Reaction milling for scalable synthesis of N, P-codoped covalent organic polymers for metal-free bifunctional electrocatalysts

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HIGHLIGHTS

- Reaction milling method was proposed to synthesize bifunctional electrocatalysts.
- Space-time yield for scalable synthesis reaches 288 kg m\(^{-3}\) day\(^{-1}\).
- RM method provides a solvent-free and scalable alternative for electrocatalysts.
- The reaction process was significantly proceeded by RM method.
- 3 days under 120 °C (tradition) V.S. 2 h under room temperature (RM).

GRAPHICAL ABSTRACT

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ABSTRACT

This study exploits an effective mechanochemical process (termed as reaction milling) to conduct Schiff-based coupling reaction with melamine and terephthalaldehyde for the synthesis of covalent organic polymer (RM-COP) as the carbon skeleton and the derivative phosphorus doped material (RM-COP-PA). Comparing with the tradition solvothermal method with reaction time of 3 days under 120 °C, the newly developed reaction milling method significantly shorten the reaction time of the synthesis to 3 h under room temperature as well as bypassing the usage for hazardous solvents. The space-time yield of the developed reaction milling method for synthesis of the bifunctional electrocatalytic precursor reaches 189 kg m\(^{-3}\) day\(^{-1}\). Significantly, the optimal products followed by further carbonization (RM-COP-PA-900) demonstrated excellent bifunctional electrocatalytic activities for an efficient ORR performance with similar commercialized Pt/C half-potential of 841 mV vs RHE as well as an IrO\(_2\)-like OER activity with a potential of 1.69 V at 10 mA cm\(^{-2}\) in alkaline media, which is better than most metal-free bifunctional catalysts. Moreover, the obtained RM-COP-PA-900 exhibits much better durability and resistance to crossover effect even than the commercial 20 wt% Pt/C catalysts. Therefore, this work will open up a rapid, solvent-free and scalable approach for, but not limit to, highly efficient electrocatalysts.

1. Introduction

With the development of the high energy conversion and storage devices such as fuel cells, Zn-air batteries, solar cells and supercapacitors [1–8], development of stable, effective and low-cost bifunctional electrocatalysts towards oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) becomes one of the major challenges for their commercial application. Recently, well-defined 2D...
Covalent organic polymers (COPs) [9,10] have been widely developed and hold the promising potential to be used as carbon skeleton due to their ultrahigh hydrothermal stability, versatile elements incorporation and controllable structures comparing with the famous carbon materials such as graphene, carbon nanotubes, fullerenes and graphite [4,5,11,12]. COP based electrocatalysts with appropriate design have shown comparable performance to noble-metal materials [13].

However, rigorous conditions, high-cost catalysts as well as slow kinetic are inevitable for the synthesis of these COP based electrocatalysts which hinder the large-scale production of COPs [9]. In addition, the using solvent with traditional synthesis methods, such as, solvothermal [14], ionothermal [15], and microwave [16], inevitably brought environmental issues, which needs solvent recovery and regeneration devices in industry application. In contrast, mechanical methods, without using of large amount of organic solvent, are applied to not only strip and mix reactants [17,18], but also enhance the reaction process due to its generated high energy in a short time by mechanical friction [19–21]. Ball milling, as one of the most efficient mechanical methods, has been applied in synthesis porous covalent triazine frameworks [22] and functional modification of the carbon materials [23] under mild condition. Besides organic synthesis in the laboratory, mechanical milling has already been applied in large-scale industrialization in many fields, such as mechanical activation of solids, mechanical alloying and the preparing of nano materials [24–27], which provides the possibility of large-scale synthesis of functional organic materials.

