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Nano-sized polydopamine-based biomimetic catalyst for the efficient synthesis of cyclic carbonates

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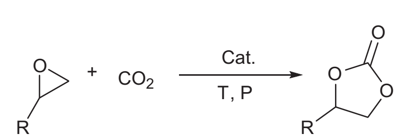
ABSTRACT

Polydopamine (PDA) is a biocompatible and biomimetic material. Herein, nano-sized PDA sphere was prepared and the combination of alkali metal halide and PDA was investigated as a catalyst for the synthesis of cyclic carbonates from epoxide and carbon dioxide. It was found that the activity of PDA could be obviously enhanced in the presence of alkali metal salts. After reaction, the catalyst and the products could be separated easily, and the catalyst was reusable. The origin of the high catalytic efficiency and the reaction mechanism were also discussed.

Recently, the increasing pressure of CO_2 released by human being promotes a high requirement of C1 conversion. As one of the most important branches of C1 chemistry, the synthesis of cyclic carbonates via the reaction between CO_2 and epoxides (Scheme 1) was investigated intensively,[1] and thus various catalysts have been developed so far including alkali metal halides based binary catalysts,[2–7] and biomass supported catalysts.[8] It is worth mentioning that the combinations of low cost, stable, and nucleophilic alkali metal halides with promoters such as β-CD,[2] cellulose,[3] formic acid,[4] lignin,[5] amino acids,[6] and H_2O[7] provide a good chance in developing cheap and environmentally benign catalysts. It is believed that continuous efforts on the development of new promoters would achieve further enhancement in efficiency under moderate conditions.

Inspired by mussels marine animals which can be glued on the rocks by their mussel adhesive proteins, most recently, Lee et al. introduced a distinctive approach to surface modification in which self-polymerization of dopamine (Fig. 1c) produced an adherent polydopamine (PDA) coating on a wide variety of materials by a simple dip-coating with dopamine solution.[9] The formed surface modification method has been explored for many applications, including improving the hemocompatibility of biomaterials and tuning the cell behaviors on their surfaces,[10,11] Li-ion batteries,[12] enzyme immobilization,[13] controlled drug release, and water treatment.[14,15] Thus, it becomes a popular method to confer multi-functionality to solid–liquid interfaces through the formed biocompatible PDA thin films.[9] Moreover, PDA could be considered as a good promoter for the synthesis of cyclic carbonates because of abundant hydroxyl groups and active N (—NH, —N=) in the structure (Fig. 1b).[4,7]

Development of cheap, efficient, and environmentally benign catalysts for the synthesis of cyclic carbonates under solvent-free conditions is still an attractive topic. Encouraged by the advantageous properties of PDA, herein, we conducted the reactions in the presence of potassium halide and PDA under solvent-free conditions for the first time, and found that the catalyst showed excellent synergetic effect on the reactions, by which high yields could be obtained for mono- and di-substituted epoxides. We believe that this efficient, stable, and ecologically safe route to synthesize cyclic carbonates has great potential in industrial application.



Scheme 1. Cyclic carbonates synthesis.

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The PDA was synthesized according to the method described in Figure 1a.[16] The corresponding results were list as follows. From Figure 2, it can be seen that the size of nano-PDA could be varied from 180 to 630 nm by controlling the dropping rate of ammonia to dopamine. The Fourier transform infrared (FTIR) spectrum of PDA in Figure 3a showed the characteristic spectral peaks of several functional groups, such as N—H, —OH, C—O, C=N, and C—N. XPS results in Figure 3b–d showed that groups such as C—N, C=N, C—O, and N—H could be found in the structure of the corresponding PDA nano-particles. The above results confirmed the structure of synthesized PDA material.

After the structure characterization, the activity of different PDA based catalysts was tested using the reaction of propylene oxide (PO) and CO_2, and the results are summarized in Table 1. PDA alone showed a little activity for this reaction, and almost no product was detected (entry 1). When using KI alone, the activity is still low (entry 2). It is surprising that the presence of alkali metal halides could result in an obvious increase in the activity of PDA (entries 3–5), and a highest PC yield of 72% as well as 99% selectivity could be realized with KI/PDA (entry 5). Furthermore, the effects of halide anion and alkali metal cation on the reaction in the presence of PDA were tested. It was found that the catalytic activity improved with the increase in leaving ability of halide anion and alkali metal cation (entries 3–8). For example, with the leaving ability increasing from Cl^-, Br^- to I^-, the corresponding activity order of anion is $Cl^- < Br^- < I^-$ (entries 3–8). Also the activity order of cation is $Na^+ < K^+$, which is in accordance with their leaving abilities (entries 3–8) (see SI, Table S1). Therefore, it can be deduced that the leaving ability is dominant for the activity. In addition, the performance of other bases, such as Na_2CO_3, K_2CO_3, and K_3PO_4, combined with PDA is provided in Table 1, entries 11–13. The results showed that their activities are unsatisfactory. Thereafter, the influence of the molar ratio of KI to PDA on the yield of PC was also investigated (Table 1, entries 5, 9, 10) with the total catalyst amount kept constant. Maximum result was obtained at the molar ratio of KI to PDA 1:1. Based on the result, KI/PDA (1:1, molar ratio) was selected for further investigation.

