Room temperature and ambient pressure deposition of Cu-BTC MOF on SBA-15 functionalized silica supports by simple spray layer-by-layer method

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ABSTRACT

Metal-organic frameworks (MOFs) have received intense interest over the past decade due to its wide application such as catalysis, membrane-based gas separation, gas adsorption, sensing, and biomedical devices. Growth of MOFs on different solid surfaces allows improving their mechanical properties. Silica is a potential candidate. Due to the difficulty of rising Cu-BTC MOF on silica substrate our group was motivated to achieve a successful coating. This work outlines the functionalization of the gold surface through the MHDA self-assembled monolayer (SAM) and the construction of a MOF film (SURMOF) of Cu-BTC upward. The same MOF was also grown onto a modified mesoporous SBA-15 silica substrate. The first obtained silica particles were previously conformed and activated to receive the MOF. The layer-by-layer method was used to deposit MOF onto the substrates. The deposited MOFs films were characterized by X- ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM) and transmission electron microscopy (TEM) showed SBA-15 as a potential MOF support.

1. Introduction

Metal-organic frameworks (MOFs) are crystalline and nanoporous materials comprised of small metal-containing clusters connected three-dimensionally by organic ligands [1]. They present a high apparent surface area, selective uptake of small molecules and a large pore size. Due to its hybrid architecture, the MOFs represent a major advance in development of ordered porous media, which have attracted significant interest in the last ten years [2,3].

This class of crystalline hybrid materials is formed by associations of metallic centers or agglomerates and organic binders and offers unique chemical versatility, large and permanent internal porosity. As such, MOFs constitute their own family of porous materials that overcome the limitations of already known porous materials (zeolites, mesoporous silica, activated carbon) [4,5].

The association of mesoporous silica materials with thin films has promoted their use into many interesting applications such as gas separation membranes, chemical sensors, optical and electrical devices, catalysis, among others [6]. Furthermore, inorganic porous membranes often show high performance to gas separation due to their defined pores in the scale of the size of molecules to be separated. In this way, membranes based on MOFs materials may offer potential to achieve similar applications [7].

The MOF $Cu_3(BTC)_2$, a coordination compound formed by copper and trimesic acid, also known as Cu-BTC and HKUST-1, is one of the widely studied MOFs [8,9] with notable potential for thin films [10]. In this sense, recent studies have been done to use mesoporous silica as support materials [11,12]. The mesoporous Santa Barbara Amorphous type material (SBA-15) presents particular features, such as uniform pore size, hexagonal and cylindrical channels and large surface area, when compared to the silica gel typical materials. In addition, the SBA-15 silica has the advantage of no need to pre-treat the surface before modification due to the silanol groups on the silica surface, as shown in Fig. 1. The presence of these groups allows the incorporation of new materials in the silica structure [6,13]. SBA-15 was chosen as a support for Cu-BTC for many reasons:

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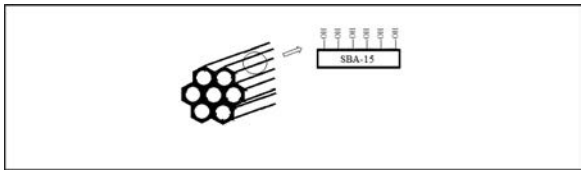

Fig. 1. Scheme of activated SBA-15 silica surface with OH-terminated groups.

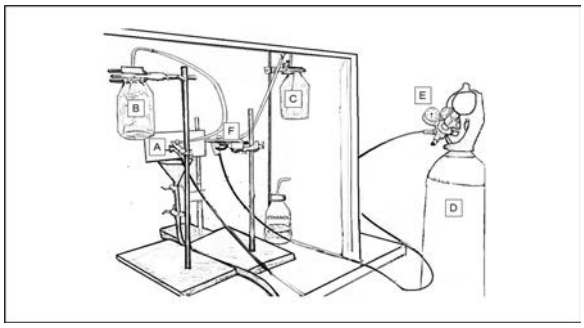

Fig. 2. Schema of simple spray method employed for the fabrication of MOF thin films: (a) sample holder, (b,c) solutions containers, (d) gas supply, (e) gas flow controller, (f) dosing valves.