In this study, we have, for the first time, prepared the bifunctional electrocatalyst with N, P co-doped carbon materials based on covalent organic polymer through the mechanical chemistry process under well-optimized conditions without using catalyst and organic solvent. Since the existence of chemical reaction, here we termed this newly developed mechanical synthesis method as reaction milling (RM) to distinguish the traditional physical mixing/grinding process. As shown in Scheme 1, melamine and terephthalaldehyde are crosslinked during the reaction process. After the construction of COP backbones, phytic acid was added to provide the phosphorous source. The application of reaction milling can significantly shorten the reaction time of the synthesis to 3 h and adopt mild synthesis conditions (Room Temperature) bypassing the need for hazardous solvents while the solvothermal method takes several days and requires heating at high temperature (usually 120°C) [28]. Furthermore, the reaction is carried out in the state where the solid reactants are continuously mixed to ensure the homogeneity and high contently doping of phosphorous with high space-time yield. The resulted RM-COP-PA-900 contained abundant mesopores and high contently doping of phosphorous with high space-time yield. The realization of mechanical synthesis applied in bifunctional electrocatalysts makes it possible for their scalable production, which has a significant for commercial needs for energy conversion and storage applications.

2. Materials and methods

2.1. Materials

Melamine (99%), terephthalaldehyde (98%) and phytic acid (70% in H2O) were purchased by Shanghai Aladdin Biochemical Technology Co., Ltd. The reaction milling synthesis was carried out in a QM-3SP planetary ball mill from Nanjing Nanda Instrument Co., Ltd. The synthesis was performed in a 100 mL grinding jar made of stainless steel with 120 g zircon oxide balls (5 mm in diameter) as milling media. Nafton solution was purchased from DuPont Company. Commercial Pt/C (20 wt%) was obtained from Alfa Aesar Chemical Co., Ltd. IrO2 was purchased from High-purity (99.99%) argon gas, oxygen gas and nitrogen gas were obtained from Shi yuan Jing ye (Beijing) Air Power Technology Development Co., Ltd.

2.2. Synthesis of catalysts

The RM-COP-PA was synthesized through reaction milling. Briefly, melamine (2 g, 1.5 eq.) and terephthalaldehyde (1.5 g, 1 eq.) were mixed by hands for 30 s and then added into the milling jar with 120 g 5 mm milling balls. The milling jar was charged with argon then milled at 500 Hz for 2 h. After milling for two hours, phytic acid (2 g) was added and kept milling for another one hour under argon atmosphere. The product after reaction milling was washed by ethanol for three times to remove the residues oligomers then vacuum dried at 80 °C. The obtained RM-COP-PA was annealed at 350 °C for 2 h, followed by heating up to 900 °C with a ramp rate of 5 °C min⁻¹ under argon atmosphere. The carbonized products were termed as RM-COP-PA-T (T represents the final carbonization temperature). To make a comparison, we synthesized the RM-COP under the same condition without the addition of phytic acid termed as RM-COP and RM-COP-T (after carbonization).

2.3. Chemical and physical characterization

The solid-state 12C and 31P measurements were performed with a Bruker AV300 spectrometer operating at 300 MHz. The morphology of RM-COP-PA-900 and RM-COP-900 materials was observed by scanning electron microscopy (SEM, S4700) equipped with an energy dispersive X-ray spectrometer (EDS), and transmission electron microscope (TEM, H7700). X-ray photoelectron spectroscopy (XPS) analysis was carried out using a commercial spectrometer (ThermoVG Fisher Scientific USA) with Al Kα as X-ray source. Raman spectra was collected on the LabRAM Aramis Raman Spectrometer (Horiba Jobin Yvon) using...
514 nm laser as the excitation source. The phase analyses of RM-COP-PA-900 was performed using X-ray diffraction (XRD) with D/MAX 2000 X-ray diffractometer 125 with Cu Kα line (λ = 1.54178 Å) as the incident beam and operating at a scan rate of 5° min\(^{-1}\). The specific surface areas were calculated using adsorption data in a relative pressure ranging from 0.05 to 0.3 by the Brunauer–Emmett–Teller (BET) method. Pore size distribution curves were computed from the desorption branches of the isotherms using the Barrett, Joyner, and Halenda (BJH) method. Fourier transform infrared spectra (FTIR) was recorded on Nicolet 8700 instrument in the wavenumber range 4000–400 cm\(^{-1}\).

