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PII: S0022-328X(20)30263-1

DOI: https://doi.org/10.1016/j.jorganchem.2020.121361

Reference: JOM 121361

To appear in: Journal of Organometallic Chemistry

Received Date: 20 March 2020

Revised Date: 17 May 2020

Accepted Date: 28 May 2020

Please cite this article as: S.A. Nafiu, M.A. Aziz, M.N. Shaikh, Shape-dependent reactivity and chemoselectivity of nanogold towards nitrophenol reduction in water, *Journal of Organometallic Chemistry* (2020), doi: https://doi.org/10.1016/j.jorganchem.2020.121361.

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Shape-dependent reactivity and chemoselectivity of nanogold towards nitrophenol reduction in water

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Abstract

Although the catalytic activity of nano-gold surfaces for the reduction of nitro compounds has been known, the effect of their shape has been rarely evaluated. Here, the synthesis, characterization, and application of both gold nanoworms (GNW) and gold nanospheres (GNS) are described. Both GNW and GNS were characterized using SEM, TEM, UV-Vis, FTIR, and XPS spectroscopy. The catalytic efficiency of GNW with an average dimensions of 2×250 nm (D×L) towards the hydrogenation of nitrophenol, a pollutant present in industrial wastewater, is higher (TOF 3675 h⁻¹) than that of spherical GNS (10±1 nm), for which TOF is 1838 h⁻¹ in water using NaBH₄ as the reductant. The selectivity of 4aminophenol is 100% for both GNS and GNW.

Keywords: Gold nanoparticles; nitrophenol; chemoselectivity; turn over frequency; azoxyarene

Introduction

Catalytic reduction of nitroarenes has gained increased attention due to its high selectivity and generation of less waste, when compared with conventional reduction reactions using metals such as iron [1], tin [2], or zinc [3]. Conventional reduction employs a toxic organic solvent and also requires hydrogen gas, which normally involves the use of a reactor capable of withstanding very high pressures. Catalytic reduction of nitrophenol is an example of catalytic transfer hydrogenation (CTH), which can be catalyzed using homogeneous catalysts including the complexes of noble metals such as Pd [4], Rh [5], Ru [6], and Ir [7], and a nonnoble metal Ni [8].

Until the 1990s, gold was considered to be catalytically inert for hydrogenation reactions due to its poor adsorption of molecules from the gaseous phase [9]. However, a major breakthrough in gold catalyzed hydrogenation was achieved when gold nanoparticles supported on a suitable oxide were employed for the selective hydrogenation of even complex organic molecules containing more than one functional group [10]. Catalytic hydrogenation of nitroarenes to their corresponding amines is among the most important hydrogenation reactions catalyzed by gold nanoparticles [11-15]. This reaction is important because functionalized anilines are intermediates in the production of pharmaceuticals [16], herbicides, polymers, and fine chemicals [17]. Aminophenols produced by the reduction of nitrophenols are also vital starting materials and intermediates in the manufacture of many indispensable chemicals, including polymers, dyes, and agricultural and pharmaceutical products [18]. For example, 4-aminophenol is employed as a developer in processing black and white photographs and as intermediate in the synthesis of paracetamol. Furthermore, 4-nitrophenol has been identified as a highly toxic environmental pollutant. Hence, catalytic hydrogenation can also be used in environmental remediation [19].

In this study, colloidal gold nanospheres (GNS) and gold nanoworms (GNW) were developed and used as heterogeneous catalysts to selectively reduce a series of nitroarenes using sodium borohydride as the hydrogen source in aqueous medium at a temperature of 50 $^{\circ}$ C. Both GNS and GNW catalysts are highly selective for the reduction of nitroarenes to aminoarenes and azoxyarenes. These AuNPs have exceptional properties and will enhance the engineering of new catalyst technology that is environmentally benign and cost effective.