- Its chemical affinity with Cu-BTC Its high mechanical resistance
- The possibility of controlling features such as surface area and pore size, which may contribute to the adsorption/separation process
- SBA-15 is a known support for different materials
- It is a relatively new technology, therefore the association between the two materials may lead to interesting results

The tests carried out in this paper were initial and meant to assess the interaction between these two materials. This investigation opens the possibility for new ways to functionalize SBA-15 with Cu-BTC and for the development of new materials.

For many advanced applications in nanotechnology, it is required the deposition of MOFs, normally obtained in the form of powders, on solid substrates [10,14]. In the literature we find several interesting applications, among them the purification, separation and storage of gases, the separation of CO_2 from gaseous emissions being one of the most promising applications [15–17]. MOFs are also being synthesized through reactions that favor the confinement effect, with dispersion of nanomaterials and carrying active ingredients of drugs with controlled release (drug delivery) [18,19].

Other interesting works address the use of MOFs applied as chemical sensors, based on magnetic and optical properties. Some MOFs have their magnetic properties altered when they store or release visiting molecules due to reversible structural transformations, either due to the change in amorphous to crystalline structure, or a transformation of crystalline phases. In this way, they can be used as molecular recognition sensors [17].

Efforts to improve the synthesis of these materials and the selections for industrial and processing applications are increasingly present in several sectors. In particular, the use of MOFs as films is one of them, which is important for many applications, such as chemical sensors and membranes.

Another interesting method of obtaining MOF is by electrochemical deposition [20]. Relevant contributions are found in the literature. Through this method it is possible to obtain multi-scale porous composite adsorbent with a micropore copper benzene-1,3,5-tricarboxylate coating on macropore copper foam [20]. It is worth mentioning that almost 50 % of the works on this theme (MOFs as coverings) were published after 2011, which corroborates the currentness of the theme [4,5,17].

Among the types of MOFs thin films, we will focus on SURMOF (surface-supported metal-organic frameworks) fabricated using layer-by-layer (LBL) spray method, where the orientation and film thickness can be well-controlled and occur at room temperature and ambient pressure [21]. Searching in the literature, it is notable the conventional functionalization of the gold surface through the MHDA self-assembled monolayer (SAM) and the construction of a MOF film (SURMOF) of Cu-BTC upward. The first studies related to the MOFs association with mesoporous silica started around 2012. This demonstrates how recent this topic is and the opportunity for new discoveries [22].

The fundamental SURMOF principle was exposing a substrate to dilute solutions of metal-containing for a period of time and then expose to linkers solution to grow highly oriented layer-by-layer MOFs [23]. In the cited spray method, (Fig. 2) an aerosol is produced by expanding solutions of the reactants through a small nozzle. When the droplets of the resulting aerosol hit the substrate, the material is deposited [21,24]. The LPE spray method has been used due to its ability to produce thin SURMOF coatings in a short time. Using this procedure, SURMOFs were obtained with a thickness in the micrometer order in just a few hours [10].

Hence, our approach relies on the optimization of the experimental parameters for the direct layer-by-layer spray deposition of Cu-BTC precursors (organic linker: BTC, metal node: copper) on the SBA-15 mesoporous silica pastilles to form CuBTC + SBA-15 SURMOF using OH-terminated groups as anchoring. Silica SBA-15 was used with its own available OH groups. Other authors have made cellulose substrates functionalization with COOH groups to increase the amount of Cu-BTC deposited [25,26]. To remove an interface from the process and make it simpler, we opted for non-functionalization of silica substrates with MHDA. The gold conventional supports were functionalized by a thiol-based SAM and the mesoporous SBA-15 silica was simply activated by water. These hybrid materials are expected to exhibit gas separation behavior and improved mechanical resistance of the MOF due to silica support [27].

2. Experimental

2.1. Materials

Copper acetate anhydride ($Cu(OAc)_2$), 1,3,5-benzene tricarboxylic acid (H_3BTC), ethanol (99.5 %) and The methylcellulose (Methocel A4M) were obtained from Sigma-Aldrich and used as received unless otherwise stated. The SBA-15 mesoporous silica powder was previously obtained employing the established synthesis [13,28] and calcined at 500 °C.

