

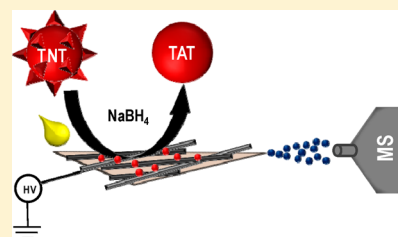
Catalytic Paper Spray Ionization Mass Spectrometry with Metal Nanotubes and the Detection of 2,4,6-Trinitrotoluene

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Supporting Information

ABSTRACT: Materials are making inroads into mass spectrometry, and an example is the use of advanced materials for enhanced ionization by transformation of a less-ionizable molecule to an easily ionizable one. Here we show the use of Pt nanoparticle-decorated nanotubes as highly active catalysts for the reduction of 2,4,6-trinitrotoluene to 2,4,6-triaminotoluene and subsequent easy detection of the product by in situ ambient ionization mass spectrometry.



The ability to generate ions under ambient condition has been one of the major developments in mass spectrometric analysis in recent years.^{1–9} Ambient ionization techniques such as desorption electrospray ionization (DESI),^{10–15} paper spray (PS) ionization,^{16–19} leaf spray (LS) ionization,^{20–22} low-temperature plasma (LTP) ionization,^{23–26} etc., made mass spectrometry more important for real-life applications²⁷ like therapeutic analysis,^{12,28} explosive detection,^{29–31} forensic applications,^{32,33} etc. Paper spray ionization, which works based on the principle of electrospray ionization, uses a triangularly cut paper as the ionization source. Ions are generated by applying a high voltage (3–5 kV) to the wetted paper on which the analyte is transferred earlier by dropcasting from a solution or by simply rubbing the paper against a surface to be investigated. The paper is made of porous cellulose fibers that help in the storage of analytes in their native form, and these transferred analytes can be dissolved by eluting them with a suitable solvent. Use of paper as the ionization source further combines the effectiveness of paper chromatography to separate a mixture of compounds into individual components, thereby removing the need for prior sample preparation.^{34,35} The availability of a variety of papers at low cost and the ability to easily couple PS sources with portable mass spectrometers while providing fast qualitative and quantitative analysis has made paper spray ionization one of the most promising ambient ionization techniques for point-of-care applications.

Fast ambient ionization in PS ionization has also enabled monitoring of chemical reactions and reaction intermediates in real time.^{36–38} Direct probing of fast chemical reactions and reactive intermediates was possible due to this direct mass spectrometric method. One of the reactants in these reactions is taken on the paper, and the other is mixed with the spray solvent. They react on the surface of the paper or inside the droplets generated, and the reaction intermediates and products are detected with MS.

Nanostructures are known to be capable of electric field enhancement at the sharp tips, which forms the basis of surface-enhanced Raman scattering (SERS),^{39–42} a technique for ultratrace detection of Raman-active molecules.^{40,43} However, application of such a phenomenon to boost the ionization efficiency in mass spectrometry has been very limited. An example of such enhancement was demonstrated from our group where carbon nanotubes (CNTs) were used to bring about ionization in PS at an applied voltage of as small as 3 V.⁴⁴ Anisotropic ionization from an aligned array of ultrathin tellurium nanowires (Te NWs) also pointed to a prominent role of such nanostructures for field ionization.⁴⁵ Nanostructures are also very active catalytically, due to their very high surface-to-volume ratio. Coupling the high catalytic efficiency with the enhancement of ionization efficiency of nanostructures is likely to further improve the scope of PS ionization.

In this Article, we demonstrate a PS-based easy vapor-phase detection of TNT (2,4,6-trinitrotoluene) by modifying the paper with platinum (Pt) nanoparticle-nanotubes (NP-NTs). Apart from being one of the commonly used explosives, TNT is highly toxic, carcinogenic, and mutagenic, hence posing a high environmental risk.⁴⁶ TNT is not easily ionized by electrospray ionization (ESI) due to the lack of easily ionizable functional groups. However, recently developed ambient ionization techniques such as atmospheric pressure chemical ionization (APCI),⁴⁷ secondary electrospray ionization (SESI),⁴⁸ desorption atmospheric pressure chemical ionization (DAPCI),¹¹ desorption electrospray ionization (DESI),²⁹ and direct analysis in real time (DART)^{49,50} can generate TNT ions. All these methods generate M^- ions of TNT. On the other hand, here we show that by using Pt NP-NTs as a heterogeneous catalyst in PS ionization (PSI)-MS, the nitro ($-\text{NO}_2$) groups are

