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ARTICLE

Naturally occurring gallic acid derived multifunctional porous polymer for highly efficient CO_2 conversion and I_2 capture

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Assembly of naturally occurring building blocks into functional materials is of great importance. Herein, we utilized plant-derived polyphenols as the building blocks to prepare porous organic polymer (POP) with multifunctional sites, and a typical POP (denoted as GA-azo-POP) could be achieved from gallic acid through an azo-coupling strategy. As a superior support, GA-azo-POP supported Ag nanoparticles could efficiently catalyze the carboxylative cyclization of propargyl alcohols with CO_2 with a very low usage of Ag (0.14 mol%). Meanwhile, GA-azo-POP showed a high capacity for I_2 adsorption (up to 287 mg/g), which was higher than that of reported solid materials under the similar I_2 concentration. More interesting, after adsorbing I_2, GA-azo-POP could efficiently catalyze the formation of cyclic carbonates from CO_2. The excellent performance of GA-azo-POP resulted from the co-existence of aromatic, azo, and phenolic OH functional groups and its porous structure.

Introduction

With the depletion of fossil resources, increasing attention has been paid to efficient utilization of naturally occurring or biomass-derived compounds.[1-7] In this regard, assembly of naturally occurring compounds for functional materials has been recognized as a highly attractive strategy.[8-11] Among various natural compounds, polyphenols, widely existing in plant tissues, have gained many applications in pharmaceutical and food industries.[12,13] Especially, functional coating and capsule materials have been successful synthesized on the basis of metal chelation feature of these polyphenols.[14-17] However, making full use of these polyphenols to prepare functional materials is still in its early stage. Novel routes for designing functional materials by using polyphenols in plants are highly desired.

Porous organic polymers (POPs) have received considerable interest due to their distinctive properties. A salient feature of POPs is that multiple functionalities can be integrated by employing different functional monomers, resulting in the wide applications of POPs in various areas.[18-23] In this respect, azo-bridged POP (azo-POP) is one of the most promising POPs. As a general route, azo-POPs can be synthesized by azo-coupling between aromatic diazonium salts and phenols.[24] The azo-POPs obtained through this route contain azo and phenolic -OH groups simultaneously, resulting in potential applications especially in catalysis and adsorption. Of interest to us is that the phenols used for the synthesis of azo-POPs can be replaced by the renewable polyphenols in plants, which could decrease the reliance of fossil-based chemicals. More importantly, the structural diversity of polyphenols in plants (Scheme S1) provides a range of possibilities for preparing various POPs with different properties.

Herein, we described for the first time the synthesis of a biomass-based POP (denoted as GA-azo-POP hereafter) using a renewable polyphenol, gallic acid, which can be obtained from tannic acid (a specific form of tannin from Chinese gall) *via* hydrolysis,[25-27] as the building block through a simple azo-coupling reaction. Due to the co-existence of azo, aromatic and phenolic -OH groups, the obtained GA-azo-POP could be used as a multifunctional material to support Ag nanoparticles for efficient CO_2 fixation, and also as an efficient solid adsorbent for I_2 capture with a very high capacity of 287 mg/g. Moreover, after adsorbing I_2, the GA-azo-POP could also be used as an efficient catalyst for cycloaddition of CO_2 to epoxides with no additional cocatalyst.

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Experimental

Synthesis of GA-azo-POP

The synthesis of GA-azo-POP was carried out in two steps. Firstly, 1,3-bis(4-aminophenoxy)benzene (6 mmol) was loaded in a 500 mL flat-bottomed flask charged with 200 mL of deionized water and 3 mL of concentrated hydrochloric acid. After stirring under ice-water bath for 15 min, the mixture was added with 30 mL of aqueous solution of sodium nitrite (12 mmol) and stirred for 25 min to make amino groups be completely converted to diazonium salts. Subsequently, the mixture was neutralized with saturated solution of Na_2CO_3, and then 30 mL of aqueous solution of galic acid (5 mmol) and Na_2CO_3 (20 mmol) was added into the mixture dropwisely in an ice-bath. After 12 h, solid sample was separated from the reaction solution by filtration and washed by the solvents several times in the order: water, methanol, THF, methanol, water and then Soxhlet extracted with methanol overnight to remove any unreacted monomers. Followed by freeze drying, the polymer sample was obtained in a high yield of 82%. Elemental analysis data: C 67.11%, H 4.09%, and N 5.49%. Other azo-POPs were prepared as the same way by the reaction of other polyphenols with different arylamines.