2.2. Substrate preparation

The Cu-BTC SURMOF membranes were synthesized on both gold and silica substrates. Gold substrates (200-nm Au/2-nm Ti evaporated on Si wafers) were at first functionalized by self-assembled monolayers, SAMs, of 16-mercaptohexadecanoic acid (MHDA), that were prepared by immersing Au substrates into 20 mM ethanolic solutions for 70–72 h. After removal of the samples from solution, they were rinsed with ethanol and dried in a stream of N_2 [24,29,30]. In the case of silica, it was prepared a mesoporous SBA-15 silica powder and then conformed in pastilles. A preparation of powder of silica was prepared by sol-gel route. Then, SBA-15 silica pastilles were prepared by mixing 1.5 g of powder of SBA-15 mesoporous silica, 0.2 g of methocel and 0.6 mL of deionized water. The solid solution was transferred to an evacuable pellet dies accessory and submitted to 500 kfg/m^2 pressure during three minutes. The samples were calcined at a rate of 1 °C/min from room temperature to 800 °C for 1 h, to remove the methocel. The obtained silica disks were activated by immersion in deionized water under ultrasound for 10 min to ensure the presence of OH groups on the surface. The OH-terminated groups are found on the silica surface in three forms:

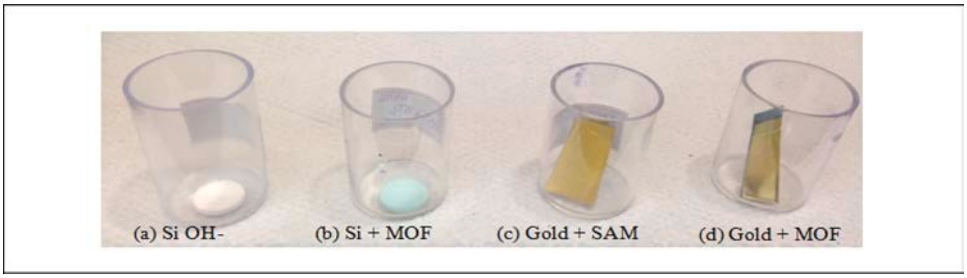

Fig. 3. Illustration of (a) activated SBA-15 silica. (b) activated SBA-15 silica with Cu-BTC deposition. (c) gold with MHDA-SAM. (d) gold with MHDA-SAM and Cu-BTC deposition.

(a) isolated free silanols, ≡SiOH; (b) geminal free silanols (or silanediols) ≡$Si(OH)_2$; (c) vicinal, H-bonded or bridged silanol groups. When these OH groups come into contact with the water, they act as centers of adsorption and the hydroxylated regions are gradually expand, until eventually the entire surface become hydroxylated [31]. This explains why gold functionalized surfaces may be replaced by SBA-15 water activated pastilles.

2.3. Procedure of deposition MOFs onto substrates

The following procedure for the Cu-BTC deposition were the same for both substrates cited types. It was used the spray layer-by-layer (LBL) method adapted from the procedure described by Arslan and coworkers [21], as shown in Fig. 2. These substrates were then placed on a sample holder (Fig. 2a) and subsequently sprayed with a 1 mM of ($Cu(OAc)_2$) ethanol solution (Fig. 2b) for 10 s and then with a 0.2 mM of H_3BTC solution (Fig. 2c) for 20 s at room temperature. Typical values of spray parameters were employed, such as, gas pressure of 1.5 psi, and distance between the nozzle and the target of 0.1 m, based on the literature [24]. Between each step the substrates were manual rinsed with ethanol. Through the number of cycles, the thickness of the SURMOF can be controlled. We work with 20 deposition cycles to obtain SURMOF layers. After the complete deposition, the sample was removed from the sample holder, washed with ethanol, and dried with N_2.

2.4. Characterization

The materials were characterized by powder X-ray diffractometer (XRD) PANalytical Empyrean X-ray in the 2θ range from 5° to 20°, using scan speed of 0.02° with an acquisition time of 20 s per step. FTIR spectroscopy (Perkin-Elmer Frontier spectrometer with aid of VARS accessory) was performed between 4000 cm^{-1} and 400 cm^{-1}, with a resolution of 4 cm^{-1} and 128 scans. Scanning electron microscope (SEM) Quanta 3D FEG FEI was used for morphologies analyses. To perform the analysis on the SEM, the samples were powdered and their surfaces were covered with a layer of about 15 nm of amorphous carbon to improve surface conductivity, avoiding the accumulation of charges during image acquisition. TEM images were obtained from Transmission Electron Microscope G2-20-SuperTwin FEI microscope.