Experimental

Materials and methods: All chemicals were purchased from Sigma-Aldrich and were used as-received unless otherwise stated. Standard procedures were followed for the production of dry and deoxygenated solvents. Deionized (DI) water (specific conductivity: 18.2 M Ω) was used in all the experiments. UV-Vis absorption spectroscopic data were obtained on a UV-Vis-NIR system, model Cary 500 from Agilent, USA within the wavelength window of 200-800 nm. TEM images were acquired on a JEOL JEM2100F transmission electron microscope. The TEM samples were prepared by dropping an ethanolic suspension on a copper grid and allowing it to dry at room temperature. The amount of nanogold in the catalyst was determined by inductively coupled plasma optical emission spectrometry (ICP-OES; PlasmaQuant PO 9000 - Analytik Jena). The samples were first digested in a dilute mixture of HNO₃ and HCl. Calibration curves were prepared for gold using standard solutions (ICP Element Standard solutions, Merk). Samples for SEM (Lyra 3, Tescan) imaging were prepared from a chunk of decorated jute stem on alumina stubs and coated with gold in an automatic gold coater (Quorum, Q150T E). The surface chemistry was determined using an X-ray Photoelectron Spectroscope (XPS) equipped with an Al-K α micro-focusing X-ray monochromator (ESCALAB 250Xi XPS Microprobe, Thermo Scientific, USA). The binding energy scale was calibrated, and base pressure used. The chamber pressure was 2 x 10^{-9} torr. Catalytic products were identified by a Shimadzu 2010 Plus gas chromatograph attached with a mass spectrometer (GC-MS, Japan). The disappearance of the reactant and sequential appearance of the product was recorded in real time, identifying the species in terms of their molecular ion (M^+) by comparing and matching them with the available Wiley library of the mass spectral database, in addition to the identification of mass fragmentation. Catalytic reactions were performed in a 10-place parallel reactor, from Bibby Scientific, UK (model# Electrothermal Onmi Series 1025).

Synthesis of gold nanospheres (GNS)

Gold nanospheres (GNS) were synthesized using a slightly modified version of a method reported in the literature [20, 21]. Briefly, 19.42 mg of pamoic acid (PA) was dissolved in 15 mL of distilled water in an Eppendorf tube and sonicated for 15 min. Following sonication, 100 μ L of 1.0 M NaOH (aq.) was added to the solution, followed by distilled water to make

the volume 25 mL and sonicated for further 15 min to obtain a clear solution of 2.0 mM PA. An aliquot of 250 μ L of 1.0 M NaOH (aq.) was added to the resulting solution and further sonicated for 1 min. Subsequently, 25 mL of 1.413 mM of HAuCl₄ solution was added to the resulting PA solution and sonicated for 15 min. Finally, the solution was allowed to stand undisturbed for 60 min for completion of the formation of GNS.

Synthesis of gold nanoworms (GNW)

Gold nanoworms (GNW) were also synthesized using a slightly modified version of a method reported in the literature [20, 21]. Initially, 80 μ L of 1 M NaOH solution (aq.) was added to 18 mL of water containing 11.53 mg of 2-naphthol (2-NP) and the solution was sonicated for 10 min. Further 200 μ L of 1 M NaOH was added to the resulting solution and the sonication was continued until 2-NP dissolved. The solution volume was then adjusted to 20 mL with water to make the final concentration of 2-NP 4.00 mM. Finally, 20 mL of 1.34 mM solution of HAuCl₄ (prepared by diluting 2 mL of 13.4 mM HAuCl₄ (aq.)) was added to the solution of 2-NP under sonication. The solution becomes a dark-grey color immediately, which confirms the formation of GNW, and the sonication was continued for another 15 min. The final solution was then allowed to stand for 60 min for completion of the formation of GNW.

Procedure for catalytic reduction of nitroarenes using GNS and GNW

0.5 mmol of nitroarene were dissolved in a solution of 25 mmol of NaBH₄ in 5 mL of distilled water. The resulting solution was stirred for 5 min. at 50 °C and 2.72 x 10^{-4} mmol of GNS or GNW were added with continued stirring. The progress of the reactions was monitored using UV-visible spectrophotometry with continued stirring till the completion of the reaction. The crude product was extracted with ethyl acetate (2 x 5 mL) and the organic layer was dried with anhydrous Na₂SO₄. The residue obtained by evaporating the solvent of the dried organic layer under vacuum was dissolved in ethyl acetate and analyzed using GC-MS to determine the percentage conversion and selectivity towards the product (azoxylarenes or aminoarenes).

Results and discussion

Synthesis and characterization

Both the gold nanospheres and the gold nanoworms were prepared using sonochemical methods. As described earlier, pamoic acid coated gold nanoshperes were synthesized using sodium hydroxide as the deprotonating agent. The guided two-dimensional growth of nanoworms was steered using 2-napthol as the coating agent by sonication under the same conditions.

