub>- $\beta$  and Ni(OH)<sub>2</sub>- $\gamma$  gave after calcination nickel oxide NPs which were designated as NiO- $\beta$ , NiO- $\gamma$  respectively (Fig. 2).

### 3.3. Characterization of NiO NPs

The morphology of NiO- $\alpha$ , NiO- $\beta$  and NiO- $\gamma$  was analyzed by using FEG-SEM which confirmed that synthesized NPs are in the nano size. The change in the capping agent has an impact on the changes of morphology of these particles. The use of  $\alpha$ -CD and  $\gamma$ -CD as capping agents results in agglomerated nanoparticles as observed in Fig.S6(a) and S6(c), whereas the use of  $\beta$ -CD provides stabilization of NiO particles in the form of nanosheets [Fig.S6(b)]. Notably, the TEM images of NiO- $\beta$  as shown in the Fig. S7 also reveal that an aerated nano-structure is obtained with NiO domains in the nano range. Such a structure is assumed to lead to enhanced specific surface area. The elemental dispersive spectrum (EDS) of NiO- $\alpha$ , NiO- $\beta$  and NiO- $\gamma$  shows the presence of only Ni and O elements (Fig.S8). Note that the presence of the carbon peak is due to the carbon tape on which is sample was placed.

After the ultrasound treatment, all nickel samples are shown to consist of a Ni(OH)<sub>2</sub> phase with a hexagonal lattice. The X-ray diffraction patterns of the samples are presented in Fig. S9.

After calcination of Ni(OH)<sub>2</sub>, the XRD pattern of NiO- $\alpha$ , NiO- $\beta$  and NiO- $\gamma$  gives lattice planes of (111), (200), (220), (311) and (222)

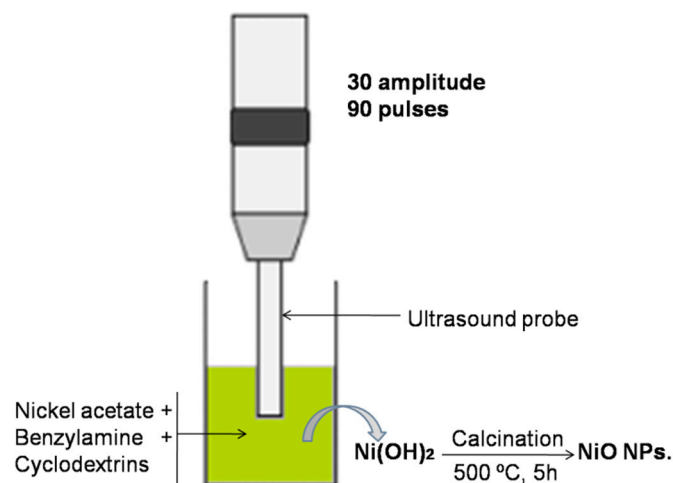


Fig. 2. Schematic representation for the synthesis of NiO NPs.

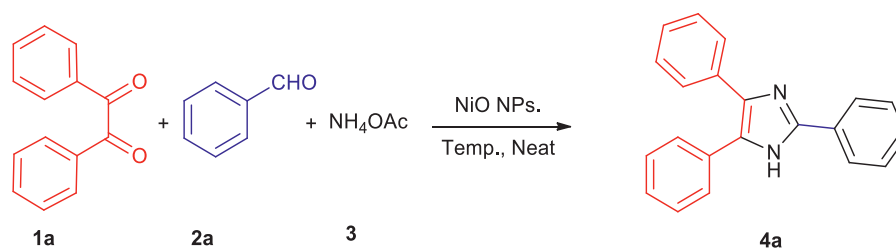
corresponding to the hexagonal lattice of NiO, which is in good agreement with the JCPDS 78-0429 file (Fig.S10) [2]. It shows that average crystallite size of NPs which was determined according to the Scherrer's equation, was found to be small (3 nm for  $\alpha$ -CD, 3.5 nm for  $\beta$ -CD and 4.5 nm for  $\gamma$ -CD).

### 3.4. Catalytic activity of NiO NPs for the synthesis of 2,4,5-trisubstituted imidazoles

The NiO NPs were used as catalysts for the synthesis of 2,4,5-trisubstituted imidazoles 4a (Scheme 1). Initially, we tested the catalytic activity of NiO- $\alpha$ , NiO- $\beta$  and NiO- $\gamma$  of 10 mg each for the model reaction of benzil (1 mmol), benzaldehyde (1 mmol) and ammonium acetate (2.5 mmol) under solvent free condition at 120 °C for one hour. The 61% yield of the product 4a obtained when NiO- $\alpha$  used (Table 1, entry 1), 97% and 69% yields of product 4a were obtained when we utilized NiO- $\beta$  and NiO- $\gamma$  (Table 1, entries 2–3). The significant higher catalytic activity of NiO- $\beta$  may be due to higher specific surface area. So we choose NiO- $\beta$  as a catalyst for further optimization for the synthesis of 4a. When, the model reaction was carried out using bulk NiO as control catalyst and without adding catalyst, we got 65% and 13% yield of the product 4a respectively (Table 1, entries 4–5).