3. Results and discussion

The surface mounted metal-organic-frameworks (SURMOF) were carried out by using SBA-15 silica, previously synthesized at Laboratory of Ceramic Materials (LMC), and silicon wafer coated with gold as substrates. Fig. 3 illustrated the comparison between the surfaces before and after the deposition of Cu-BTC, where Fig. 3a shows the substrate of SBA-15 silica and Fig. 3b shows the substrate of SBA-15 silica after deposition of Cu-BTC, bluish surface. The noted color of the silica substrate was characteristic of the formation of Cu-BTC. In the case of gold substrate, the Fig. 3c shows the MHDA-SAM without Cu-BTC and Fig. 3d the MHDA-SAM with Cu-BTC.

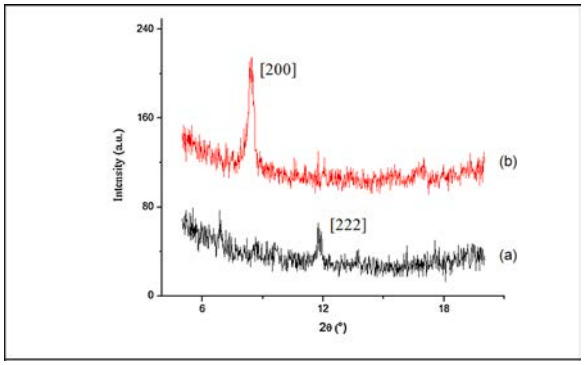

Fig. 4. Out-of-plane data for $Cu_3(BTC)_2$ (a) growth on OH activated SBA-15 silica substrate and (b) growth on MHDA SAM on gold substrate.

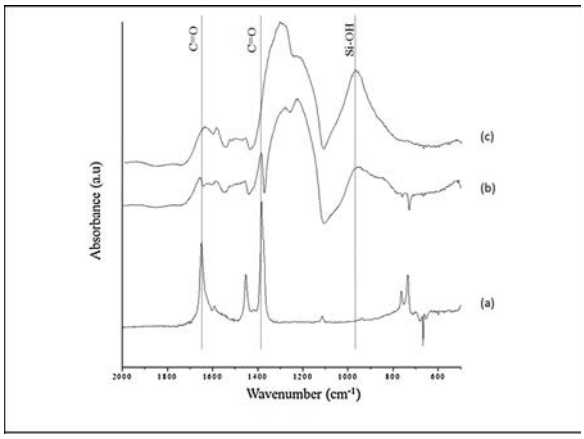

Fig. 5. FTIR spectra of (a) Cu-BTC on gold substrate, (b) Cu-BTC on SBA-15 silica substrate and (c) SBA-15 silica.

The Fig. 4 shows the XRD patterns of the resulting SURMOFs obtained by using layer-by-layer spray method. As previously described, SURMOFs were prepared step by step thorough and directly on the substrates, so no pure MOF data was presented. They need support for growth. We compare XRD data for Cu-BTC SURMOF prepared using 20 cycles on activated SBA-15 silica substrate (Fig. 4a) with a typical data for Cu-BTC SURMOF fabricated on MHDA functionalized gold conventional substrate (Fig. 4b). The XRD patterns demonstrated the success of the adapted spray method and that MOF material has been deposited on SBA-15 silica substrate. The gold functionalized with MHDA COOH-terminated substrate, presented the growth of [$Cu_3(BTC)_2$] along the [200] direction. On the other hand, the OH-terminated SBA-15 silica surface presented MOF-layers with a [222] orientation. These results using SBA-15 OH-terminated substrate corroborate the researches conducted with others anchoring organic reagents, such as 11-