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converted to easily ionizable amine ($-\text{NH}_2$) groups in situ, which facilitated the mass spectrometric detection of this compound, generating +ve ion derived from TNT. The process enables the detection of TNT in any form, solid, liquid solution (either in organic or aqueous solvents), or gas. It also enables the detection of TNT from any surface, allowing for monitoring environmental and forensic samples. We have shown the detection of TNT from solid surfaces by this method by first extracting the analyte from the surface using methanol. The same catalyst (Pt NP-NTs)-modified paper could be used several times as a PSI source without any significant loss of catalytic activity. This demonstrates the possibilities of using PSI-MS for nanostructure-catalyzed detection of socially important nonionizable molecules as well as for the study of reaction mechanisms in nanoparticle catalysis.

MATERIALS AND METHODS

All the chemicals were commercially available and were used without further purification. Tellurium dioxide (TeO_2 , 99.9%) powder, hydrazine monohydrate ($\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$, 99–100%), and PVP (polyvinylpyrrolidone, K30) were supplied by Alfa Aesar, Fischer Scientific, and SD Fine Chemicals, respectively. Ethylene glycol (LR) and sodium hydroxide (NaOH) pellets were procured from RANKEM, India. H_2PtCl_6 from Sigma-Aldrich, India, was used as the Pt source. MeOH was purchased from Finar Chemicals India Pvt., Ltd. Locally available deionized (DI) water was used.

Synthesis of Te NWs. Ultrathin Te NWs were synthesized by hydrothermal reduction of Te(IV) precursor with hydrazine hydrate.⁵¹ In this modification of a reported synthetic strategy,⁵² 66.5 mg of TeO_2 was dissolved in 2 mL of 2 M NaOH solution. This solution was mixed with a polyvinylpyrrolidone (PVP) solution containing 500 mg of PVP (K30) in 30 mL of distilled water in a Teflon-lined stainless steel autoclave. To this, 2.5 mL of 25% aqueous ammonia solution was added dropwise under constant magnetic stirring followed by the injection of 500 μL of 99% $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$. This mixture was further stirred for 15 min, and the mixture then was maintained at 180 °C for 3 h. Formation of a dark-blue-colored suspension indicated the formation of Te NWs, which was subsequently confirmed by optical absorption spectroscopy and transmission electron microscopy (tens of micron long wires of ~ 8 nm diameter).

Synthesis of Pt NP-NTs. Pt NP-NTs were synthesized following a reported methodology.⁵² In a typical synthesis, as-synthesized Te NWs (0.05 mM) were dispersed in ethylene glycol (20 mL) through vigorous magnetic stirring at room temperature. An H_2PtCl_6 solution in ethylene glycol (1.5 mL, 80 mM) was then added to this homogeneous dispersion of Te NWs, and the mixture was maintained at 50 °C and stirred at 300 rpm on an IKA C-MAG H7 magnetic stirrer/hot plate for 15 h. The products were collected by centrifugation at a speed of 12 000 rpm for 15 min. After this, the precipitate was washed thoroughly with distilled water and absolute alcohol to obtain a black precipitate, which was further characterized to confirm the formation of Pt NP-NTs.

Preparation of Paper Spray Emitters. For all the paper spray experiments, Whatman 42 filter paper was cut in the shape of an isosceles triangle of 10 mm long and 5 mm wide at the base. Then the paper was coated with Pt NP-NTs by dropcasting an ethanolic suspension of Pt NP-NTs on the paper and subsequently drying it under ambient conditions. Mass spectra were collected using an ion trap LTQ XL

(Thermo Scientific, San Jose, California) mass spectrometer. For all mass spectrometric experiments, the following parameters were used: source voltage 3–3.5 kV, capillary temperature 150 °C, capillary voltage ± 35 V, and tube lens voltage ± 100 V. All the paper spray mass spectrum shown are an average of 50 scans. Tandem mass spectrometric study was performed using collision-induced dissociation.

