



Efficacy of synthesized azo dye for development of latent fingerprints on Non-porous and wet surfaces

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ABSTRACT

Latent fingerprints (LFPs) play a key role in illegitimate investigations in most of the crime. Mostly, physical evidence is used to establish a relationship between crime scenes and criminal in the justice procedure. We developed a novel protocol for enhanced development of LFPs on non-porous and wet surfaces by physical powder dusting method. The azo-dye was obtained from β -naphthol and aniline by the diazo-coupling reaction. The wet finger-print gives excellent results up 10 days and developed LFPs were visualized on 11 different surfaces. In the present work we report; a simple, rapid, less toxic, efficient, cost-effective alternative method for the development of LFPs by powder method. Characterization of azo dye was done by HR-MS, FT-IR, UV-VIS and TLC.

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1. Introduction

Forensic investigators are regularly encountered with the latent fingerprints (LFPs) development and detection tasks. The human fingerprints have characterized the pattern of raised papillary ridges and depressed furrows. The formation of fingerprints on different non-porous surfaces like paper, plastic, glass, wooden and metal articles due to physical touch. When the hands are touches to various surfaces subsequently the oily substances and sweat present on the fingertip of the skin may shift and deposited on respective the surface [1]. The features of human fingers have three types of fingerprints nature. The first types of feature deals with pattern include arch, loop, or whorl, core and delta. The second type of feature indicates the natures of ridges like ridge endings, bifurcations, dots. The third type of feature deals with the details of minute each friction ridge such as edge shapes, and sizes. These characteristic patterns are unique every human being and remain persists throughout life span [2,3]. In a few crime scene cases, the impression of the suspected fingerprints maybe gets contaminated by environmental, social and personal factors like air, dust, blood, water and paint. In most of the criminal cases, the fingerprints left at crime scenes side was not immediately identified

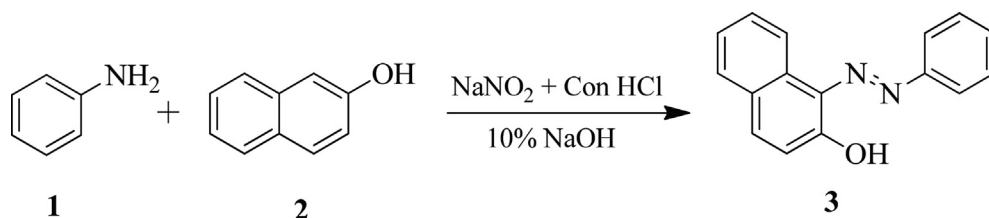
and visualized by naked eyes. It needs to be developed LFPs by proper techniques for visualization and analysis [4]. The LFPs have probability with the contamination chances with drugs metabolite, explosives residues, and other chemicals [5]. The chemical composition latent fingerprints residue have a mixture of amino acids water, salts and fatty acids, exclusively the developing agent selectively attacks the amino acids and fatty residues to provides a nice contrast between the surface and fingerprint ridges [6].

In the recent few decades, common methods are used for the visualization of LFPs in various non-porous surfaces includes powder dusting, cyanoacrylate fuming, iodine fuming, ninhydrin dipping, and silver nitrate soaking [7]. Forensic experts most frequently used the powder dusting method in crime scene investigation due to the wide range of high applicable efficiency [8]. The colored or fluorescent powders are mostly used for the development of LFPs become a burning topic in today's era [9]. Besides, the powder dusting method has features like low toxicity, time-saving, cheap and highly sensitive [10]. Nevertheless, these traditional protocols used for the development and detection of LFPs not always effective. Hence, the researcher community focused on the improvement of existing methods used for clear and effective visualization of LFPs [11].

The number of advanced dyes is used in the powder dusting method to validate for the development of LFPs on various non-porous surfaces has been demonstrated. There are few commer-

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Scheme 1. Synthesis of azo-dye by diazotization.