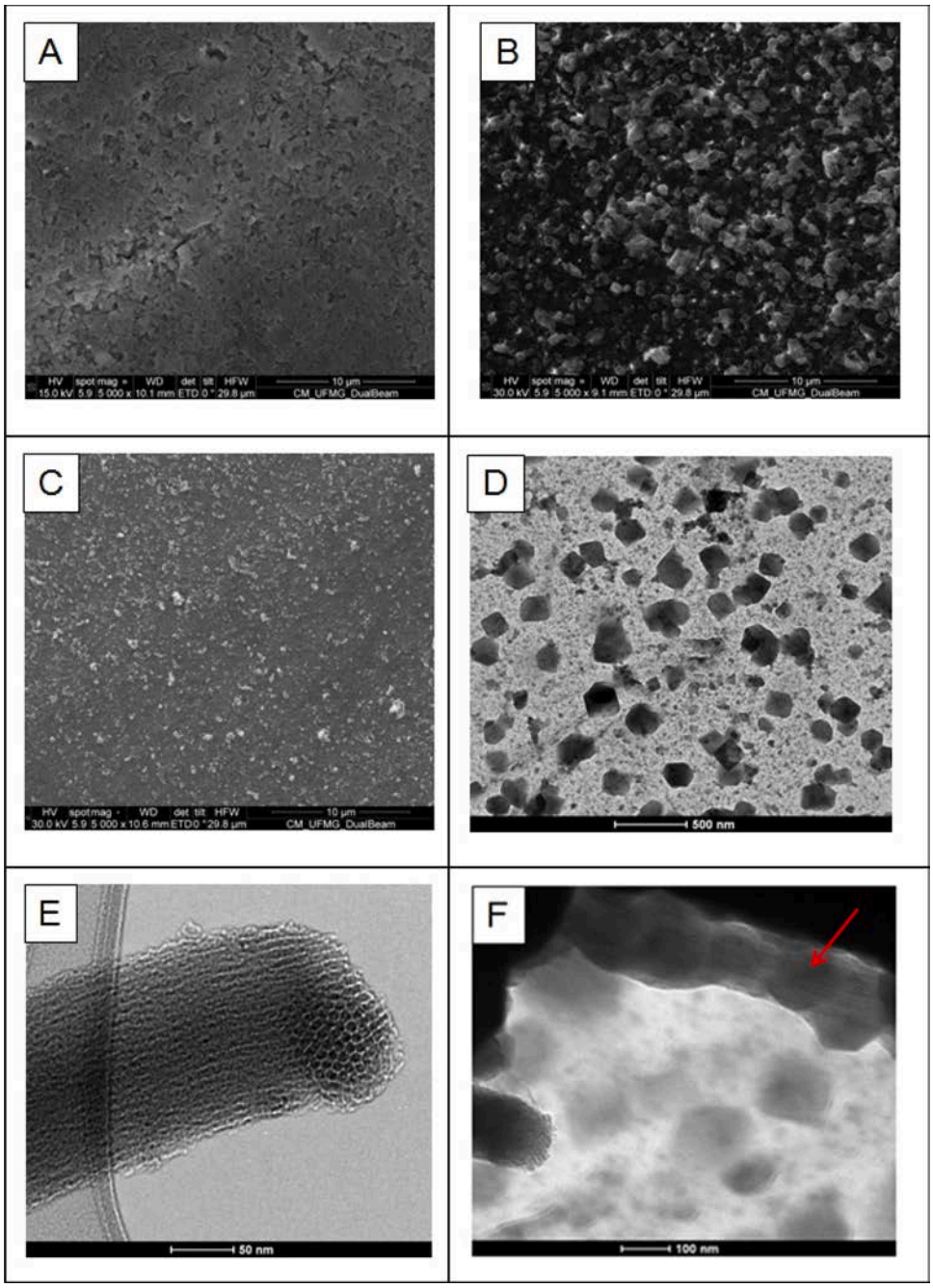

Fig. 6. SEM images of (a) SBA-15 pastille, (b) SBA-15 + Cu-BTC by LBL spray method, (c) gold substrate + MHDA-SAM + Cu-BTC and TEM images of (d) gold + MHDA SAM + Cu-BTC (e) SBA-15 silica and (f) SBA-15 + Cu-BTC by LBL spray method.

mercaptoundecanol (MUD), which presented the growth in the same [222] direction [32]. In addition, the SBA has amorphous walls that do not appear in the DRX, which emphasizes that the peak presented refers to the built MOF [33]. Thus the different substrate termination controls the growth direction of the MOF. The FTIR results indicated the formation of a Cu-BTC SURMOF on SBA-15 silica supports, which is consistent with results obtained from XRD.

