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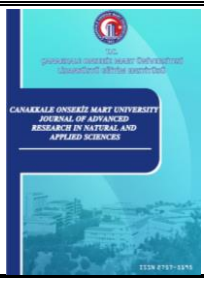

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Hydrothermal Synthesis of CuO Nanoparticles: Tailoring Morphology and Particle Size Variations for Enhanced Properties

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Abstract − Transition metal oxides, particularly copper oxides, have garnered significant attention due to their intriguing photochemical, photomagnetic, photo-thermal, and photoconductive properties. Among these, CuO stands out as a p-type semiconductor having narrow bandgap energy ranges from 1.2 to 2 eV, finding versatile applications such as gas sensing, magnetic storage, solar energy conversion, photocatalysis, supercapacitors, field-emission emitters, and optical switches. Additionally, it serves as a crucial component in materials designed for lithium-ion electrodes. In this study, five different CuO nanoparticles were synthesized by simple and cost-effective hydrothermal method with various reaction temperatures and times in a teflon lined stainless steel autoclave. Copper (II) chloride dihydrate was used as copper source in this process. Various characterization techniques were conducted including X-ray powder diffraction (XRD), Raman spectroscopy, and transmitting electron microscopy (TEM). The effect of temperature and time on synthesis process was characterized and discussed. TEM images show that particle size of CuO increase with the temperature and reaction time. First reaction had the smallest particle sizes (mostly around 9-11 nm). This can be attributed to its lowest reaction temperature and shortest reaction time. For the other reactions, two of them accumulate around 19-35 nm and two around 27-45 nm range. However, the rise in the particle's diameters is not directly proportional to temperature and time. As a result, CuO nanoparticles have been produced with simple method for the market. It can be produced in large quantities for heat exchangers, gas sensing, magnetic storage, solar energy conversion, photocatalysts, supercapacitors, etc.

Keywords − *CuO, nanoparticle, hydrothermal, particle size*

1. Introduction

Transition metal oxides are a significant characteristic of semiconductors that have been extensively ex-plored due to their unique features for possible applications [1]. Copper oxides are one type of transition metal oxide that have gained a lot of interest because of their fascinating photochemical, photomagnetic, photo-thermal and photoconductive characteristics. Cu_2O and CuO are two examples of the several stoichiometries and phases that copper oxides (CuxO) may exist in, have narrow bandgap energy ranges from 1.2 to 2 eV. CuO is a p-type semiconducting material has many different ap-plications including gas sensing, magnetic storage, solar energy conversion, photocatalysts, supercapacitors [2-4] , field emission emitters, photocatalysts, optical switches, and materials for lithium-ion electrodes [5]. In addition, it is essential for a variety of chemical reactions, including oxidation of carbon monoxide, hydrocarbons, fine compounds, the degradation of nitrous oxides and the selective catalytic reduction of nitric oxide with ammonia [6, 7].

These various applications have led to appear numerous chemical routes to synthesize CuO such as sol-gel for

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more complex and high-tech methods, solid-state reaction, precipitation-stripping, alkoxide-based synthesis, sonochemical production, microwave irradiation and precipitation-pyrolysis [8, 9]. Moreover, thermal oxidation [10], hydrolysis [11], solvothermal [12], microemulsion system [13] and the hydrothermal method are also in use for synthesizing CuO particles.

The synthesis of nanomaterials using hydrothermal method may occur at temperatures ranging from ambient temperature to extremely high temperatures. Hydrothermal technique has several advantages comparing the other methods. For instance, low-pressure or high-pressure circumstances can be used to control the size and shape development of the materials, based on the vapor pressure of the primary component in the reaction. Hydrothermal synthesis allows for the production of nanomaterials with well-controlled compositions due to liquid phase or multistage chemical processes [14] . Nanomaterials which are unstable at high temperatures can be produced by this method. High vapor pressure nanomaterials can be produced using the hydrothermal technique with the least amount of material loss [15]. This method also stands out as a convenient approach for copper oxide synthesis, yielding nanoparticles characterized by exceptional dispersibility, strong crystallinity, high purity, and distinct morphologies of varying dimensions [16, 17].