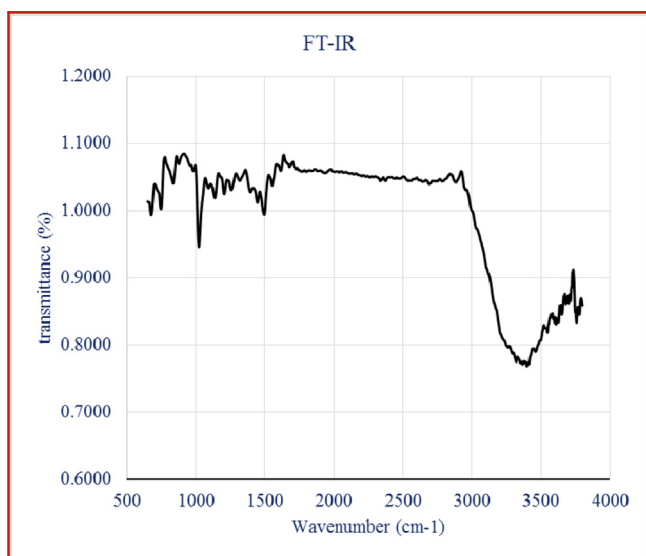


Fig. 1. FT-IR spectra of synthesized azo dye.

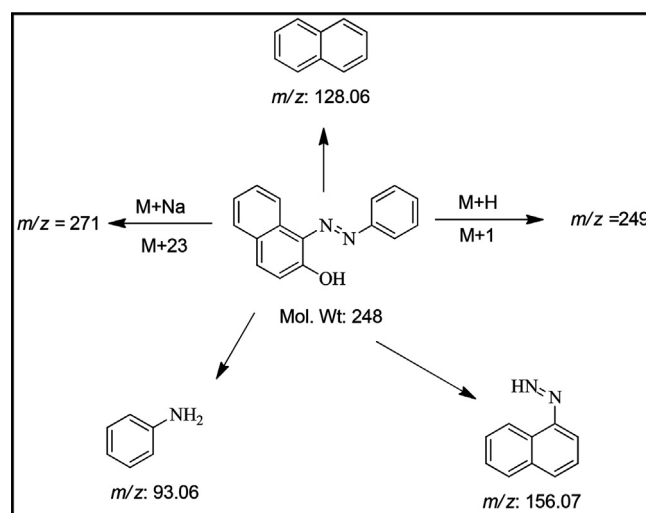


Fig. 3. Fragmentation pattern analysis of HR-MS spectra of azo dye.

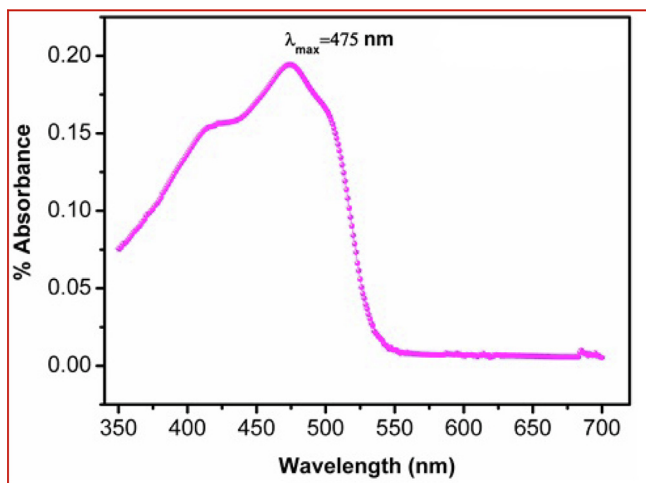


Fig. 2. UV-VIS spectra of synthesized azo dye.

cially available dyes used for detection of LFPs such as Robin® powder blue [12], benzophenoxazine derivative [13], tetraphenylethene-based dye [14], acid-modified Imperata cylindrica powder [15], pararosanine and crystal violet tagged montmorillonite [16], ninhydrin or DFO-treated [17], poly(3,4-ethylenedioxythiophene) [18], poly(allylamine hydrochloride) (PAH) functionalized with the 7-amino-quinolinium [19]. Azo dyes are organic moieties that possess azo functional group ($-\text{N}=\text{N}-$) in their molecular skeleton. The azo dye has remarkable applications in various fields like textile [20], food [21], dyeing on polyester fabric [22], biomedical sterilization [23], and polarizing films [24].

However, the less toxic and effective colored dyes are used for easy detection of LFPs by powdered dusting methods.