The FTIR spectrum illustrated in Fig. 5 shows the comparison between the synthesized $Cu_3(BTC)_2$ on MHDA-SAM on gold substrate (Fig. 5.a), $Cu_3(BTC)_2$ on OH-terminated SBA-15 mesoporous silica (Fig. 5.b) and powder of SBA-15 mesoporous silica (Fig. 5.c). For $Cu_3(BTC)_2$ (Fig. 5a), the peaks at 1652 cm^{-1} and 1384 cm^{-1} were respectively attributed to the asymmetric and symmetric stretching vibrations of C═O existing in the BTC ligands [11]. For the SBA-15 (Fig. 5c), the main bands are from 1300 to 1000 cm^{-1}, due to Si—O—Si asymmetric stretching vibrations [13]. The characteristic vibrational band related to the Si—OH groups was seen around 982 cm^{-1} [11]. As presented in Fig. 5b, it was found that the FTIR spectra of the synthesized Cu-BTC SURMOF on OH-terminated SBA-15 silica substrate presented the peaks of Cu-BTC on gold substrate. Furthermore, the OH functional groups appeared in the FTIR spectra of pure SBA and then decreased in the peak of OH in the MOF + SBA suggesting a decreasing of available OH on the silica surface and the MOF adhesion to the surface of the support, which corroborates the results of XRD. This shows that the OH-terminated groups bind to the MOF and assisted in the orientation of its structure.

The SEM and TEM images shown in Fig. 6 demonstrated the morphologies of the $Cu_3(BTC)_2$ prepared by using spray layer-by-layer

method. The Fig. 6a presents the formation of the homogeneous pastille of pure SBA-15 silica. Some research has been done to recover silica substrates with SURMOF without much success [34]. As shown in the SEM images in Fig. 6b, in this work we achieve an homogeneous distribution of the Cu-BTC SURMOF film on SBA-15 silica pastilles and proved the success of the LBL spray method to prepare this coating on silica supports without any organic functionalization. Fig. 6c showed the Cu-BTC SURMOF on conventional gold substrate functionalized with the COOH organic group, by using MHDA-SAM. The Fig. 6d presents the regular octahedral morphology of Cu-BTC with a size around 150 nm growth on gold with MHDA-SAM substrate. In the Fig. 6e it was observed the highly ordered mesoporous structure of original SBA-15. On the other hand, Fig. 6f suggested the phase distributions of Cu-BTC crystals on SBA-15. It is possible to observe the regular arrangement of MOF forms interacting with the SBA-15 substrate. Furthermore, the Cu-BTC nanocrystals were attached on SBA-15 silica substrate and grew along the direction under silica influence due to the presence of OH-terminated group. These results were in line with the findings from the FTIR and XRD measurements and demonstrated that the room temperature layer-by-layer spray method is well-suited for the growth of such MOF thin film on mesoporous supports.

4. Conclusions

In conclusion, we have successfully synthesized and characterized a Cu-BTC MOF on mesoporous SBA-15 silica substrate by using a new approach of the layer-by-layer spray method. The obtaining of SBA-15 pastilles and its simple activation with water was enough to provide the necessary OH-terminated groups to anchor the MOF on the silica surface. The chosen method, besides allowing the formation of MOF at room temperature and ambient pressure, allowed the oriented growth of the structure, as confirmed by instrumental analysis. Furthermore, both SBA-15 silica and gold substrates modified with MHDA allow the growth of the MOF and they proved to be suitable for using as support for Cu-BTC. Silica SBA-15, however, as a porous substrate, allows to explore different applications such as porous gas separation membranes [10,11, 27,35]. While modified gold substrates are more attracted to sensor applications [24,36]. Hence, this study opens the way for further research on the association of MOF with ceramic membranes, encourages studies on the performance of these materials and contributes significantly to the recent studies related to the synthesis of SURMOF on mesoporous materials.

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.

Acknowledgments

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