Instrumentation. Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) were performed at an accelerating voltage of 200 kV on a JEOL 3010, 300 kV instrument equipped with a UHR polepiece. A Gatan 794 multiscan charge-coupled device (CCD) camera was used for image acquisition. Energy-dispersive spectra (EDS) were collected on an Oxford Semistem system housed on the TEM. Samples were dropcast onto 300-mesh, carbon-coated copper grids (spi Supplies, 3530C-MB) and dried under ambient condition before examining in TEM. Ultraviolet–visible (UV–vis) spectra were measured with a PerkinElmer Lambda 25 instrument in the wavelength range of 200–1100 nm.

RESULTS AND DISCUSSION

Pt NP-NTs structures were synthesized by taking advantage of a galvanic replacement reaction, in which ultrathin tellurium nanowires (Te NWs) were used as sacrificial templates. A typical large-area TEM image of these ultrathin Te NWs is shown in Figure 1A. A high-resolution transmission electron microscopy (HRTEM) image of the same is shown in the inset of the figure which confirms their single-crystalline nature. Addition of PtCl_6^{2-} ions in the solution initiates the following reaction.

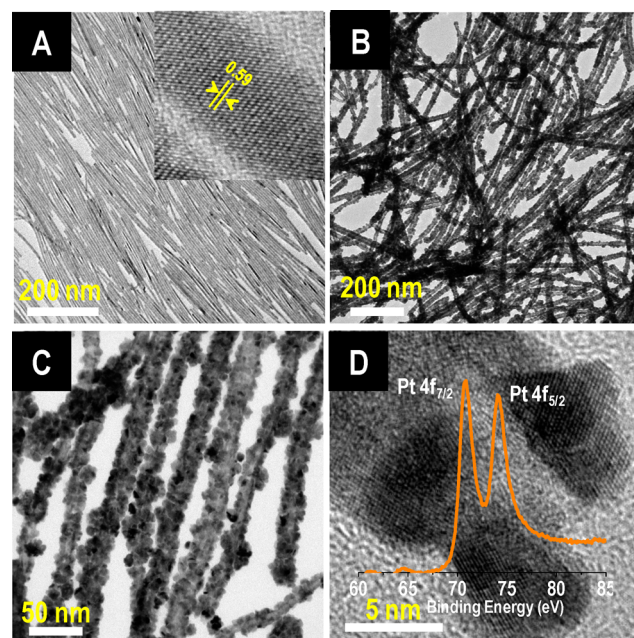
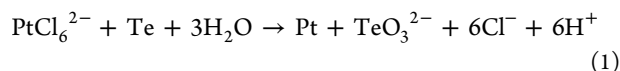


Figure 1. TEM images: (A) Te NWs used as sacrificial templates (inset shows HRTEM image of the same), (B) PtNTs after washing (with saturated Na_2CO_3) process, showing uniform coating of PtNPs, (C) higher-magnification image of the same showing PtNP-coated PtNTs, and (D) higher-magnification image showing the tubular structure. Inset shows XPS spectrum of PtNTs, showing the pure metallic nature of it.



Elemental Pt formed in this reaction deposit over the NW body and created a Pt shell. A definite difference in contrast across the diameter after 10 h of reaction (Figure S1) indicated a hollow morphology, forming nanotubes (NTs). Outward diffusion of the soluble TeO_3^{2-} ions (oxidation product of Te) is most likely responsible for this hollow morphology. Formation of nanoparticle aggregates on some of the regions of these NTs was also observed. Monitoring of the Pt concentration in the supernatant through inductively coupled plasma mass spectrometry (ICPMS) suggested the completion of the reaction after 15 h. The nanostructures formed at this stage appeared to be of different morphologies (Figure 1B). A higher-magnification image (Figure 1C) revealed these to be NP-decorated NTs (NP-NTs). The presence of well-crystalline ultrasmall NPs (size of individual NP being ~ 5 nm) attached across the diameter of the ultrathin tubular structure was evident from the high-resolution TEM image (Figure 1D). Lattice distance (0.392 nm) of these NPs matches exactly with the (111) plane of Pt (Figure S2A), and EDS spectra collected from these showed the presence of only Pt, thus confirming these to be Pt NP-NTs.