The morphological structure of the prepared material was evaluated using transmission electron microscopy (TEM). TEM images show the uniform distribution of surface coated gold nanospheres with an average diameter of 10 ± 1 nm (Fig 1a), which was confirmed by measuring the diameter of the particles using the dynamic light scattering (DLS) technique(Fig 1b). Moreover, the low standard deviation indicates the monodispersity of GNS. A uniform and homogeneous distribution of 2-naphthol coated nanoworms, which appear like worms, with dimensions of 2 nm × 255 nm (D x L) were confirmed by TEM micrographs, supplemented by DLS (Figs. 1c and d). HRTEM image revealed the atomic structure of GNW (Fig 1e). UV-Vis spectra show absorption peaks at 520 nm (GNS) and flattened absorption spectra (GNW), indicating the formation of nanogold (Fig 1f). The size



of both GNS and GNW is reproducible and they are uniformly dispersed under the described conditions.

Fig. 1 GNS: (a) TEM image (b) DLS for particle distribution; GNW: c) TEM image (d) DLS for particle distribution (e) HRTEM of GNW and (f) UV-Vis spectra of GNS and GNW.

X-ray photoelectron spectroscopy (XPS) was performed on the as-synthesized nanomaterials to determine the electronic states of gold (Fig 2). The XPS spectra indicate the presence of C and Au in both GNS and GNW. The formation of metallic gold (Au^o) in GNS is confirmed by the appearance of peaks at binding energies of 84.33 and 87.97 eV corresponding to the



 $4f_{7/2}$ and $4f_{5/2}$ gold orbitals respectively [20, 22] (Fig 2a). The peaks at binding energies at 284.48, 285.48, and 289.78 eV clearly indicate the presence of -C-C- bond, -C-O- and -C=O group, respectively [20, 23]. The presence of this functional group indicates that the GNS is carboxylic acid functionalized. A similar trend was observed for GNW, with the presence of the peaks

Fig 2. XPS curve fitting of GNS a) gold b) carbon and GNW of c) gold d) carbon

at 84.3 eV and 88.0 eV which reveal the formation of metallic gold (Fig 2c). Besides, the presence of -C-C- bond (peak at 284.6 eV) (Fig. 2d) is appeared in GNW. Another broad peak between binding energies at 284.7 eV and 292 eV (Fig. 2d) is appeared which might be presence of -C-O and C=O i.e. presence of -COO- along with other -C-O on GNW. The

lower intensity of this broad peak indicates the presence lower amount of -COO- on AuNW compared to that of GNS. Perhaps this -COO- was generated by the degradation of 2-NP during the reduction of Au^{3+} ion. The generated -COO- and -C-O on GNW helped to make stable GNW aqueous solution.

Catalytic performance of GNS and GNW

The catalytic activity and selectivity of GNS and GNW were evaluated using 4-nitrophenol (4-NP) as the benchmark substrate for the catalytic hydrogenation in water, and the results are summarized in Table 1. The efficacy of the catalyst was investigated by varying the amount of the hydrogen source, i.e., NaBH₄, temperature, and the duration of the reaction. The progress of the reaction was monitored using GC-MS and solution-state UV-Vis spectroscopy. 4-aminophenol (4-AP) is not produced in the absence of NaBH₄ or the catalyst, i.e., GNS or GNW. Hence, the catalytic activity of nanogold plays an important role in the reduction of the nitroarenes to the corresponding aminoarenes in water using NaBH₄.



Fig 3. Variation of the UV-Vis absorption spectra with time of the 4-nitrophenol reduction with NaBH₄ in water in the presence of a) GNS b) GNW at 50 $^{\circ}$ C.