2.4. Electrochemical characterization

The RM-COP-PA-900 catalyst ink was prepared by dispersing the catalyst (5 mg) in Nafton (DuPont, 0.5 wt%, 20 μL) dispersion solution in ethanol (980 μL) via sonication for 30 min to form a homogeneous suspension. Then, the catalyst ink (10 μL) was pipetted onto the glassy carbon (GC) electrode (0.197 cm\(^2\)) and dried at room temperature. The catalyst loading for the prepared catalyst on the GC electrode was 0.25 mg cm\(^{-2}\). By using the same electrode configuration, RM-COP-PA-800, RM-COP-PA-1000, RM-COP-900, RuO\(_2\) and Pt/C catalysts with the same amount were also studied for comparison. Electrochemical measurements were conducted with a CHI660e electrochemical working station (CH Instrument) at room temperature in O\(_2\)/N\(_2\) saturated 0.1 M KOH electrolyte for ORR/OER. A typical three-electrode system was employed, using a glass carbon rotating disk electrode (RDE) covered by catalyst as working electrode, a platinum wire as counter electrode, and an Ag/AgCl electrode (saturated with KCl) as reference electrode. All potentials in this study were converted to potential vs. reversible hydrogen electrode (RHE) according to the equation (\(E_{\text{RHE}} = E_{\text{AgCl}} + 0.197 + 0.0592 \times \text{pH}\)). As for ORR experiment, O\(_2\) or N\(_2\) was bubbled for 30 min prior to the test and maintained in the headspace of the electrolyte throughout the testing process. The catalyst loaded working electrode was cycled by cyclic voltammetry (CV) at a scan rate of 50 mV s\(^{-1}\), until stabilized current was obtained.

3. Result and discussion

3.1. Structure and chemical composition of the catalysts

The successful network formation was analyzed by the solid-state \(^{13}\text{C}\), \(^{31}\text{P}\) NMR and FTIR spectroscopy. From the corresponding carbon bond position of Solid-state \(^{13}\text{C}\) NMR, we confirm the generation of C=N bond (Fig. 1a), which is a sign of the reaction between melamine with terephthalaldehyde. As we know, the \(^{31}\text{P}\) NMR spectrum shift of phosphate groups on phytic acid is 0 ppm, however, from solid-state \(^{31}\text{P}\) NMR spectra of RM-COP-PA, the \(^{31}\text{P}\) NMR spectrum shifts to low-frequency region (Fig. 1b), which may be the reason that the oxygen of hydroxyl group attached directly to phosphorus has changed into nitrogen causing the electron cloud density around the phosphorus becomes smaller [11]. Otherwise, the spectrum has only one peak without miscellaneous peak, further confirming the uniqueness of combination between phytic acid with RM-COP. Fourier-transform infrared spectra (FTIR) was recorded on Nicolet 8700 instrument in the wavenumber range 4000–400 cm\(^{-1}\).

Fig. 1. (a) Solid-state \(^{13}\text{C}\) NMR spectra of RM-COP with the corresponding bond position. (b) Solid-state \(^{31}\text{P}\) NMR spectra of RM-COP-PA. (c) FT-IR spectra of RM-COP.
of the peaks has no obvious shifting and the relative intensity of primary amine peaks decreases, indicating the addition of phytic acid with multiple phosphate groups did not change the COP framework, in other words the doping occurred on the edge functional group (marginal amino) of RM-COP to form a cross-linked network structure through reaction milling, which is further confirmed by XRD of RM-COP and RM-COP-PA for the position of the peak did not change, except the relative intensity (Fig. S2). The edge doping play a critical role for electrocatalyst performance compared with the basal doping [33,34].