It is to be noted that we used a higher concentration of H_2PtCl_6 in the reaction than suggested by the reaction stoichiometry, and this resulted in the formation of a uniform coating of Pt NPs on the NT body. Ethylene glycol has been used as both the solvent and the reducing agent to synthesize various metal nanostructures at elevated temperatures (polyol method) and is likely to be responsible for the reduction of excess PtCl_6^{2-} ions into Pt NPs. Decoration of ultrathin Pt NTs with these ultrasmall NPs is expected to provide increased surface area for enhanced catalytic activity. The X-ray photoelectron spectrum (XPS) shown in the inset of Figure 1D proves that these NTs are made of Pt(0) metal. The XPS spectrum shows peaks corresponding to Pt $4f_{5/2}$ and Pt $4f_{7/2}$.

Catalyst-assisted reactive paper spray experiments were performed using Pt NP-NTs-coated paper. Pt NP-NTs act as catalytic nanostructures for instant in situ conversion of $-\text{NO}_2$ into $-\text{NH}_2$, the latter with increased ease of ionization resulting in enhanced mass spectrometric detection. The coating was done by a simple dropcasting method. An ethanolic dispersion of the Pt NP-NTs was dropcast on the paper and kept for drying under laboratory conditions. Once the paper was dried, it turned black in color, due to the presence of Pt NP-NTs on it. Using these catalyst-coated papers, we have detected 2,4,6-TNT in its vapor phase. Figure 2A shows a schematic representation of the experimental setup. In a typical experiment of vapor detection, 2,4,6-TNT was taken in a closed 5 mL glass bottle and it was pumped using a vacuum pump. The bottle was maintained at 60°C during the experiment, as the vapor pressure of TNT is very low (0.0002 mmHg) at 20°C (The National Institute for Occupational Safety and Health Pocket Guide to Chemical Hazards, <https://www.cdc.gov/niosh/npg/npgd0641.html>). Then, for collecting the vapor of TNT, a PtNT-coated paper was held in the path of the air flow. After 30 min of collection, the paper was cut into a triangular shape and the paper spray experiment was carried out. In this case, the paper was eluted with an aqueous solution of NaBH_4 . Figure 2B shows the schematic of the paper spray experiment. Figure 2C shows the mass spectrum collected from the above-mentioned experiment. The presence of a few other

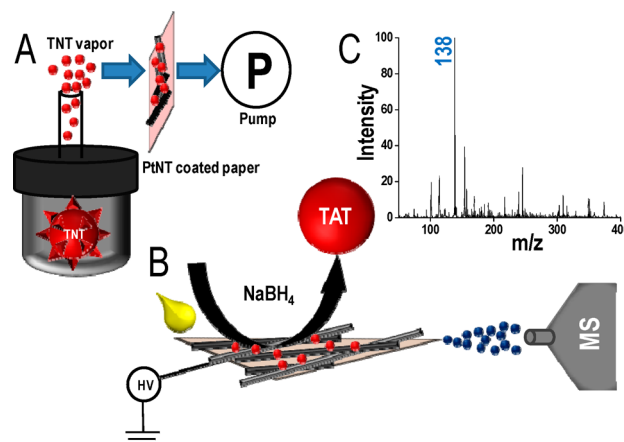


Figure 2. (A) Schematic of the process for accumulation of TNT vapor on PtNT-coated paper, (B) schematic of a typical paper spray ionization process, showing that, after eluting the TNT-adsorbed Pt NP-NT-coated paper with NaBH_4 solution, it transformed to triaminotoluene (TAT), and (C) typical mass spectrum showing peak of TAT at m/z 138.

peaks along with the peak at m/z 138 (for 2,4,6-TAT) was visible in the mass spectrum; these may be impurities present in the sample or in the paper itself. The amount of TNT collected on the paper was calculated from the vapor pressure of TNT at 60°C . It was found that ~ 4.5 ng of TNT was collected during this time. This shows the high detection efficiency of this method. Formation of the product was also confirmed by tandem mass spectrometry. Figure S3 shows MS^2 spectra of m/z 107, 123, and 138, respectively. In all these cases, we see a loss of 17 mass units, a loss of an NH_3^+ .