Recently, there has been extensive research into the controlled shaping of various nanostructures, as the physical and chemical properties of nanocrystals are strongly influenced by factors such as sizes, shapes, compositions, and structures. This paper describes the hydrothermal synthesis of CuO nanostructures in the presence of sodium hydroxide (NaOH), utilizing a simple and surfactant-free technique. The study explores the effects of hydrothermal temperature, and time on crystal growth, and shape through simple and cheap hydrothermal method with integration of heat and time parameters.

2. Materials and Methods

All of the compounds utilized in this work were analytical grade and did not require any additional purification. Copper (II) chloride dihydrate ($CuCl_2 \bullet 2H_2O$, ≥99% purity), NaOH (≥99% purity), ethanol (CH_3CH_2OH, 99,8%) and distilled water were used in the experiments for preparing and cleaning samples. $CuCl_2 \bullet 2H_2O$ were supplied by Merck, sodium hydroxide was purchased from Interlab and absolute technical grade ethanol supplied by Panceac.

CuO nanoparticles synthesized by simple hydrothermal method. Synthesis procedure adapted from Wang and his co-workers' published paper [3]. Different sized and shaped nanoparticles were obtained by changing the reaction parameters such as time and temperature. Nanoparticles were formed by thermal decomposition of $CuCl_2 \bullet 2H_2O$ and precipitation in aqueous solution. The preparation procedure was started with dissolving of $CuCl_2 \bullet 2H_2O$ in distilled water, 0,01 mol $CuCl_2 \bullet 2H_2O$ dissolved in 25 ml distilled water and stirred for 15 minutes at room temperature. After that 20 ml of 1mol/L NaOH solution was slowly added to this solution in 20 minutes under the continuous magnetic stirring. Stirring was kept on extra 10 minutes more after adding NaOH solution to obtain homogenous mixing. Afterward, solution was transferred to teflon lined stainless steel autoclave for hydrothermal process. Autoclave was transferred to hot air oven for various temperatures and times as given in Table 1. Finally black colored CuO nanoparticles were collected and washed several times with ethanol and distilled water (Figure 1). As a last step of the process particles were dried in oven for 24 hours at 65 ^{o}C. All the samples produced with the same method but with particular experimental conditions (Table 1) and characterized with several techniques.

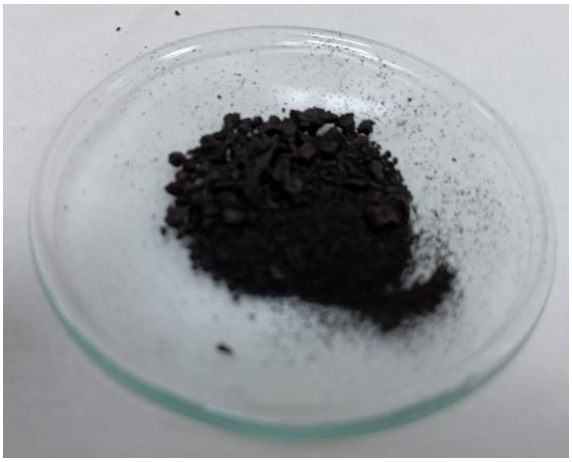


Figure 1. Successfully synthesized CuO nanoparticles after washing and drying procedures

Table 1. Temperature and time parameters of hydrothermal reactions

Sample	Temperature (°C)	Time (h)
1	110	2
2	150	2
3	190	2
4	110	4
5	110	6

2.1. Characterizations

Produced CuO nanoparticles were characterized using Malvern Panalytical model X-ray powder diffraction (XRD) with a scanning angle range of 2θ = 5-80, and a scanning rate of 0.02° per minute, utilizing Cu-Kα radiation (Figure 2). For the further structural analyse CuO nanoparticles were characterized using a Witec Alpha model 300RA Raman spectrometer (Figure 3). The particle size analyses of the samples were conducted using a JEOL JEM-1400 transmitting electron microscope (TEM). Nanoparticles should be clean for to get clear TEM images. Particles have washed multiple times with ethanol and water. Synthesized particles pounded in a mortar to obtain smaller grains for sample preparation. CuO nanoparticles do not need any conductive coating because of their conductivity. The percentage distributions of nanoparticles in the nano size range were analyzed from TEM images (Figure 4).

