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Solvent-Directed Morphological Transformation in Covalent Organic Polymers

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Synthesis of bi-functional covalent organic polymers in two distinctive morphologies has been accomplished by simply switching the solvent from DMF to DMSO when 1,3,5-tribenzenecarboxyldehyde and 2,5-diaminobenzene sulfonic acid were reacted *via* Schiff base condensation reaction to afford covalent organic polymers (COPs) encompassing flower (F-COP$_{DMF}$)- and circular (C-COP$_{DMSO}$)-type morphologies. Chemical and morphological natures of the synthesized COPs were compared by characterization using TEM, SEM, XRD, FT-IR, and XPS analysis techniques. Besides diverse morphology, both the polymeric materials were found to comprise similar chemical natures bearing protonic acid–SO$_3$H and Lewis base–C=N functionalities. Subsequently, both the COPs were evaluated for the synthesis of hydroxymethylfurfural (HMF) by the dehydration of fructose to investigate their morphology-dependent catalytic activity.

Keywords: covalent organic polymer, HMF, morphology-dependent activity, biomass upgradation, morphological transformations

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INTRODUCTION

The synthesis of covalent organic polymers with diverse functionalities and morphology has always been a desirable pursuit in terms of their broad applicability (Li et al., 2017; Chen et al., 2021; Namsheer and Rout, 2021). Organic polymers comprise an important class of nanomaterials, which includes porous polymer networks (PPNs) (Yuan et al., 2011), polymers of intrinsic microporosity (PIMs) (McKeown, 2017), conjugated microporous polymers (CMPs) (Lee and Cooper, 2020), covalent organic frameworks (COFs) (Guan et al., 2020; Li et al., 2020), hyper-cross-linked polymers (HCPs) (Masoumi et al., 2021), crystalline triazine-based frameworks (CTFs) (Guo et al., 2021), porous organic frameworks (POFs) (Zhang et al., 2018), porous polymer frameworks (PPFs) (Zhu et al., 2013), polymeric organic networks (PONs) (Jeon et al., 2012), and porous aromatic frameworks (PAFs) (Yuan and Zhu, 2019). This area of research has witnessed a prodigious growth in terms of both synthetic diversity as well as applicability in the field of gas storage (Ahmed et al., 2018), energy storage (Magu et al., 2019), separation (Li et al., 2019a), sensors (Anik et al., 2019), and heterogeneous catalysis (Li et al., 2019b). Generally, these nanomaterials are synthesized *via* boronic acid condensation (Kubo et al., 2015), imine formation (Segura et al., 2016), Suzuki coupling (Zhou et al., 2019), and Friedel-crafts alkylation (Troschke et al., 2017). C-N linked organic polymers such as triazine-, imine-, and hydrazone-linked polymers are comparatively stable and do not decompose easily in the presence of moisture and thus are widely accepted, including the catalysis arena. Their physical properties, namely, morphology, crystalline/amorphous nature, and porous nature, depend on the reaction conditions such as catalyst, solvent system, temperature, and substrates. Additionally, the intrinsic geometrical features of the building blocks dictate the chemical nature and final topology of the materials. It has been well documented that the morphology and functionality of a nanomaterial significantly affect its catalytic activity and thus can be tuned as per the target applications (Zhuang et al., 2015). Moreover, morphological changes themselves have been found to be effective in various applications because of the morphology–activity correlation (Mondal et al., 2014; Ghorbanloo et al., 2017). Consequently, the synthesis of covalent organic polymers (COPs) with substituted back bone structure and nanoscale morphologies is an emerging field of research. However, it is challenging to acquire the morphology-controlled nanostructure due to the unrestricted kinetic of polymerization (Trewin and Cooper, 2010). Various synthesis methods have been developed involving template-assisted, external cross-linkers, and solvent knitting methods (Thomas et al., 2008; Zhao et al., 2013; Wang et al., 2017; Gao et al., 2019; Giri et al., 2022). Although a wide range of substrates have been used to design and synthesize newer types of COPs, most of these approaches require either an external cross-linker or a catalyst. Therefore, the development of a facile method to synthesize the bi-functional COPs with diverse morphology could be desirable for the organocatalytic applications (Gharpure et al., 2013; Khan et al., 2018; Lambat et al., 2019a; Lambat et al., 2019b; Khan et al., 2020; Chopra et al., 2021).