The Further, we investigated the effect of the reaction time, temperature, type of solvent and catalyst loading for the synthesis of 4a. The reaction time has a significant influence on the yield of 4a. When the reaction was carried for 20 min, only 53% yield of the 4a, was obtained (Table 1, entry 6) while the further increase in the reaction time up to 50 min provided the increase in the yield of 4a up to 91% (Table 1, entries 7–9). The maximum yield of 4a, was obtained when the reaction was carried for 60 min (Table 1, entry 2). The increase in the reaction temperature was also found to be effective for the synthesis of 4a. When, the reaction carried out at 80 °C, a lower yield of 51% of 4a, was observed (Table 1, entry 10) and the 4a product yield increased when the reaction temperature rose from 90 °C to 110 °C (Table 1, entries 11–13). The highest yield of 97% of 4a, was observed when the reaction was carried out at 120 °C (Table 1, entry 2). The nature of the solvent has also a marked effect on the final yield of the product. Thus, the use of water, acetonitrile and ethanol were evaluated as solvents under their reflux conditions and only gave a yield of 4a of 28%, 55% and 53%, respectively (Table 1, entries 14–16), as compared to the value of 97% obtained under neat conditions (Table 1, entry 2). In case of neat condition as there is no solvent and other reagents including catalysts are same, effective catalyst concentration is very high and therefore it gives higher yield. Finally, we studied the effect of the catalyst loading. When the reaction was carried out using 5, 10 mg of catalyst, we observed 90%, 97% yield of the product 4a respectively (Fig. 3). A Further increase in the catalyst loading from 15 to 20 mg leads to a marginal increase in the yield of the product. So, the 10 mg of the catalyst was the optimum loading for the synthesis of product 4a.

Hence, the optimized reaction conditions are: catalyst (NiO- $\beta$ ), catalyst loading: 10 mg, time: 60 min, temperature: 120 °C under solvent free conditions. The above optimized reaction conditions were readily extended to the one-pot synthesis of other substrates of 2,4,5 trisubstituted imidazoles in a one pot synthesis using different derivatives of aldehydes, and 1,2-diketones in the presence of ammonium acetate as the starting nitrogen source. The reaction of benzil 1a, benzaldehyde 2a gave excellent of 2,4,5 trisubstituted imidazole 4a (Table 3, entry 1). Then, keeping benzil 1a different derivatives of benzaldehyde were also investigated in this MCR. Thus, with benzaldehyde substrate bearing an electron donating groups such as 2-hydroxyl 2b, 4-*N,N*-dimethyl 2c, 4-methoxy 2d, 3,4-dimethoxy 2e gave the excellent yield of the product 4b-4e (Table 3, entries 2–5). In the same vein, the presence of electron withdrawing groups on benzaldehyde such as 4-fluoro 2f, 2-chloro 2g also gave excellent yields of their corresponding products 4f-4g (Table 2, entry 6–7). Finally, the methyl derivatives of benzil 1b gave the 85% yield of their corresponding