3. Results and Discussion

Crystal structure of the first CuO nanoparticle is given in Figure 2. The exceptional crystalline quality of the particles is shown by the strong and sharp diffraction peaks. Primary diffraction peaks corresponding to the (002) and (111) planes were observed at 2θ values of 35.57 and 38.75, respectively. Additionally, other diffraction peaks such as (110), (202), (020), (202), (113), (022), (220), and (311) are also visible. The (002) and (111) peaks are the most prominent, indicating that the growth model of CuO crystals occurs predominantly along the (002) and (111) planes. These peaks are correlated with previous studies [3, 18].

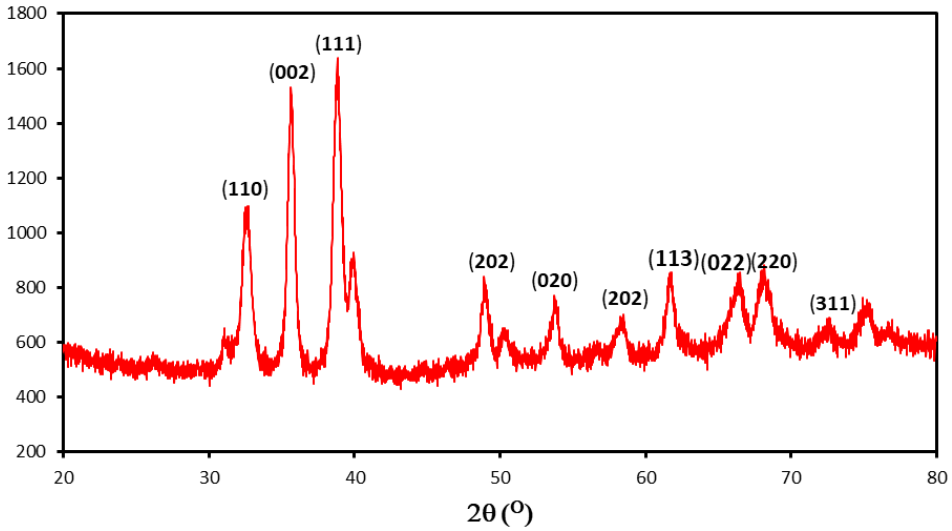


Figure 2. XRD pattern of first CuO nanoparticle synthesized at 110 °C in 2 hours

Figure 3 shows first CuO nanoparticles Raman spectra. A popular optical method for identifying deformations, structural problems, and defect chemistry in materials is Raman spectroscopy. CuO is a p-type semiconductor with a monoclinic structure belonging to the C^6_{2h} (c^2/c) space group [19]. This space group has twelve vibrational modes at the center, including three normal acoustic modes ($A_u + 2B_u$), six infrared active modes ($3A_u + 3B_u$) and three Raman active modes ($A_g + 2B_g$) at peaks 294, 332, 626 cm-1 [20]. The peak at 294 cm^{-1}, corresponding to the monoclinic phase of CuO, belongs to the A_g mode, and the peaks at 332 and 626 cm^{-1} belong to the B_g modes and matches the previously reported data [21].