In this present study, we report a novel method for the development and examination of latent fingerprints on various nonporous and wet surfaces. The azo-dye (Scheme 1) was synthesized by the diazo-coupling reaction of aniline and β -naphthol at minimum temperature. On the other hand, the application of less toxic azo-dyes fully obeys to the concept of sustainable chemistry.

2. Materials and methods

2.1. Chemicals

Aniline, β -naphthol, sodium nitrite and sodium hydroxide were purchased from Sigma Aldrich and SD fine Pvt. Ltd. and used without further purification.

2.2. Synthesis of azo dye

20 mL aniline was added into 250 mL Erlenmeyer flask containing in 16 mL of con. HCl and 20 mL distilled water was added into the reaction mixture for diluted. This flask was kept in the ice bath for cooling up to temperature fall below 5°C . 4 gm of sodium nitrite was dissolved in 20 mL distilled water and kept this beaker in the ice bath for cooling. Then, Erlenmeyer flask reaction was subject for diazotization by slowly addition of sodium nitrite solution into Erlenmeyer flask solution with constant stirring and maintain solution temperature below 5°C . After the complete addition of sodium nitrite solution, the reaction mixture was tested for the presence of free nitrile by placing it on a starch-iodine paper which will turn blue in the presence of free nitrous acid.

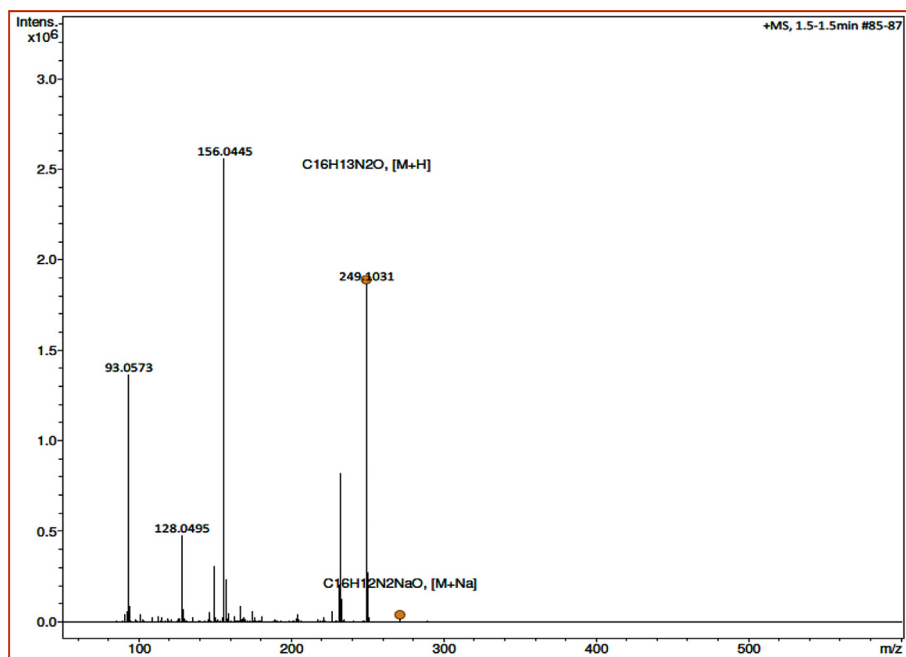


Fig. 4. HR-MS spectra of recrystallized azo dye.