In this study, we have investigated the role of organic solvents in switching the morphology of organic polymers employing benzene-1,3,5-tricarboxaldehyde and 2,5-diaminobenzene sulfonic acid as the building blocks *via* the Schiff condensation process without the deployment of any catalyst and external cross-linkers. The choice of the sulfonic acid functional groups substituted substrate as one of the building blocks was intentional, to afford acidic COPs for targeting their applications in biomass upgradation. Carbohydrates represent 75% of the annual renewable biomass for the synthesis of various value-added chemicals of tremendous importance (Kumar et al., 2014; Verma et al., 2016; Verma et al., 2017a; Verma et al., 2017b; Tadele et al., 2017; Den et al., 2018) where HMF has been listed as one of the valuable biomass-derived products, and thus, its production involving fructose is of enormous interest (Sayed et al., 2020); it serves as an active intermediate for the preparation of value-added chemicals including dimethyl furan and levulinic acid (Aljammal et al., 2019). Thus, the ensued COPs bearing the Brønsted acidic sites were accordingly utilized as acid catalysts for the HMF production by fructose dehydration (Baig et al., 2016).

EXPERIMENTAL

Synthesis of Covalent Organic Polymers (F-COP$_{DMF}$ and C-COP$_{DMSO}$)

For COP synthesis, 0.2 mmol of benzene-1,3,5-tricarboxaldehyde and 0.2 mmol of 2,5-diaminobenzene sulfonic acid were taken in 20 ml of dimethylformamide and 20 ml dimethylsulfoxide, and the solutions were sonicated for 5 min at room temperature. The resulting homogeneous wine-colored solutions were flushed with nitrogen and heated at 130°C for 24 h. After the reaction, solid materials were separated *via* centrifuge and washed with dehydrated solvents until the supernatant appeared colorless and then dried under vacuum at 60°C to yield brown-colored materials, represented here as F-COP$_{DMF}$ and C-COP$_{DMSO}$. The other organic polymer, Fe-COP$_{DMF}$, was prepared following the same procedure, except using an additional 0.2 mmol of iron chloride salt while maintaining the same molar ratio of the reacting components, benzene-1,3,5-tricarboxaldehyde and 2,5-diaminobenzene sulfonic acid.

Dehydration of Fructose to HMF

The catalytic activity of the prepared COPs was evaluated in the synthesis of HMF *via* the dehydration of fructose. For the synthesis of HMF, a 10-ml pressure tube (Sigma Aldrich) was charged with 0.3 mmol of fructose and 20 mg of the COFs (F-COP$_{DMF}$ or C-COP$_{DMSO}$) as catalyst and 2 ml DMSO as solvent. The pressure tube was transferred into a preheated oil bath at 130°C, and then the stirring continued for 3 h. After the completion of the reaction, the catalyst was separated by centrifugation. The yield of HMF was calculated to be 83 and 76% for F-COP$_{DMF}$ and C-COP$_{DMSO}$, respectively, and determined by using the UV-visible spectroscopy technique as described in the literature (Zhang et al., 2013).

RESULTS AND DISCUSSIONS

One of the widely used strategies for the synthesis of COPs involves the condensation among the aromatic amines and aromatic aldehydes to afford the comparably stable imine-based polymeric network structures. In this case, COP materials with two different morphologies were successfully synthesized by taking equimolar amounts of benzene-1,3,5-tricarboxaldehyde and 2,5-diaminobenzenesulfonic acid in two different solvents. The application of DMF and DMSO solvents resulted in the nano flower and circular disk type morphology, respectively, under the same reaction conditions. The morphology transformation could be related to the polarity and chemical nature of the solvents. It was observed that 2,5-diaminobenzenesulfonic acid was not fully dissolved in most of the organic solvents because of the presence of sulfonic acid and amino functional groups and thus behaved as zwitterion. However, one of the imperative conditions for the facile growth of organic polymers is to have a better solubility of the substrates in the solvent system. Therefore, different solvent systems have been reported for the synthesis of assorted organic polymers. DMF and DMSO are nitrogen- and sulfur-containing highly polar organic solvents, which can provide the better solubility for a range of substrates. Moreover, the presence of substituted groups in the substrates evidently affects the nature of the polymerization and, thus, the physical and chemical properties of the ensuing polymeric material (Kim et al., 2001; Gao et al., 2020). Bulky groups are prone to destabilizing the