In the case of solution-phase detection, the Pt NP-NT-coated paper was held in front of the mass spectrometer inlet, at a distance of 5 mm, using an alligator copper clip, and high voltage of the order of 3–3.5 kV was applied. The paper was eluted with 20 μL of 1:1 reaction mixture of 2,4,6-TNT (0.5 ppm, MeOH solution) and sodium borohydride (250 mM, aqueous solution), and the mass spectrum was collected immediately. Figure 3A shows a positive-mode mass spectrum collected from the above-mentioned experiment. The peak at m/z 138 is due to 2,4,6-TAT. In this reaction, NaBH_4 was used as a reducing agent, and Pt NP-NTs act as a catalyst. In the absence of Pt NP-NTs, with only NaBH_4 , complete reduction of nitro to amino group did not happen within a significant time (30 min). Figure S6 shows a mass spectrum collected from the reaction mixture of 2,4-dinitrotoluene (in MeOH) and NaBH_4 (in water), without the presence of catalyst, after 30 min of mixing. Without Pt NP-NTs, reduction stops at the intermediate stage, forming the azo compound. TNT can be detected from solid surfaces also. In this process first it was extracted with methanol followed by reactive paper spray. The same experiment was also tried with different other nitro aromatic compounds like 2,4-dinitrotoluene (2,4-DNT) and *p*-nitrotoluene (*p*-NT). In both cases reduction of nitro to amino group was observed. Parts B and C of Figure 3 show the mass spectrum collected for reduction of 2,4-DNT and *p*-nitrotoluene, respectively. Peaks at m/z 123 and m/z 107 are due to the formation of 2,4-diaminotoluene (2,4-DAT) and *p*-aminotoluene. In both cases, the color of the solution turned red just after the addition of NaBH_4 . In the case of 2,4-DNT (Figure 3B), the mass spectrum shows a peak at m/z 301, which is an intermediate of the reduction process. We speculate

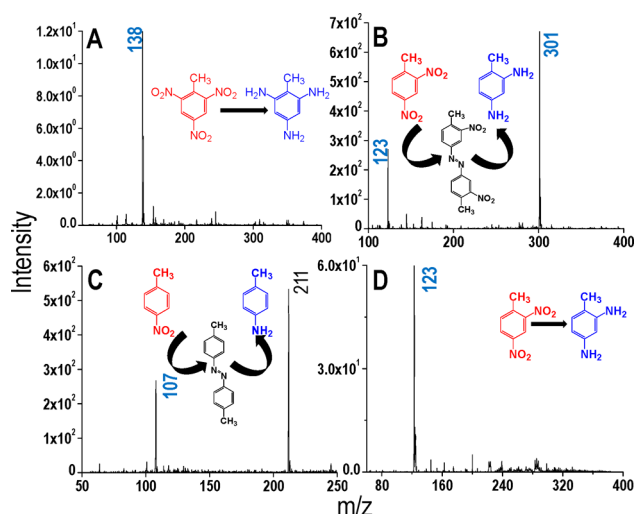


Figure 3. PtNTs-assisted paper spray mass spectrum for (A) trinitrotoluene, showing the product peak at m/z 138, (B) dinitrotoluene, showing both the intermediate and product peaks at m/z 301 and m/z 123, respectively, (C) *p*-nitrotoluene, showing both the intermediate and product peaks at m/z 211 and m/z 107, respectively, and (D) mass spectrum corresponding to the vapor-phase detection of dinitrotoluene.

this intermediate to be an azo compound. The azo intermediate was also visible in case of *p*-NT.