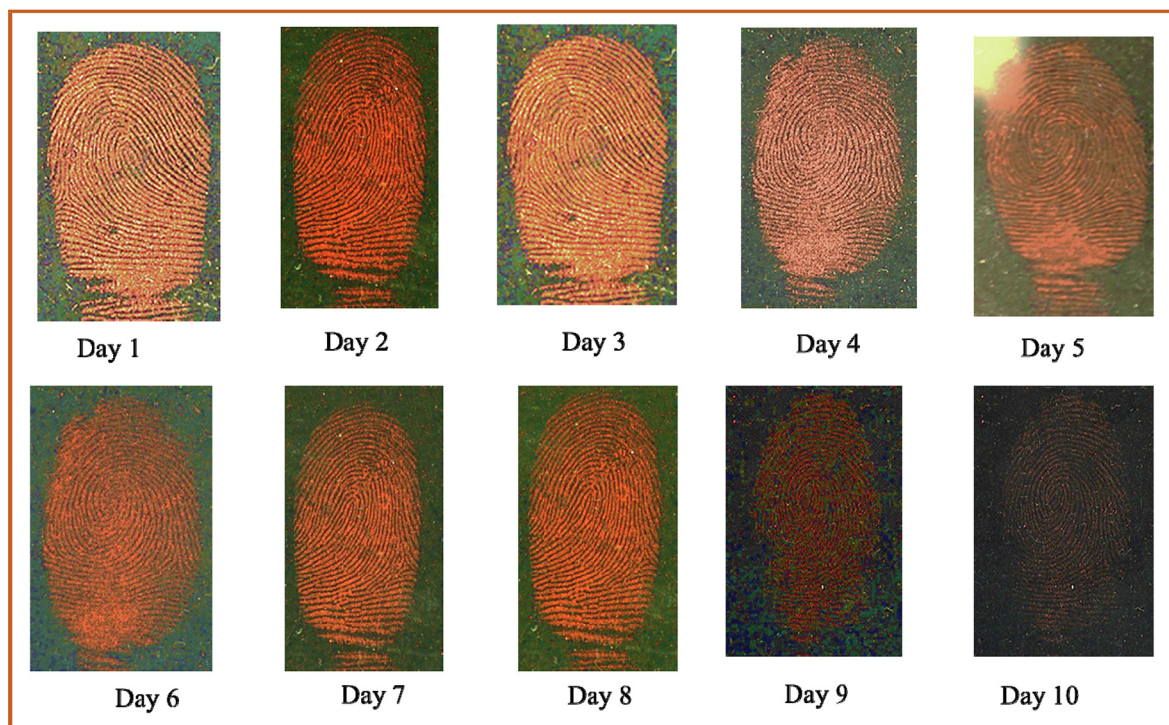


Fig. 5. Successfully developed wet fingerprints using azo dye up to 10 days.

In another 250 mL beaker, 7.8 gm of β -naphthol was dissolved in 50 mL of 10% NaOH solution and this solution was cooled in an ice bath. The cold diazonium salt solution was poured into the β -naphthol solution very slowly and with stirring. The synthesis of orange-red color azo dye was formed immediately after the completion of the addition. The synthesized azo dye was recrystallized in acetic acid or ethyl alcohol.

2.3. Specification of sophisticated instrumentations

The instrumental analysis of synthesized azo-dye using (Fourier transform infrared spectroscopy) FT-IR analysis was done on BRUKER made instrument having OPUS software of version 7.0.129. UV-VIS Perkin Elmer, lambda scan-35 system. The melting point of the recrystallized azo dye was recorded in capillaries open at