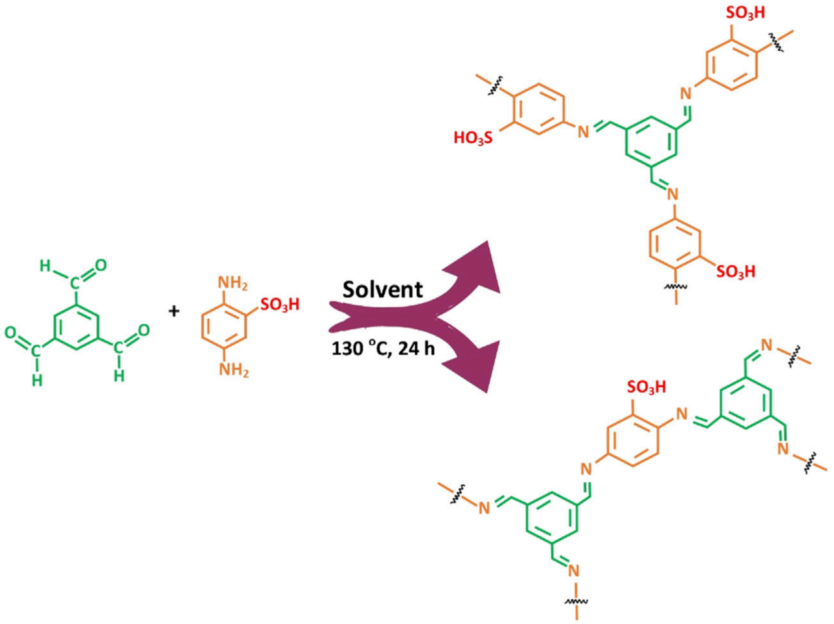


FIGURE 1 | Synthesis of organic polymers with two possible repeating units.

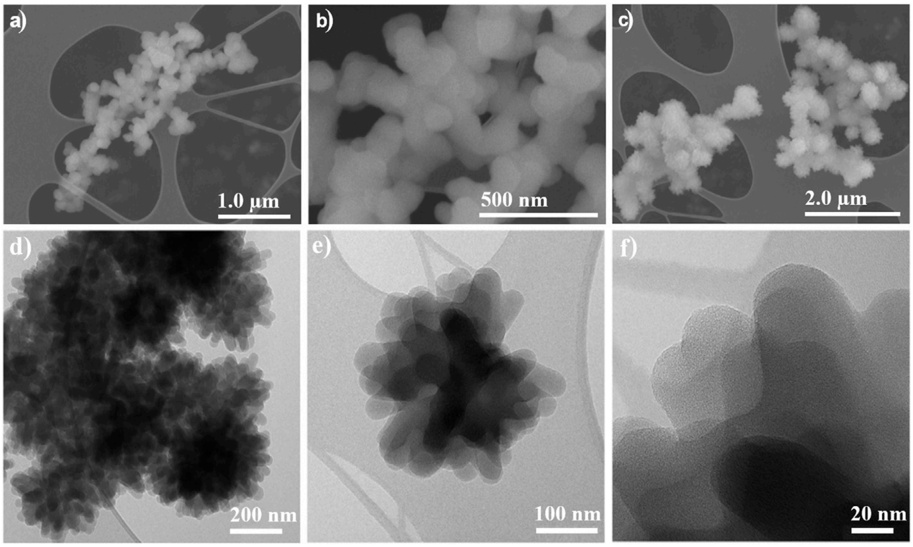


FIGURE 2 | (A,B) SEM images of C-COP$_{DMSO}$; **(C)** SEM image; and **(D–F)** TEM images of the F-COP$_{DMF}$ with different size scales.

framework structure due to the steric hindrance and may lead to the crosslinking of the substrates. In this case, the sulfonic acid functional group is a bulky substituted group and could be responsible for strained intermediate formation due to the lack of keto-enol tautomerization, thus facilitating the crosslinking polymerization (Peng et al., 2016). Moreover, different chemical interactions between solvents and substrates might be playing a vital role in stabilizing the intermediates, resulting in two different morphologies (Gao et al., 2018). There could be two possible different growth patterns in the respective solvents as shown in **Figure 1**. Therefore, we can conclude that the polar and chemical natures of the solvents are the factors, which has not only resulted in the reaction to ensue but also provided diverse morphologies.