Hence, the possible reaction scheme may be conversion of $-\text{NO}_2$ groups to $-\text{NH}_2$ groups, one by one. We could not detect the other intermediates because the reaction is very fast. The absence of the intermediate in the case of TNT is likely to be due to the reduced concentration (0.5 ppm) of it, used in comparison to DNT. The large excess of catalyst surface area facilitates the rapid conversion of the intermediate to the product. Increasing the concentration of TNT to observe the intermediate was not feasible due to its explosive nature. In real applications, vapor-phase detection of explosives is more important than solution-phase detection. We detected these nitro compounds in their vapor phase using this reactive paper spray mass spectrometric technique. Figure 3D shows a mass spectrum where 2,4-DNT was reduced and detected from its vapor phase. The peak shown at m/z 123 is due to 2,4-DAT. In this case, the peak at m/z 301 was not detected. Presence of very less amount of analyte molecules, with respect to the catalyst resulting in the rapid conversion of the analyte to the product, may be the reason for this. Pt NP-NT-catalyzed reduction of 2,4-DNT was also confirmed by absorption spectroscopy. Figure 4A shows time-dependent absorption spectra collected for the reduction reaction of 2,4-DNT by NaBH_4 , using Pt NP-NT as catalyst. The spectra show that with time the peak due to the nitro group goes down and a peak near 350 nm comes up, which is due to a feature of 2,4-DAT. Parts B and C of Figure 4 show the photograph of the reaction mixture just after adding NaBH_4 (Figure 4B) and the same reaction mixture after 20 min (Figure 4C). In the absence of the Pt NP-NTs, the reaction stops at an intermediate stage. Any catalyst is useful if it regains its catalytic activity after the reaction. The reusability of PtNTs for the reduction of 2,4-DNT to 2,4-DAT was checked. Figure 4D shows that, up to 20 cycles, the catalyst works with more or less similar efficiency. In Figure 4D the maximum intensity of the product, in the mass spectrum (average of 100 scans) collected from the reduction

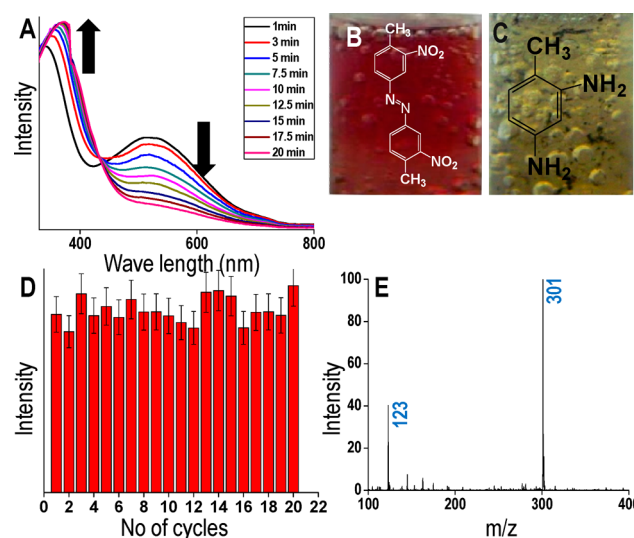


Figure 4. (A) UV-vis spectrum of the reaction mixture with time, showing the peak for nitro group, which goes down slowly, and the peak due to amino group coming up, (B) photograph of the reaction mixture in the intermediate stage, (C) photograph of the reaction mixture after completion of the reaction, (D) plot of signal intensity (considering 10% RSD) of the product peak (m/z 123) vs number of cycles, showing that a single paper substrate can be reused for a number of times, and (E) average mass spectrum during these cycles.

reaction, was plotted against the number of cycles. Figure 4E shows the corresponding mass spectrum. These data show nearly similar catalytic activity for the nanotubes. TEM imaging of the PtNTs after catalysis reaction was also done, to prove that the catalyst is the same before and after the reaction. Figure S4 shows TEM images of the PtNTs after reaction, at different magnifications.

CONCLUSIONS

We show a method of preparing PtNTs with rough surfaces, which involves the use of sacrificial Te NW templates. The roughness on the surface gives more surface area, and hence more catalytically active areas. The PtNTs were used as highly active catalysts for the reduction and detection of 2,4,6-TNT. Vapor-phase detection of the explosive was also shown. Sensitivity in the range of 4.5 ng was demonstrated. Simultaneous chemical conversion and detection provides additional advantage for such modified ionization platforms.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.analchem.7b02288.

TEM images of PtNTs after 10 h reaction, HRTEM and EDX spectrum, tandem mass spectra for all product peaks, TEM images of PtNTs after catalysis reaction, tandem mass spectra of m/z 211, and mass spectrum collected from the reaction mixture of 2,4-dinitrotoluene and NaBH_4 (PDF)

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Notes

The authors declare no competing financial interest.

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