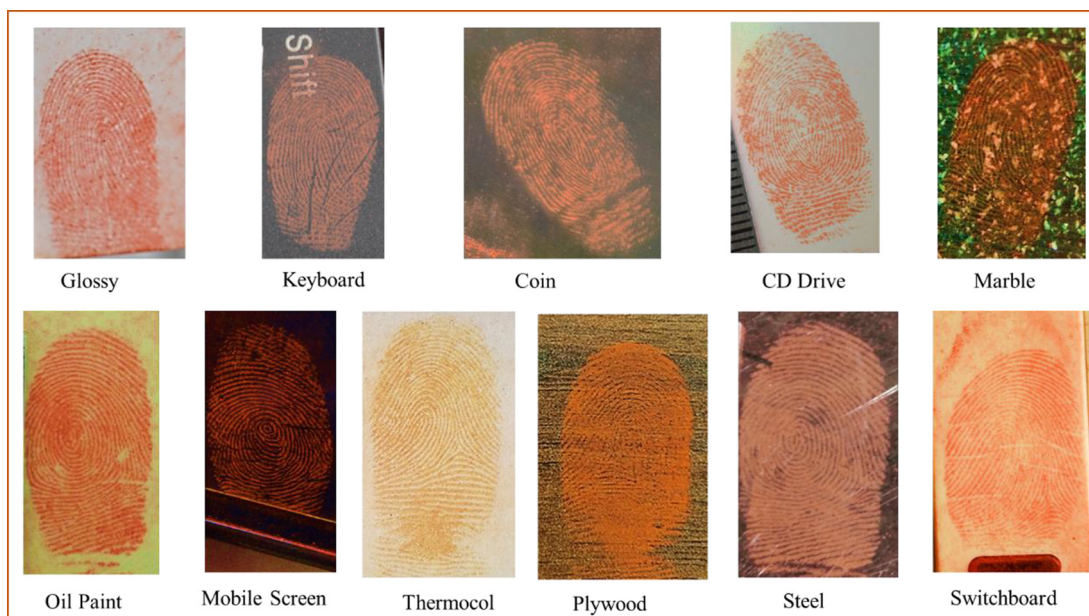


Fig. 6. Developed LFPs on 11 different surfaces using azo dye.

one end and was uncorrected using an Electrothermal Mk3 apparatus. Thin layer chromatography (TLC) was monitored using Merck pre-coated silica gel and the components were visualized under a UV cabinet.

3. Results and Discussion:

(a) Characterization and analysis of synthesized azo-dye using various techniques

In search of the best experimental protocol initially, we optimized the reaction of aniline (**1**) and β -naphthol (**2**) by diazotization reaction. Initially, we took aniline, sodium nitrite and con. HCl in the Erlenmeyer flask. Cooled and shake the reaction mixture for some time. Simultaneously, we took β -naphthol and 10% NaOH into another beaker. This reaction mixture was shaken vigorously till β -naphthol get completely dissolved in 10% NaOH solution. Mixed these two reaction mixtures gently with constant stirring. The orange-red color (*E*)-1-(phenyl diazenyl)naphthalen-2-ol azo dye (**3**) was formed after completion of the addition. The synthesized azo dye was analyzed and confirmed by physical and spectral techniques.

The FT-IR (Fourier-transform infrared spectroscopy) analysis of azo-dye gives stretching frequencies of various function groups as: 3338 cm^{-1} (O-H) bond stretching, 2883 cm^{-1} (C-H) bond stretching, 1552 cm^{-1} (C=C) bond stretching, 1615 cm^{-1} (C=N) bond stretching, 1496 cm^{-1} (C=C) bond stretching, 1226 cm^{-1} (C-N) bond stretching, 1021 cm^{-1} (C-C) bond stretching (Fig. 1) [25]. The UV-VIS (UV-VIS spectroscopy) analysis of azo-dye in methanol solvent gives absorption at 475 nm [26]. The azo-dye gives absorption in the visible region and it gives preliminary confirmation of the synthesized azo-dye (Fig. 2). The TLC analysis of azo-dye in gives R_f value at 0.74 in-solvent system n-Hexane: ethyl acetate (9:1 v/v) [27]. Melting points of the recrystallized azo dye were recorded in capillaries open at one end Electrothermal Mk3 apparatus and it was found that the recrystallized azo dye melt at $138\text{--}140^\circ\text{C}$. The HR-MS (High resolution mass spectrometry) analysis gives peaks as (Molecular Formula $\text{C}_{16}\text{H}_{12}\text{N}_2\text{O}$): $m/z = 271$ ($M + 23$), 249 ($M + 1$), 248 (M^+), 156 , 128 ,

93 (Figs. 3-4). While, an analysis of HR-MS fragmentation of (*E*)-1-(phenyl diazenyl)naphthalen-2-ol few prominent fragments confirmed the structure of azo dye includes m/z : 248 (molecular ions peak), 271 (molecular ions + sodium ions), 248 (molecular ions + hydrogen ions).