The reduction of 4-NP to 4-AP does not occur at room temperature and at 40 $^{\circ}$ C with GNS after 30 minwhen 0.5 mmol of NaBH₄, an equimolar amount of 4-NP, is used. Only the conversion of 4-NP to the 4-nitrophenolate intermediate takes place. Hence, the amount of NaBH₄ was increased by 10-fold to 5 mmol, and also the reaction temperature was increased from 40 $^{\circ}$ C to 50 $^{\circ}$ C. After 40 min, 4-nitrophenolate intermediate still accounted for almost

60% of the conversion. However, with the increase of the amount of NaBH₄ to 25 mmol and prolonging the reaction time to 60 min, the reaction mixture contained only 4-aminophenol and not even traces of the 4-nitrophenolate intermediate was detected, as shown in Fig 3a. Hence, the combination of 25 mmol of NaBH₄ and 50 $^{\circ}$ C are the most suitable conditions for the complete conversion of 0.5 mmol 4-NP to 4-AP in 1 h using 2.72 x 10⁻⁴ mmol of GNS as the catalyst. Optimized conditions determined for the GNS catalyst were also found to be most suitable for the reduction with the GNW catalyst using the same substrate in 30 min.

The progress of the reaction was further monitored by UV-Vis absorption spectroscopic studies at 50 °C and the results are shown in Fig 3. UV-Vis spectra of the reaction mixture were obtained at 10, 20, 30, 40, 50, and 60 min (Fig. 3a), and more than 60% of 4-aminophenol was formed after 40 min. The peak due to 4-nitrophenolate is negligible after 50 min and after 60 min only the 4-aminophenol peak at 300 nm is present. As indicated in Fig 3b, the 4-AP peak at 300 nm begins to appear at t = 3 min and the amount of nitrophenolate gradually decreases after the addition of the GNW catalyst, and in 30 min all nitrophenolate is reduced to 4- aminophenol at 50 °C.







Aminoarene



Entry	Catalysts	Substrate	Conv.	Selectivity $(\%)^b$		$TOF(h^{-1})$
			(%)"			
				Amine	Azoxy	
1	GNS	$R_1 = R_2 = R_4 = H; R_3 = OH$	100	100		1838
2	GNW		100	100		3675
3	GNS	$R_1 = R_2 = R_3 = R_4 = H$	91	11	89	1672
4	GNW		100		100	3675
5	GNS	$R_1 = Me; R_2 = R_3 = R_4 = H$	86	23	77	1580
6	GNW		100	100		3675
7	GNS	$R_1 = R_3 = R_4 = H; R_2 = Me$	93	30	70	1709
8	GNW		100	100		3675
9	GNS	$R_1 = R_2 = R_4 = H; R_3 = Me$	96	9	91	1764
10	GNW		100	91	9	3675
11	GNS	$R_1 = R_2 = R_4 = H; R_3 = Br$	96	28	72	1764
12	GNW		100	36	64	3675

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12	CNS	$\mathbf{P} = \mathbf{P} = \mathbf{P} = \mathbf{H} \cdot \mathbf{P} = C\mathbf{I}$	02	26	74	1601
13	GNW	$K_1 - K_2 - K_4 - 11, K_3 - C1$	92 66	100	/4	2426
15	GNS	$R_1 = R_2 = R_4 = H; R_3 = NH_2$	100	100		1838
16	GNW		100	100		3675
17	GNS	$\mathbf{R}_1 = \mathbf{R}_2 = \mathbf{M}_{\mathbf{P}} \cdot \mathbf{R}_2 = \mathbf{R}_2 = \mathbf{H}$	100	100		1838
18	GNW	$n_1 - n_4 - m_5, n_2 - n_3 - m_1$	100	100		3675
					0	

^{*a*}For the reaction of 0.5 mmol of nitrophenol and 25 mmol of NaBH₄ in 5 mL water at 50 $^{\circ}$ C with GNS (for 60 mins) or GNW (30 mins) as the catalyst, determined by gas chromatography (GC); ^{*b*}Confirmed by gas chromatography-mass spectrometry (GC-MS).