The morphological identification of both materials was confirmed by using SEM and TEM analytical techniques, and the images are depicted in **Figure 2**. In case of C-COP$_{DMSO}$, the TEM images clearly showed the presence of agglomerated and

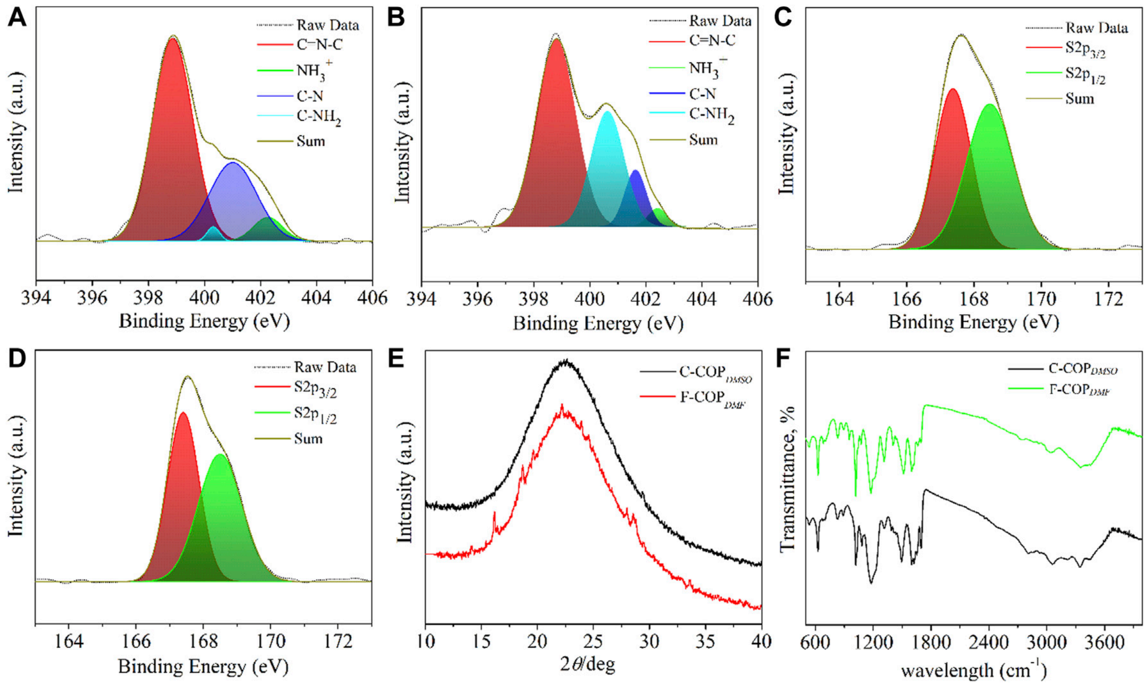


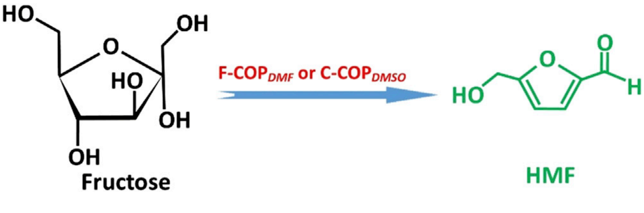
FIGURE 3 | (A) N1s of F-COP$_{DMF}$; **(B)** N1s of C-COP$_{DMSO}$; **(C)** S2p of F-COP$_{DMF}$; **(D)** S2p of C-COP$_{DMSO}$; **(E)** XRD spectra; and **(F)** FT-IR spectra.

stacked circular disks with the size in the range of 100–200 nm. However, TEM images F-COP$_{DMF}$ indicated the presence of nanoflowers, with the sizes varying from 150 to 250 nm. A sheer dissimilarity between both the organic polymer structures is evident and thus confirmed the distinct effect of the solvent. Moreover, the morphology of the C-COP$_{DMSO}$ was found to be like that of the Cu_2S bonded sulfonated organic polymers (Kumar et al., 2020). Interestingly, these results prompted us to envision that not only the solvent but also the presence of metal can play a vibrant role in determining the final morphology of the materials. Adhering to this thought, we synthesized the Fe-COP$_{DMF}$ material using iron chloride salt to recognize any possible effect on the morphology under the same reaction conditions. The synthesized material was characterized by the SEM and TEM analysis and shown in **Supplementary Figure S1**. In the SEM images, a mixed type of morphology containing disk as well as spherical domains in the range of the 200–500 nm were observed. In case of TEM images, Fe-COF$_{DMF}$ showed a high degree of resemblance in their bulk structures. It was difficult to find the individual domain due to the high agglomeration, and the morphology was found to be of the distorted spherical type. This study provided clear evidence that not only the solvent but also the type of metals can significantly affect the morphology of the resulting materials, as is evident in previous reports (Gao et al., 2018; Giri et al., 2022); further studies relating to the effect of metal are presently under progress in our group. In order to stick to the metal-free morphology transformation, we further study the chemical nature of the F-COP$_{DMF}$ or C-COP$_{DMSO}$ using the XPS analysis.