From the transmission electron microscopy (TEM) image in Fig. a, we observed that the RM-COP-PA-900 synthesized by reaction milling possess good stratified and mesoporous structure, which is formed during the reaction milling and pyrolysis process, respectively (Fig. S3). The layer structure formed through reaction milling processes good thermal stability, meanwhile during pyrolysis process the release of ammonia gas from melamine decomposes under 300 °C produced a macroporous structure [35] (Fig. S4), which is beneficial for both the ORR and OER process [36]. A scanning electron microscopy (SEM) image and associated elemental mapping (Fig. 2b–d) identified the homogeneous distribution of N and P for a sample pyrolysis at 900 °C (RM-COP-PA-900). In conclusion, the materials synthesized by reaction milling, which is further confirmed by XRD of RM-COP-PA-900 samples can be divided into four different bands at 398.4, 399.3, 400.4 and 401.4 eV (Fig. 2h), which correspond to pyridinic N (N1), nitrile N (N2), pyrrolic N (N3) and graphitic N (N4), respectively [45–48]. Considering the high content of pyridinic N and graphitic N in the RM-COP-PA-900 (Fig. 2e), excellent catalytic performance of the material was anticipated toward oxygen redox catalysis [49–53], for the former improved the onset potential for ORR, while the latter determined the limiting current density [4,54].

The Raman spectrum of RM-COP-PA after carbonization given in Fig. 2j shows the D-band at 1334 cm$^{-1}$ associated with the E_g mode [55]. The high graphitization degree of the RM-COP-PA-900 is evident from the high ratio of I_D/I_G (1.1), leading to an improved electrical conductivity. The corresponding X-ray diffraction (XRD) pattern (Fig. S6) shows two broad graphitic (0 0 2) and (1 0 1) diffraction peaks centered appeared at about 24.3 and 43.8° [56]. We also performed N$_2$ adsorption measurements to determine the specific surface area and pore structure of the RM-COP-PA-900. It was found that the BET surface area was 943 m$^2$ g$^{-1}$ (Fig. 2k), which significantly higher than RM-COP-900 (670 m$^2$ g$^{-1}$) (Fig. S7). The type IV isotherm curve with an obvious hysteresis confirms the presence of mesoporous.
The rapid N₂ uptake \((P/P₀ > 0.9)\) is attributable to the existence of secondary, much larger pores. Barrett–Joyner–Halenda (BJH) pore size distribution curves derived from the N₂ desorption confirm the presence of the main mesoporous with diameters between 3 and 13 nm of RM-COP-PA-900 (Fig. 2I), and the amount and uniformity are better than RM-COP-900 (Fig. S8). Clearly, therefore, the RM-COP-PA-900 with stereoscopic holes possesses a large surface area, high pore volume and wide pore size distribution for facilitating the electrocatalysis.

3.2. Electro catalytic performance of the catalysts

To understand the effect of the phosphorus, we compared the catalytic properties of RM-COP-900 and RM-COP-PA-900. As shown in Fig. 3a, b, we can see that the addition of phytic acid can improve the ORR and OER performance obviously, possibly for the influence of a synergistic effect of N, P co-doping and the edge doping effect of phosphorous by changing the charge distribution and electronic properties, which is beneficial for enhancement of electrocatalytic activity and electrochemical kinetics. Meanwhile, the post-addition of phytic acid leads the phosphorus mostly distributed in the periphery of COP skeleton, which is the active site for the ORR process more favorable than the middle of carbon surface [57,58]. The charge-transfer mechanism in ORR and OER process of RM-COP-900, RM-COP-PA-900 and noble metal based catalysts were measured by electrochemical impedance spectrum (EIS) ranging from 10⁶ to 0.05 Hz to investigate the electrode kinetics in the alkaline electrolyte (0.1 M KOH) under their respective half-wave potential (ORR) and the potential corresponding to 10 mA cm⁻² (OER). EIS is an effective method to study interfacial properties and processes of electrodes. Furthermore, the Nyquist plots clearly reveals that RM-COP-PA-900 catalyst shows the much smaller semicircle radius than RM-COP-900 and Pt/C, indicating the higher charge-transfer rates of RM-COP-PA-900, which is beneficial for ORR in the kinetic process (Fig. 3c). Also, in the OER process, the catalyst with phosphorus has smaller semicircle diameter at low frequency area and steeper slope at high frequency, due to the higher speed of charge-transfer and mass-diffusion [59] (Fig. 3d). To further explore the influence phosphorus doping for the increase of ORR performance, we measured the electrochemically active surface area of RM-COP-900, RM-COP-PA-900 and Pt/C (20 wt%) based on double-layer capacitance method in the potential range of 0.2–0.4 V vs. RHE, where no obvious Faradic current were observed for each catalyst. Then, the differences of capacitive currents \(1/2[I⁺−I⁻]@1.1 V\) were plotted as a function of the scanning rates (Eq. S1, Figs. S9, S10, S11), their slopes are equal to the electrochemical double-layer capacitance \((C_{dl})\) (calculated by Eq. S2). The results demonstrated that the RM-COP-PA-900 had a large catalytically active surface area, which was evaluated by the \(C_{dl}\) for the linearity with the area. Catalytically active surface area of RM-COP-900 was evaluated to be 4.35 cm⁻².
For the better reversible oxygen electrode [65]. The RM-COP-PA-900 exhibited a ΔE of 0.84 V (Fig. 4f), which is smaller than other temperature, even better than precious metal catalysts (shown in Table S1) and other recently reported meta-free bifunctional catalysts (shown in 4. Conclusion