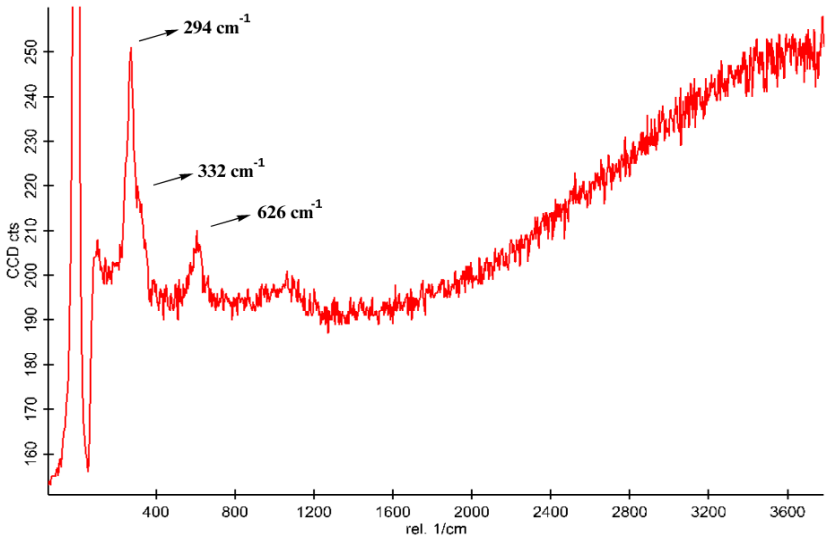
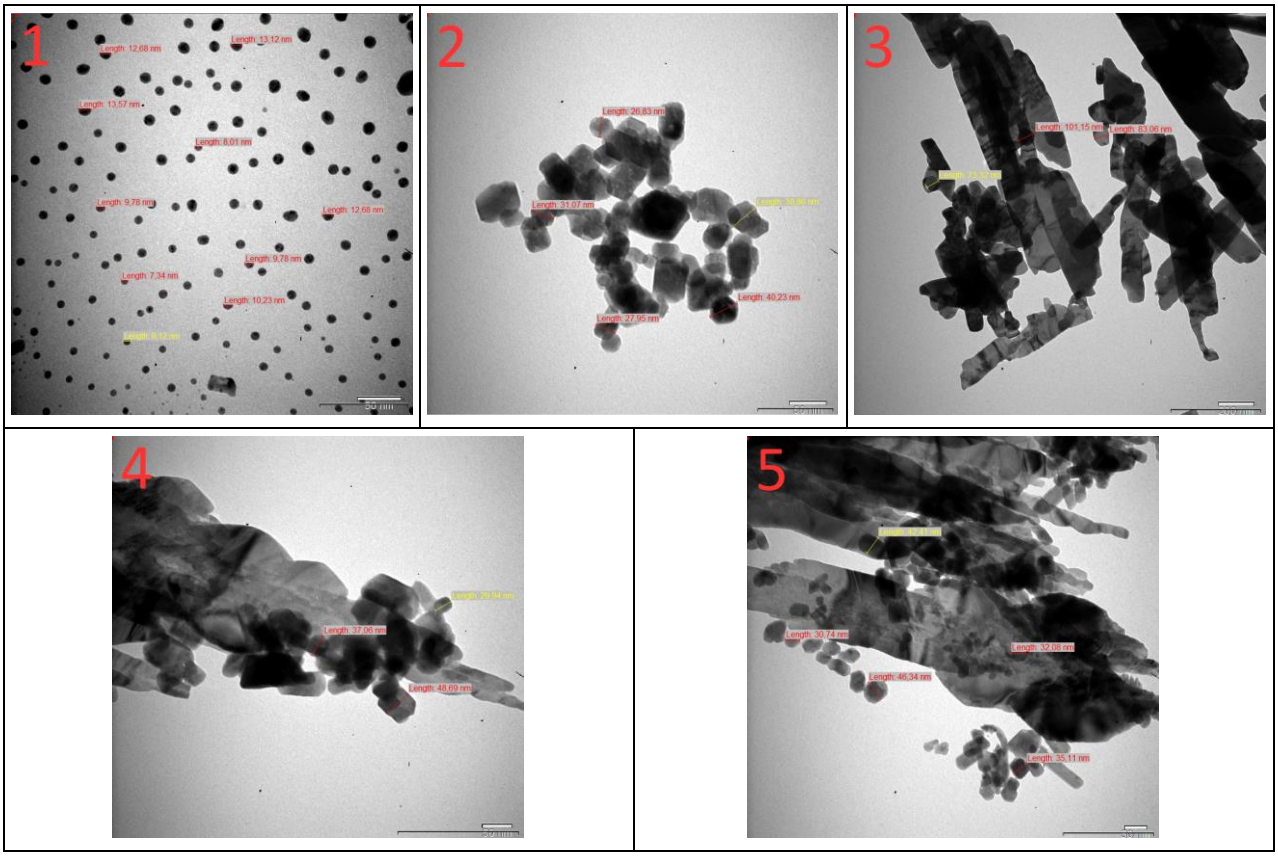


Figure 3. Raman spectrum of CuO nanoparticles synthesized at 110 °C in 2 hours

TEM images are given in Table 2. Spherical-shaped nanoparticles are more common in first and second synthesis. Hydrothermal reaction times were the same (2 hours) for the first 3 synthesis, but reaction temperatures were different (Table 1). It is obvious that spherical-shaped nanoparticle numbers decreased and became more polyhedron-like structures as the temperature elevated. The temperature had great impact on the accretion of CuO nanostructures. The precursor's disintegration and CuO's expansion all increased with rising temperatures. Because the nanocrystals tended to orient the crystal lattices in the direction of growth at higher temperatures. The thermal movement of the molecules in the elements for growth accelerated and subsequently sped up the formation of the crystal cores [22].