Having established the catalytic activity of GNS and GNW catalysts for the reduction of 4-NP, the catalytic reduction was applied to a series of nitroarenes with structurally divergent functional groups to evaluate their comparative conversion and selectivity, and the results are presented in Table 1. For the GNS-catalyzed reaction, 86%, 93%, and 96% of 2-nitrotoluene (2-NT), 3-nitrotoluene (3-NT), and 4-nitrotoluene (4-NT), respectively, were converted to their corresponding reduced products (azoxytoluene and aminotoluene) in 1 h with a selectivity of 77%, 70%, and 91% for azoxyarene, respectively. The increase of the conversion is most likely due to the decrease of the steric hindrance in going from 2-NT, through 3-NT to 4-NT, which in turn increases the reactivity (Table 1, entries# 5, 7, and 9). Meanwhile, quantitative conversion (100%) of 2-NT, 3-NT, and 4-NT with a selectivity of 100%, 100%, and 91% for the amine, respectively, were recorded in the presence of the GNW catalyst (Table 1, entries# 6, 8, and 10). The reactivity of the GNS-catalyzed reduction of halogen-substituted nitrobenzenes was also evaluated and 96% and 92% of 1-bromo-4nitrobenzene and 1-chloro-4-nitrobenzene, respectively (Table 1, entries# 11 and 13), is reacted in 1 h. In the case of the GNW-catalyzed reduction, 100% and 66% conversion of 1bromo-4-nitrobenzene and 1-chloro-4-nitrobenzene, respectively, were achieved in 30 min (Table 1, entries# 12 and 14) without the formation of even traces of the dehalogenation product. The lower conversion of 1-chloro-4-nitrobenzene is most likely due to the higher electron withdrawing ability of chlorine compared to bromine, which implies that electron withdrawing substituents lower the reactivity of nitroarenes [24, 25]. GNS and GNW catalyzed reduction of 4-nitroaniline selectively produced the amines in 1 h and 30 min, respectively, (Table 1, entries# 15 and 16).

The turnover frequency (TOF) is calculated on the basis of the number of nitroarene molecules reacted per mole of GNS or GNW catalyst per hour. A very high TOF of 3675h⁻¹

was achieved with the GNW catalyst compared to spherical nanogold, which results in a turnover frequency of 1838 h^{-1} for the reduction of 4-NP to 4-AP at 50° C. Thus, GNW demonstrates better catalytic efficiency over its spherical counterpart in terms of both conversion and selectivity. This may be due to the higher surface area of GNW allowing a higher number gold atoms on the surface to interact with sodium borohydride to form the gold-hydride intermediate, which is mainly responsible for the reduction of the nitro group to its amine.

Kinetics study of GNS and GNW

The performance of the GNS catalyst was evaluated at the optimized reaction conditions using 4-NP as the model substrate and sodium borohydride as the reductant in water. The reduction of 4-NP was then monitored using UV-Vis absorption spectroscopy at 40, 50, and 60 °C, and the results are shown in Fig. 4a. An absorption peak at 300 nm corresponding to the 4-aminiphenol is present after 1 and 10 min at 50 °C for GNW and GNS catalyzed reduction of 4-NP respectively. Almost all the 4-NP is reduced to 4-AP after 20 and 40 min using GNW and GNS catalyst respectively at 50 °C (Fig. 3).

The optimized conditions were determined using 25 mmol of NaBH₄ and 0.5 mmol of 4-NP, and thus, the reduction is expected to follow a pseudo-first order reaction with respect to 4-nitrophenol [26]. The rate of the GNS catalyzed reaction was calculated at 40, 50, and 60 °C. The plot of $ln(C_t/C_o)$ vs. reduction time reveals that the rate of the reduction increases as the temperature is varied from 40 °C to 60 °C and to 50 °C in that order. The rate constants (k) obtained from the slope of the respective plots are 2.44 x 10⁻³ mol L⁻¹ min⁻¹, 4.52 x 10⁻³ mol L⁻¹ min⁻¹, and 2.64 x 10⁻³ mol L⁻¹ min⁻¹ at 40, 50, and 60 °C, respectively (Fig. 4a). A similar kinetic study of the GNW catalyzed 4-NP reduction indicates that the rate constants (k) are 7.79 x 10⁻⁴ mol L⁻¹ min⁻¹, 5.20 x 10⁻³ mol L⁻¹ min⁻¹, and 1.57 x 10⁻³ mol L⁻¹ min⁻¹ at 40, 50,



and 60 °C, respectively (Fig. 4b).

Fig. 4 Plot of $\ln(C_t/C_0)$ versus time for a) GNS and b) GNW catalysts

General mechanisms for the reduction of nitroarenes with GNS or GNW

The reduction of nitroarenes to the corresponding aminoarenes involves a direct reduction pathway (Scheme 1). In this pathway, nitroarenes are converted into nitrosoarenes and then to N-phenylhydroxylamines, which are further reduced to produce aminoarenes. However, the condensation of nitrosoarene and N-phenylhydroxylamines results in the formation of azoxyarenes. This is referred to as the condensation pathway (Scheme 1).