Thereafter, the effect of various conditions on the reaction for the synthesis of PC was carried out using KI/PDA as the catalyst. As can be seen in Table 2, the reaction temperature has an obvious

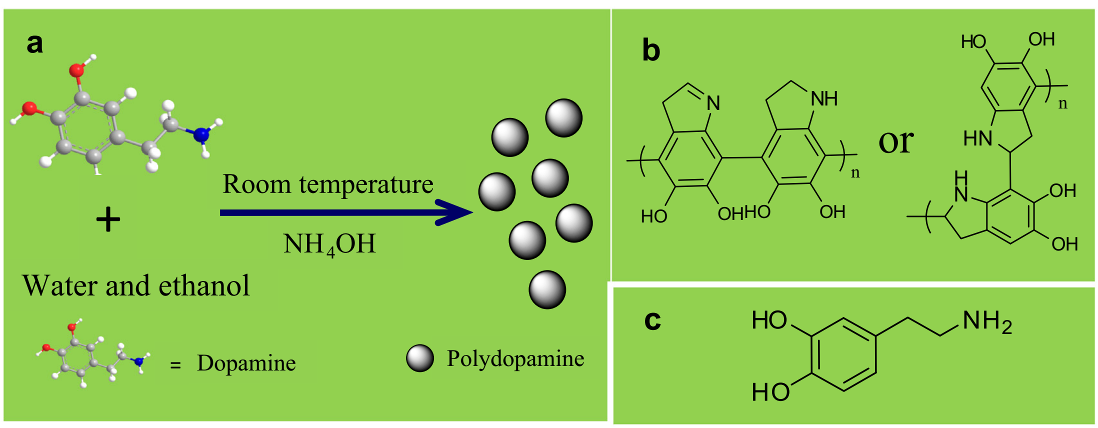

Figure 1. (a) Schematic illustration of the synthesis of PDA. (b) The suggested structure of PDA. (c) The chemical structure of dopamine.

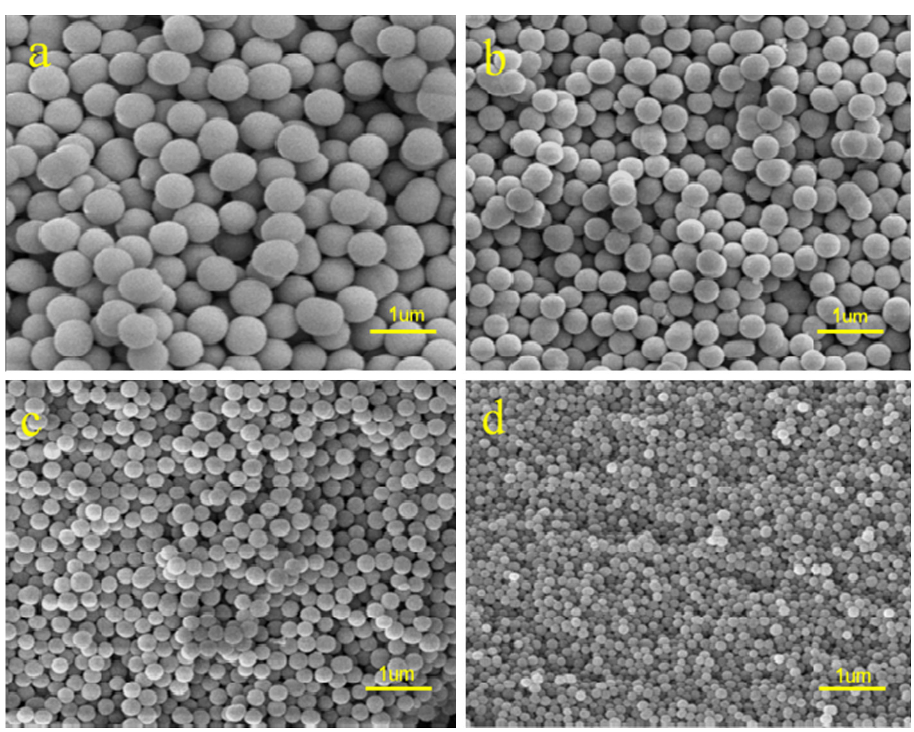

Figure 2. SEM images of PDA with different diameters (from a to d: 630, 450, 320, and 180 nm).