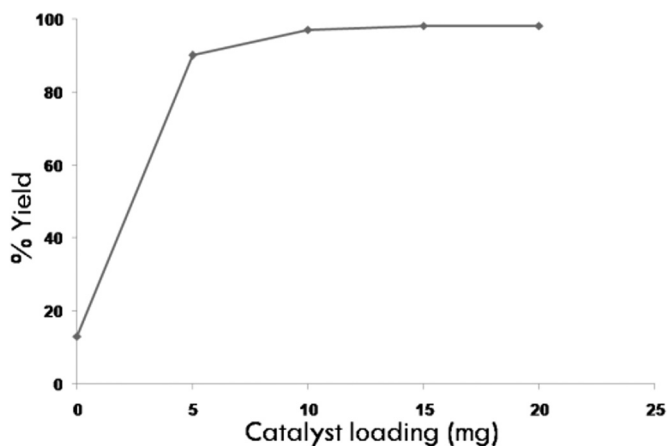


**Scheme 1.** Synthesis of 2,4,5-trisubstituted imidazoles catalysed by NiO NPs.

**Table 1**  
Optimisation of reaction for the synthesis of substituted imidazoles.<sup>a</sup>

Entry	Catalyst	Temp.(°C)	Solvent	Time (min.)	Yield [%] <sup>b</sup>
1	NiO- $\alpha$	120	–	60	61
2	NiO- $\beta$	120	–	60	97
3	NiO- $\gamma$	120	–	60	69
4	Bulk NiO <sup>c</sup>	120	–	60	65
5	–	120	–	60	13
6	NiO- $\beta$	120	–	20	53
7	NiO- $\beta$	120	–	30	60
8	NiO- $\beta$	120	–	40	74
9	NiO- $\beta$	120	–	50	91
	–	120	–		
10	NiO- $\beta$	80	–	60	51
11	NiO- $\beta$	90	–	60	65
12	NiO- $\beta$	100	–	60	72
13	NiO- $\beta$	110	–	60	83
14	NiO- $\beta$	120	Water	60	28
15	NiO- $\beta$	120	Acetonitrile	60	58
16	NiO- $\beta$	120	Ethanol	60	53

<sup>a</sup>Reaction conditions: Benzil (1.0 mmol), Benzaldehyde (1.0 mmol), NH<sub>4</sub>OAc (2.5 mmol), NiO NPs (10 mg), <sup>b</sup> Isolated Yield, <sup>c</sup>commercial, neat.



**Fig. 3.** Effect of catalyst loading for the synthesis of 4a (Reaction conditions: time: 60 min., neat, temp: 120 °C).

product 4 h (Table 2, entry 8).

The comparison of catalytic activity of NiO NPs with reported catalytic systems for the synthesis of 2,4,5-trisubstituted imidazoles is shown in Table 3. It can be seen that the reported protocols have certain limitations such as longer reaction time, lower yields of product. The catalyst Yb(OPf)<sub>3</sub>, Fe<sub>3</sub>O<sub>4</sub>@CS gave good yields of the products, but has longer reaction time as compared with reported protocol.

### 3.5. Recyclability study

The present protocol is based on Lewis acid based NiO NPs which are heterogeneous in nature and hence recyclable. These NPs could be were

**Table 2**  
Synthesis of 2,4,5-trisubstituted imidazoles catalysed by NiONPs.<sup>a</sup>

Entry	1,2-diketone	Aldehyde	Products	Yield [%] <sup>b</sup>
1				97
2				81
3				88
4				85
5				98
6				82
7				87
8				85

<sup>a</sup> Reaction conditions: 1,2-diketone (1.0 mmol), aldehyde (1.0 mmol), NH<sub>4</sub>OAc (2.5 mmol), NiO NPs (10 mg), temperature (120 °C), time: 60 min., <sup>b</sup> Isolated Yield.

separated from reaction mixture and recycled. After the completion of the reaction, the catalyst was readily separated by ultracentrifugation and the recovered catalyst was thoroughly washed with water-and ethanol- and finally dried in the oven (80 °C, overnight) before reusing it. Thus, the reusability of the  $\beta$ - NiO catalyst was examined and the tests showed that the catalyst was reusable up to four times without much loss of catalytic activity (Fig. S11).

**Table 3**

The comparison of catalytic activity of NiO NPs for the synthesis of 2,4,5-trisubstituted imidazoles.

Entry	Catalyst	Condition	Time [min.]	Yield	Ref.
1	Yb(OPD) <sub>3</sub>	Fluorous solvents, 80 °C	360	97	[31]
2	InCl <sub>3</sub> · 3H <sub>2</sub> O	MeOH, RT	720	70	[32]
3	Zr(acac) <sub>4</sub>	EtOH, reflux	150	90	[33]
4	N-acetyl glycine	Neat, 150 °C	120	78	[34]
5	Fe <sub>3</sub> O <sub>4</sub> @CS	EtOH, reflux	120	95	[15]
6	NiCl <sub>2</sub> ·6H <sub>2</sub> O/ Al <sub>2</sub> O <sub>3</sub>	EtOH, reflux	60	89	[23]
7	NiO NPs	Neat, 120 °C	60	97	This work

### 3.6. The catalytic mechanism of NiO NPs for the synthesis of 2,4,5-trisubstituted imidazoles

The proposed reaction mechanism for the synthesis of 2,4,5-trisubstituted imidazoles 4a catalysed by NiO NPs is shown in Fig. S12. NiO NPs coordinate with the carbonyl group of an aldehyde thereby increasing the electrophilicity of this aldehyde, which then allowed the subsequent coupling (or the condensation, the insertion) with two ammonia molecules to form the diamine intermediate A. Then, the intermediate A combines with the benzil to form the intermediate B which undergoes rearrangement to form 2,4,5-trisubstituted imidazoles 4a [35].

### 3.7. Characterization data of products

2,4,5-triphenyl-1H-imidazole 4a (Table 2, entry 1).

<sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>, ppm) δ 12.65 (s, 1H), 8.05 (d, *J* = 7.3 Hz, 2H), 7.51 (d, *J* = 7.5 Hz, 2H), 7.43 (dt, *J* = 11.6, 7.5 Hz, 6H), 7.34 (t, *J* = 7.3 Hz, 2H), 7.27 (t, *J* = 7.4 Hz, 2H), 7.19 (t, *J* = 7.1 Hz, 1H).

2-(4,5-diphenyl-1H-imidazol-2-yl)phenol 4b (Table 2, entry 2).

<sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>, ppm) δ 13.00 (s, 1H), 12.91 (s, 1H), 8.00 (d, *J* = 7.8 Hz, 1H), 7.59–7.08 (m, 10H), 6.92 (dd, *J* = 16.5, 8.1 Hz, 2H).

4-(4,5-diphenyl-1H-imidazol-2-yl)-*N,N*-dimethylaniline 4c (Table 2, entry 3).

<sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>, ppm) δ 12.32 (s, 1H), 7.91 (d, *J* = 8.6 Hz, 2H), 7.53–7.17 (m, 10H), 6.79 (d, *J* = 8.8 Hz, 2H), 2.96 (s, 6H).

2-(4-methoxyphenyl)-4,5-diphenyl-1H-imidazole 4d (Table 2, entry 4).

<sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>, ppm) δ 12.48 (s, 1H), 7.98 (d, *J* = 8.8 Hz, 2H), 7.49 (s, 2H), 7.47 (s, 2H), 7.29 (d, *J* = 26.8 Hz, 6H), 7.01 (d, *J* = 8.8 Hz, 2H), 3.78 (s, 3H).

2-(3,4-dimethoxyphenyl)-4,5-diphenyl-1H-imidazole 4e (Table 2, entry 5).

<sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>, ppm) δ 12.54 (s, 1H), 7.66 (d, *J* = 7.3 Hz, 2H), 7.52 (dd, *J* = 16.1, 7.1 Hz, 4H), 7.46–7.20 (m, 6H), 7.06 (d, *J* = 8.5 Hz, 1H), 3.85 (s, 3H), 3.80 (s, 3H).

2-(4-fluorophenyl)-4,5-diphenyl-1H-imidazole 4f (Table 2, entry 6).

<sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>, ppm) δ 12.66 (s, 1H), 8.17–7.11 (m, 14H).

2-(2-chlorophenyl)-4,5-diphenyl-1H-imidazole 4g (Table 2, entry 7).

<sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>, ppm) δ 12.64 (s, 1H), 7.79 (dd, *J* = 5.9, 3.4 Hz, 1H), 7.62–7.58 (m, 1H), 7.54 (d, *J* = 8.1 Hz, 2H), 7.50–7.41 (m, 6H), 7.37–7.29 (m, 3H), 7.22 (t, *J* = 7.4, 1H).

2-phenyl-4,5-di-*p*-tolyl-1H-imidazole 4h (Table 2, entry 8).

<sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>, ppm) δ 12.58 (s, 1H), 8.07 (d, *J* = 7.4 Hz, 2H), 7.50–7.42 (m, 4H), 7.37 (t, *J* = 9.3 Hz, 3H), 7.24 (d, *J* = 7.9 Hz, 2H), 7.10 (d, *J* = 7.9 Hz, 2H), 2.34 (s, 3H), 2.24 (d, *J* = 25.3 Hz, 3H).

## 4. Conclusion

The present protocol reports ultrasound assisted synthesis of the NiO NPs using Ni(OAc)<sub>2</sub> as a precursor, benzylamine as a base and cyclodextrins as a capping agent. The nature of capping agent such as α-CD, β-CD or γ-CD leads to different morphology of NiO NPs. The NiO nanosheets were formed with β-CD while the agglomerated NiO NPs were observed with α-CD and γ-CD. The catalytic activity of NiO NPs was evaluated for the synthesis of 2,4,5-trisubstituted imidazoles. The excellent yields of the products were obtained for different types of trisubstituted imidazoles. Also, the NiO NPs shows the excellent recyclability up to four recycles without significant loss of its catalytic activity.

## Author contributions

Aravind L. Gajengi: Experiments, Data Analysis, Writing Manuscript.

Shivkumar Chaurasia: Data Analysis.

Eric Monflier: Experiments, Writing, Cyclodextrin preparation and Characterization.

Anne Ponchel: Experiments, Writing, Cyclodextrin preparation and Characterization.

Jeremy Ternel: NMR Analysis.

Bhalchandra M. Bhanage: Manuscript Writing, Experiment Design, Funding.

All authors commented on and amended both the manuscripts. All Authors discussed and contributed to the work.

## Declaration of Competing Interest

None.

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## Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.catcom.2021.106366>.

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