Scheme 1. General mechanisms for the reduction of nitroarenes using GNS and GNW.

Comparison of the GNS and GNW catalysts with literature data

The efficacy of the GNS and GNW catalysts were established by comparing the data obtained from the GNS and GNW catalyzed nitrophenol reduction into aminophenol with the results

of other gold nanoparticles in the literature under similar reaction conditions as shown in Table 2. TOF values shown in Table 2, revealed that the GNS (TOF 1838 h^{-1}) and GNW (TOF 3675 h^{-1}) catalysts employed in this study display much higher catalytic activity and far superior to other AuNPs used for this reaction.

Table 2. Comparison of the results obtained with the GNS and GNW catalysts for the nitrophenol reduction with previously reported results in the literature							
Serial	Catalytic system	Reaction condition	Conv.	TOF	Ref.		
NO.			(%)	(h ⁻¹)			
1	NAP-Mg-Au(0)	NaBH ₄ , H ₂ O	100	845	25		
2	Starch-crt@Au	NaBH ₄ , $H_2O:EtOH(1:1)$	90	1.53 X10-3	27		
3	Au(0)TpPa-1	NaBH ₄ , H ₂ O	100	3	28		
4	Au-CeO	NaBH ₄ , H ₂ O	100	1.75 X10-4	29		
5	Au@BSA	$NaBH_4$, H_2O	100	1	30		
6	Fe ₃ O ₄ @PDA@Au	$NaBH_4$, H_2O	100	302	31		
7	Colloidal AuNPs	NaBH ₄ , H ₂ O	100	15	32		
8	Colloidal GNPs	NaBH ₄ , H ₂ O	100	941	33		
9	Colloidal GNS	NaBH ₄ , H ₂ O	100	1838	This		
10	Colloidal GNW	NaBH ₄ , H ₂ O	100	3675	work		

Acknowledgements

MNS gratefully acknowledges the National Plan for Science, Technology and Innovation (MAARIFAH)-King Abdulaziz City for Science and Technology through the Science and Technology Unit at King Fahd University of Petroleum and Minerals (KFUPM), the Kingdom of Saudi Arabia, award number 15-NAN4650-04.

Conclusions

Colloidal GNS and GNW catalysts were developed, characterized, and applied for heterogeneous catalytic hydrogen transfer reactions. The catalysts developed displayed excellent reactivity towards the reduction of a range of nitroarene compounds in the presence of NaBH₄ as the reducing agent in water at 50° C, resulting in up to 100% conversion. The results show that the reduction of nitroarenes produces aminoarenes and/or azoxyarenes. GNW was found to be more selective towards the amine than with the GNS. The formation of only aminoarene product when both 4-nitrophenol and 4-nitroaniline are reduced is an indication that the mechanism for the reduction of these two compounds involves only the direct pathway (Scheme 1). However, the mechanism for the reduction of nitroarenes, which leads to the formation of both aminoarene and azoxyarene products, involves a combination of both the direct and condensation pathways (Scheme 1).

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Highlights

- 1. Spherical (10±1 nm) and wire (250 nm long) of nanogold are prepared using pamoic acid and naphthol as reducing agents, respectively.
- 2. The prepared catalyst was thoroughly characterized using SEM, TEM, XPS and other analytical and spectroscopic techniques.
- 3. Reported for the first time, nitroarene has been selectively reduced to aromatic amine in water in 30 min (conversion 100%) using GNW as the catalyst.
- 4. Turnover frequency was calculated and it is very high (3675 and 1838 h^{-1})
- 5. Rate constant at different temperatures were determined for both GNS and GNW.
- 6. *Results were compared with the literature data.*

Johngi Prendr

Author declaration

1. Conflict of Interest

Potential conflict of interest exists:

We wish to draw the attention of the Editor to the following facts, which may be considered as potential conflicts of interest, and to significant financial contributions to this work:

The nature of potential conflict of interest is described below:

 \boxtimes No conflict of interest exists.

We wish to confirm that there are no known conflicts of interest associated with this publication and there has been no significant financial support for this work that could have influenced its outcome.

2. Funding

Funding was received for this work.

All of the sources of funding for the work described in this publication are acknowledged below:

[List funding sources and their role in study design, data analysis, and result interpretation]

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Not applicable for this work

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