(b) Development and analysis of latent fingerprints using Azo-dye

Herein, we demonstrate the feasibility of azo dye for the development of LFPs on nonporous and wet surfaces. Firstly, we immersed ten different glass slides with a fingerprint impression into the water bath for 10 days. Removed gently daily one slide from the water bath using forceps for the next 10 days. The wet slide was allowed to stand for air drying before the development of LFPs by the powder dusting method. The fingerprints were developed on a dry glass slide by the physical method using $90\text{ }\mu\text{m}$ fine particle size of azo-dye. The particle size of the recrystallized dye was measured by the sieve method, $90\text{ }\mu\text{m}$ particle size of azo dye was determined by the sieve method. The high definition ridge patterns of wet fingerprints were observed for up to nine days. The first nine days of wet fingerprint gives the best contrast with distinct ridges details in images of the first nine days of wet fingerprints. But, the minutiae of 10th day's developed slide was found to be quite blurred as compared to the first nine days result (Fig. 5). We were observed that, as the period pass the quality of the developed fingerprint is decreased, due to in water sweat was react with water and it leads to disturbing the ridge details. We also studied practicability of synthesized azo dye for the development of LFPs on eleven non-porous surfaces includes, mobile screen, glossy, keyboard, CD drive, plywood, switchboard, mobile screen, thermocol-sheet, coin, oil paint surfaces (Fig. 6). The azo dye show excellent result of developed fingerprints by powder method on each surface. The developed fingerprint shows clear-cut ridges and minutiae pattern (Fig. 7). The features of the developed LFPs on eleven non-porous surfaces and ten days of wet fingerprint have excellent ridges pattern with clear and sharper image quality. The analysis of minutiae of the first day developed wet fingerprints have distinct minutiae pattern having features like delta, bifurcation, core, ulnar loop, ridge bifurcation, ridge end, sweat pore and fork [28].

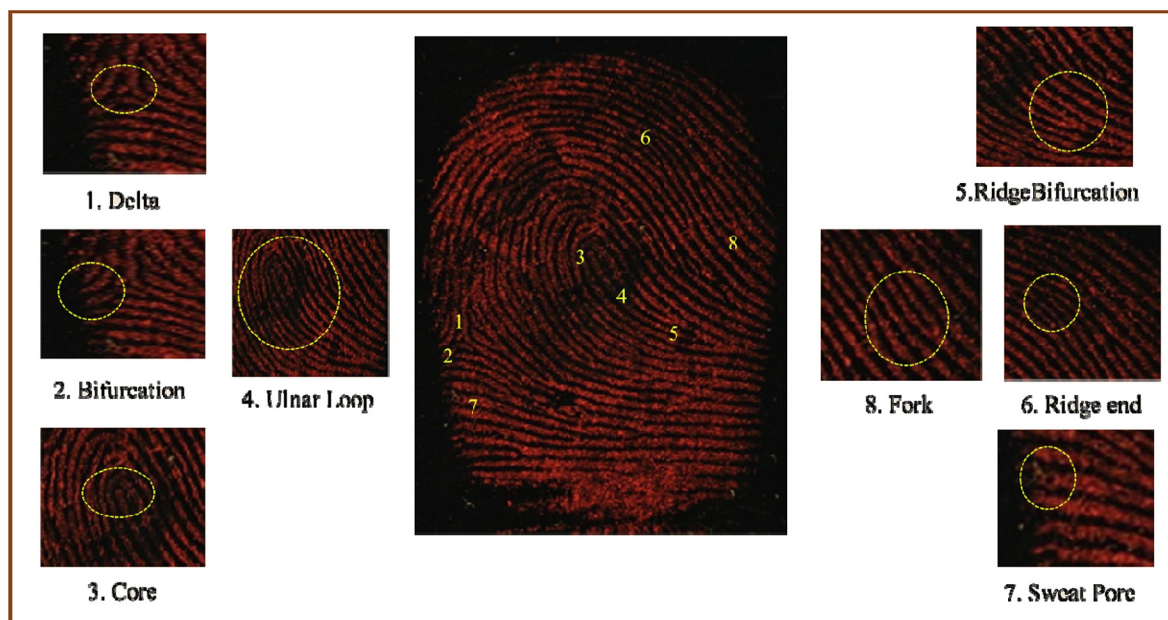


Fig. 7. Minutiae analysis of the first day developed wet fingerprints.

4. Conclusion

In summary, we developed the novel protocol for the visualization of LFPs on non-porous and wet surfaces by the powder dusting method. The synthesized azo used successfully for the development of latent fingerprints on eleven different non-porous surfaces and shows better efficiency to develop wet fingerprints up to ten days. This reported study is beneficial for the development of LFPs due to; rapid, non-corrosive, efficient, easy synthesis of azo dye protocol, less-toxic, and economically affordable. The developed LFPs have high selectivity and good contrast promising practical applicability in forensic. The synthesized azo dye could be used for development Latent fingerprints in the real crime scenes.

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Ethical approval

Approval was not required.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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