For the fourth and fifth synthesis, reaction temperatures kept constant and reaction times were changed comparing the first synthesis. It's seen that nanoparticle shapes became more plate-like unlikely the first synthesized nanoparticles. This was also observed by Janene et al. They investigated the effect of different reaction times and synthesized CuO nanoplates with 2 to 24 hours reaction times [23].

Table 2. TEM images of five different CuO nanoparticles synthesized at different temperatures and reaction time



Particle size distributions of synthesized nanoparticles are given in Figure 4. Particle size measurements were conducted via ImageJ on TEM images including Table 2 and more images. First reaction has the smallest particle sizes (mostly around 9-11 nm). This can be attributed to its lowest reaction temperature and shortest reaction time [24].

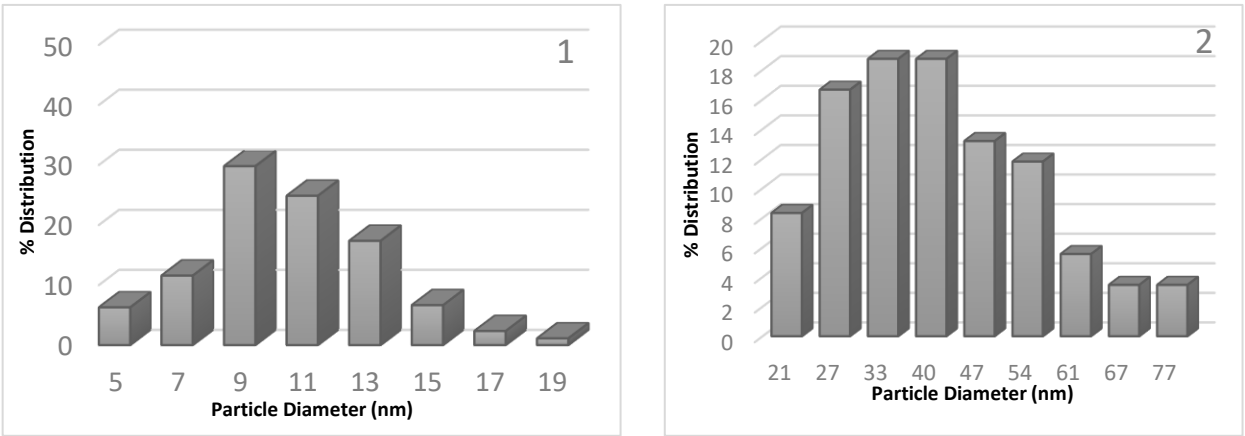


Figure 4. Particle size distributions of CuO nanoparticles synthesized at different temperatures and reaction time