In summary, we have developed a mechanical synthesis method, termed as reaction milling, for scalable synthesis of covalent organic polymer as the carbon skeleton (i.e., RM-COP) and derivative phosphorus doped material (i.e., RM-COP-PA). The space-time yield of RM-COP-PA during reaction milling process reaches 189 kg cm$^{-2}$ day$^{-1}$. The pyrosied N, P-doped COP has macroporous structure, high content of nitrogen and phosphorus, as well as possesses a large specific surface area (943 m$^2$ g$^{-1}$). Meanwhile, it shows excellent bifunctional electrocatalytic activity towards OER (onset potential = 1.50 V vs RHE, potential at 10 mA cm$^{-2}$ = 1.69 V) and OER (onset potential = 1.50 V vs RHE, potential at 10 mA cm$^{-2}$ = 1.69 V). Moreover, RM-COP-PA-900 displays better electrocatalytic activity with a limit current ($j_\text{lim}$) of 6.12 mA cm$^{-2}$ and a half-wave potential ($E_{1/2}$) of 841 mV towards OER (Fig. 4e), which is comparable to most metal-based electrocatalysts [62,63]. Meanwhile for OER the onset potential of RM-COP-PA-900 is 1.5 V and the potential corresponded to 10 mA cm$^{-2}$ is 1.69 V. The Tafel slopes showed that the catalyst under 900 °C was lower than other conditions, indicating that the catalytic reaction with faster decrease of current towards both OER and ORR process (Fig. 4c,d). This is because the higher carbonization temperature leads to higher degree of graphitization with higher conductivity for improving the catalytic activity, which, in turn, excessive temperatures can cause decomposition of the polymer along with the active sites such as nitrogen and phosphorus [64]. To further confirm the best performance of RM-COP-PA-900 as OER and ORR bifunctional catalyst, we measured the RM-COP-PA-T, Pt/C and IrO$_2$ by sweeping the RDE potential between 0.2 and 1.8 V vs RHE in a 0.1 M KOH electrolyte. The overall oxygen activity of the RM-COP-PA-T as a bifunctional catalyst can be evaluated by the potential difference (ΔE) between the $E_{1/2}$ for OER and $E_{1/2}$ for ORR (i.e., ΔE = $E_{1/2}$ − $E_{1/2}$, with the OER potential being taken at a current density of 10 mA cm$^{-2}$ while the ORR potential being taken at half-wave) with the smaller ΔE for the better reversible oxygen electrode [65]. The RM-COP-PA-900 exhibited a ΔE of 0.84 V (Fig. 4f), which is smaller than other temperature, even better than precious metal catalysts (shown in Fig. 4g) and other recently reported meta-free bifunctional catalysts (shown in Table S1).

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durability and resistance to methanol crossover effect than commercial Pt/C (20 wt%) and a four-electrode transfer pathway, suggesting the direct reduction of oxygen to water during the ORR process. Accordingly, our study provides the possibility for mechanical fabrication of bifunctional catalysts towards ORR and OER through reaction milling, which is a solvent-free, time-efficient, and scorable alternative to common synthetic routes.

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Appendix A. Supplementary data
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