X-ray photoluminescence spectroscopy (XPS) is a widely deployed surface technique to study the elemental composition and the probable bond connectivity. Subsequently, both the materials (F-COP$_{DMF}$ and C-COP$_{DMSO}$) were subjected to the XPS analysis to provide the survey scan and high resolution XPS spectra of individual elements present in the different samples as shown in **Figures 3A–D** and **Supplementary Figures S2B,C**. The survey scan spectra of both the samples were similar in terms of presence of elements and thus confirmed the availability of C, O, N, and S atoms in both the samples. However, elemental compositions of both the materials were found to be different (**Supplementary Figure S2B**). The elemental composition was calculated to be C = 70.7; N = 10; O = 16.5; S = 2.8 at% for F-COF$_{DMF}$ and C = 76.4; N = 6.3; O = 15.3; and S = 2 at% for C-COF$_{DMSO}$. In case of F-COF$_{DMF}$, the atomic percent of S is found to be higher than that in C-COF$_{DMSO}$, indicating the presence of higher sulfur-containing groups. Notably, F-COF$_{DMF}$ was synthesized using sulfur-free organic solvent, DMF, thus excluding the possibility of the role of solvent used in doping of the materials. High-resolution deconvoluted spectra of the respective elements recognized different bonding patterns. The peaks at 167, 284, 400, and 532 eV can be correlated with S2p, C1s, N1s, and O1s, respectively (**Supplementary Figure S2A**). In both the samples, the peak for C1s further splits into three peaks positioning at 284.7, 285.6, and 288.7 eV and thus can be correlated with the C–C/C=C, C=N/C-S linkages and oxidized carbon, respectively, as depicted in **Supplementary Figures S2C,D**. These peaks are presumably stemming from the aromatic regions and imine bond creation because of polymeric structure formation, while these peaks can be further corroborated from the high-resolution S2p and N1s XPS spectra. The presence of uncondensed -NH_2 groups can be identified with the help of N1s spectra. The peak at 400.6 eV in N1s spectra reveals the presence of uncondensed–NH_2 groups. In the case of C-COP$_{DMSO}$, the intensity was higher than that of F-COP$_{DMF}$, indicating the higher number of uncondensed amino groups. Moreover, lower intensity of the peak at 401.6 eV related to the C-N bonds, further affirming the lack of imine bond formation. The peak responsible for C=N-C linkage positioned at 398.8 eV was present in both the spectra (**Figures 3A,B**). The peaks at 167.6 eV for the S2p spectra of both the samples are the characteristic peaks ascribable to the availability of sulfonic acid groups on the surface of the polymeric materials. Furthermore, the peak position of deconvoluted S2p XPS spectra showed two peaks at 167.4 and 168.5 eV corresponding to the S2p3/2 and S2p1/2, which further authenticates the existence of the sulfonic acid group (**Figures 3C,D**). Notably, no other sulfur-containing functional groups such as thiol were observed in both the materials. The bonding pattern of the respective elements in each material was found to be similar, with a very small change in the peak positions. All these results authenticate the successful formation of COPs.

X-ray powder diffraction was utilized to determine the amorphous/crystalline nature of both the COPs (F-COP$_{DMF}$ and C-COP$_{DMSO}$). A broad amorphous halo centered at 23° 2θ presented in both cases is indicative of the amorphous nature of the materials (**Figure 3E**). (Murthy and Minor, 1990; Yildirim and Derkus, 2020) These results appear to support the hypothesis that the size of surface-exposed functional moieties affects the crystallinity of the polymeric materials because of steric hindrance that causes angle strain between the substrates. Moreover, the low-intensity diffraction peaks observed in the diffraction pattern of F-COP$_{DMF}$ could be attributed to the generation of micro-crystallites in the material.