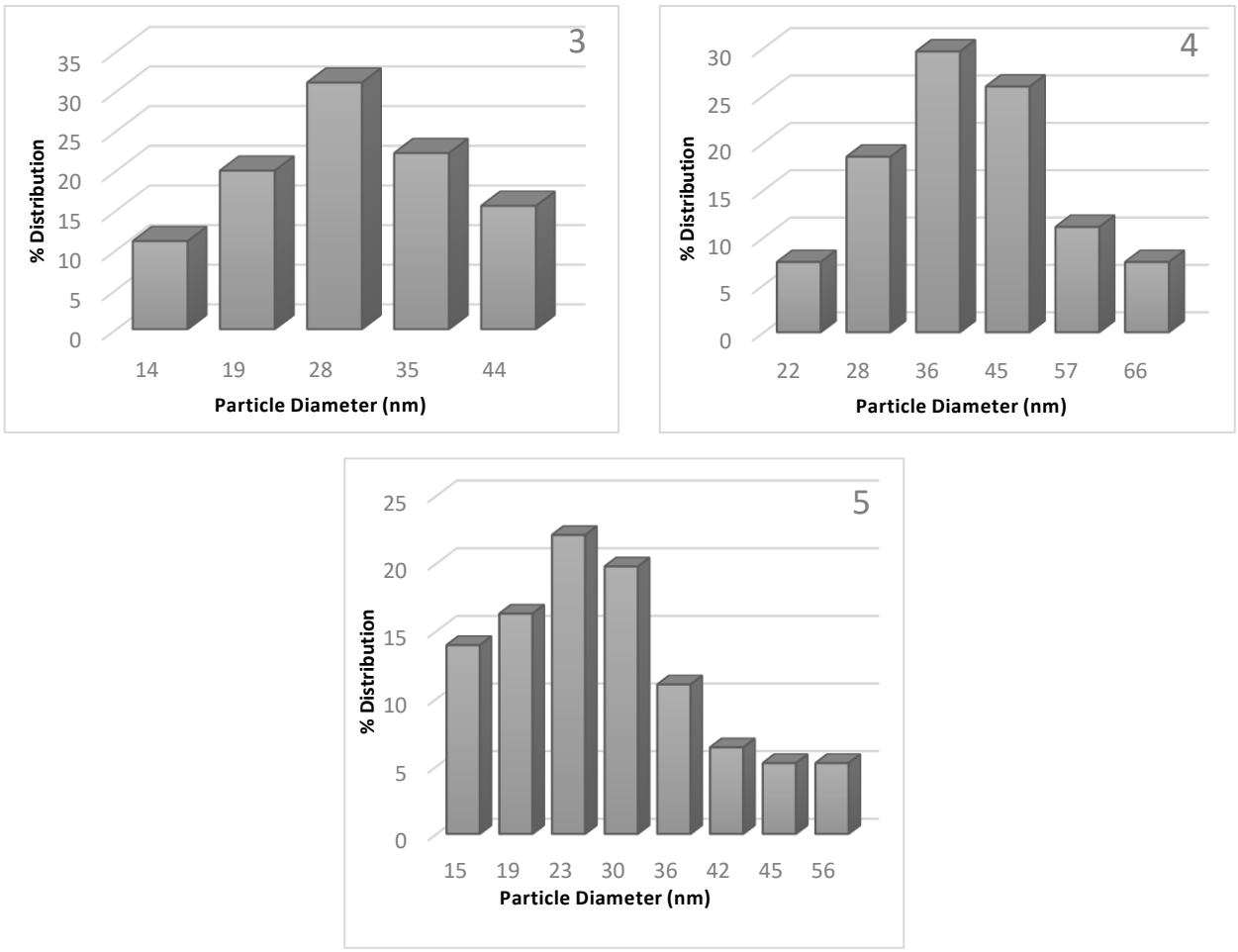


Figure 4. (Continued) Particle size distributions of CuO nanoparticles synthesized at different temperatures and reaction time

During hydrothermal treatment, uniform heating within the reaction system significantly impacts the morphology of CuO nanoparticles. The morphological characteristics of these nanoparticles are intricately tied to both temperature and partial pressure inside the autoclave throughout the synthesis process. Furthermore, the morphology of CuO nanocrystals is influenced by temperature and reaction time. Incomplete reactions occur at lower temperatures, while at higher temperatures, reduction of CuO takes place, aligning with findings reported by other researchers [25-27].

4. Conclusion

The ultimate goal of this study was to produce CuO nanoparticles practically for the market. CuO nanoparticles were successfully synthesized via simple hydrothermal method with several reaction temperatures and times. Copper (II) chloride dihydrate was used as copper source. Various characterization techniques were conducted including XRD, Raman spectroscopy and TEM. First synthesis was more spherical-shaped comparing the other four reactions, they had more rod-like structures. TEM images show that particle size of CuO increase with the temperature and reaction time. However, rise in the particle's diameters are not directly proportional to temperature and time. Finally, CuO nanoparticles have produced with simple method for the market. It can be produced in large quantities for heat exchangers, gas sensing, magnetic storage, solar energy conversion, photocatalysts, supercapacitors etc.

Author Contributions

All the authors equally contributed to this work. They all read and approved the final version of the paper.

Conflicts of Interest

All the authors declare no conflict of interest.

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