The FT-IR spectra of F-COP$_{DMF}$ or C-COP$_{DMSO}$ were scanned in the range of 400–4000 cm^{-1} and compared to witness any possible changes in the form of functional groups attributable to the DMF- and DMSO-assisted solvothermal condensation (**Figure 3F**). The characteristic stretching vibrations for the C=N functional groups at 1629 cm^{-1} appeared, thus affirming the successful condensation between benzene-1,3,5-tricarboxaldehyde and 2,5-diaminobenzenesulfonic acid. However, the intensity was diminished more for F-COP$_{DMF}$ in the region of 3200–3600 cm^{-1}, which is primarily responsible for the availability of uncondensed -NH_2 groups, indicating a higher extent of condensation than C-COP$_{DMSO}$. Furthermore, symmetric and asymmetric vibration modes corresponding to the sulfonic groups at 1019, 1078, and 1218 cm^{-1} indicate that the sulfonic groups are well intact on their surface. The other common peaks could be associated to various stretching and bending vibrations of functional groups in the materials. XPS and FTIR techniques confirmed the presence of sulfonic acid functional groups on the surface of the polymeric material without showing any possible reduction of sulfonic acid into thiol groups during the synthesis process and thus come out to be a potential candidate as an acid catalyst. Moreover, the nitrogen adsorption-desorption isotherms were recorded to determine the surface area. F-COP$_{DMF}$ and C-COP$_{DMSO}$ presented type-II curves with Brunauer–Emmett–Teller (BET) surface areas of 50.03 and 48.89 m^2/g, respectively (**Supplementary Figure S3**).



SCHEME 1 | Dehydration of fructose into HMF.

Subsequently, the catalytic activity of the prepared organic polymers (F-COP$_{DMF}$ or C-COP$_{DMSO}$) was assessed and compared relating to the HMF formation *via* the dehydration of fructose in terms of yields (**Scheme 1**). The experiments were carried out in a 10.0-ml glass tube encompassing the fructose and catalyst in DMSO. The reaction was continued for 3 h under stirring at 130°C. After completion of the reaction, the glass tube was cooled in an ice bath, and the catalyst was separated by filtration. The resulting reaction mixture was analyzed using the UV-Vis spectroscopy technique by following the procedure documented elsewhere (Zhang et al., 2013).

The maximum yield of HMF under the optimized reaction conditions using F-COP$_{DMF}$ or C-COP$_{DMSO}$ was found to be 83 and 76%, respectively. Although, F-COP$_{DMF}$ showed better catalytic activity in terms of HMF yield, we cannot conclude that it is because of only morphological change. It could be due to the higher percentage of sulfonic acid groups. Therefore, at this stage, we can only determine that the DMF helps to retain higher percentage of sulfur in the possible form of sulfonic acid groups that could in turn effect the higher activity of the resulting material.

CONCLUSION

We have successfully synthesized two organic polymers (F-COP$_{DMF}$ or C-COP$_{DMSO}$) with two distinct morphologies using a similar set of substrates but different solvent systems. Based on the experimental results, the solvent system not only dictated the final morphology outcome but also helped to retain the higher concentration of sulfur in the form of sulfonic acid groups on the surface of the material. Moreover, higher condensation is observed while using the DMF as solvent. In addition, the role of metal in determining the morphology was evaluated, and the ensued materials were evaluated for the synthesis of HMF; higher activity of the catalysts might be due to the presence of acidic groups. In case of HMF synthesis, dehydration of fructose to HMF is catalyzed by Bronsted acidic groups. This interesting protocol certainly opens the door to further material development by deploying a single solvent for synthesis and morphological variation of the material. Results also suggest that the product yields attained are almost similar in both the materials and have no morphological effect on the catalytic activity.

DATA AVAILABILITY STATEMENT

The original contributions presented in the study are included in the article/**Supplementary Material**; further inquiries can be directed to the corresponding authors.

AUTHOR CONTRIBUTIONS

SK and XC conceptualized the work and wrote the manuscript. IN analyzed and interpreted XRD data. JK performed the BET analysis. RV checked and edited the manuscript. All authors contributed to the article and agreed on the submitted version.

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SUPPLEMENTARY MATERIAL

The Supplementary Material for this article can be found online at: https://www.frontiersin.org/articles/10.3389/fmats.2022.889679/full#supplementary-material

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