Synthesis of Ag/GA-azo-POP

500 mg GA-azo-POP was dispersed in 100 ml deionized water under continuous stirring firstly, and then 10 mg silver nitrate was dissolved in 10 ml deionized water. The aqueous solution of silver nitrate was added into the mixture slowly with intense stirring. The mixture was stirred for another 5 hours. The Ag nanoparticles could be uniformly dispersed on the GA-azo-POP due to the reduction effect of the phenolic -OH groups. The Ag loaded GA-azo-POP was then collected by filtration, washed by deionized water several times and dried under vacuum (60 ^oC, 24 h).

Typical procedures for the synthesis of α-alkylidene cyclic carbonates from propargyl alcohols and CO_2

In a typical experiment, propargyl alcohols (1 mmol), DBU (1 mmol), 20 mg Ag/GA-azo-POP and THF (2 mL) were charged into a stainless reactor with a Teflon tube (22 ml inner volume) equipped with a magnetic stirrer. After sealing, CO_2 was charged into the reactor until the desired pressure was reached. Then, the reactor was put into a constant temperature air bath at room temperature, and the stirrer was started. After a certain reaction time, the reactor was placed into ice water and CO_2 was released slowly passing through a cold trap containing the corresponding solvent to absorb the trace amounts of reactant and product entrained by CO_2. After depressurization, the solvent in the cold trap and the internal standard 1,3,5-trioxane were added into the reactor. The reaction mixture was analyzed quantitatively by Bruker Avance III HD 400 MHz NMR spectrometer. To obtain the isolated yields of some typical α-alkylidene cyclic carbonates, the reaction mixture was concentrated and purified by column chromatography (silica gel with petroleum ether/EtOAc = 20:1). Meanwhile, the pure product was characterized by ^1H NMR and ^{13}C NMR (Data in supporting information).

Reusability of Ag/GA-azo-POP

To examine the reusability of Ag/GA-azo-POP, the catalyst was recovered by centrifugation and washed with ethyl ether (5 × 10 mL). After drying under vacuum at 80 ^oC for 12 h, the recovered catalyst was reused for the next cycle.

Typical procedures for the synthesis of cyclic carbonates from various epoxides and CO_2

In a typical experiment, desired epoxide (10 mmol) and 50 mg I_2/GA-azo-POP were charged into a stainless reactor with a Teflon tube (22 ml inner volume) equipped with a magnetic stirrer. After sealing, CO_2 was charged into the reactor until the desired pressure was reached. Then, the reactor was put into a constant temperature air bath at desired temperature, and the stirrer was started. After a certain reaction time, the reactor was placed into ice water and CO_2 was released slowly passing through a cold trap containing ethanol to absorb the trace amounts of reactant and product entrained by CO_2. After depressurization, ethanol in the cold trap and internal standard n-butanol were added into the reactor. The reaction mixture was then analyzed quantitatively by GC (Agilent 6820) equipped with a flame-ionized detector.

Results and discussion

Synthesis and characterization of GA-azo-POP

The GA-azo-POP was synthesized through a catalyst-free diazo-coupling reaction between biomass-derived gallic acid and 1,3-bis(4-aminophenoxy)benzene under alkaline aqueous conditions (Scheme 1), and detail information was described in the Experimental Section. Fourier transform infrared (FT-IR) spectroscopy (Fig. S1) showed two bands around 1200 and 1400 cm^{-1}, which were the characteristic symmetric and asymmetric vibrations of the azo group,[24,28] suggesting the formation of -N=N- functionality in the as-prepared GA-azo-POP.[29] The solid UV-vis adsorption of GA-azo-POP showed strong optical adsorption from 200 to 800 nm (Fig. S2), further verifying the formation of -N=N- functionality.[24,30] N_2 adsorption-desorption isotherm showed that the GA-azo-POP was a porous material with a broad mesopore-size distribution as determined by the Barrett-Joyner-Halenda (BJH) method (Fig. 1A), which showed the same tendency with some POP materials,[24] and the mesopores probably originated from the hydrogen bonding interaction between the gallic acid and water, and water acted as a soft template. Meanwhile, Brunauer-Emmett-Teller (BET) surface area and pore volume were 143 m^2/g and 0.61 cm^3/g, respectively, and the relative low surface area may be caused by the geometry structure of the gallic acid and the 1,3-bis(4-aminophenoxy)benzene.[24] XRD pattern indicated that the GA-azo-POP had low crystallinity (Fig. 1B), and the broad peak at $2\theta = {\sim}20^o$ suggested that the GA-azo-POP was a layer material to some extent, and the interlayer distance was 4.43Å calculated by the Bragg equation. Furthermore, SEM and TEM images also demonstrated that the GA-azo-POP was porous (Fig. 1C, D and Fig. S3), which agreed

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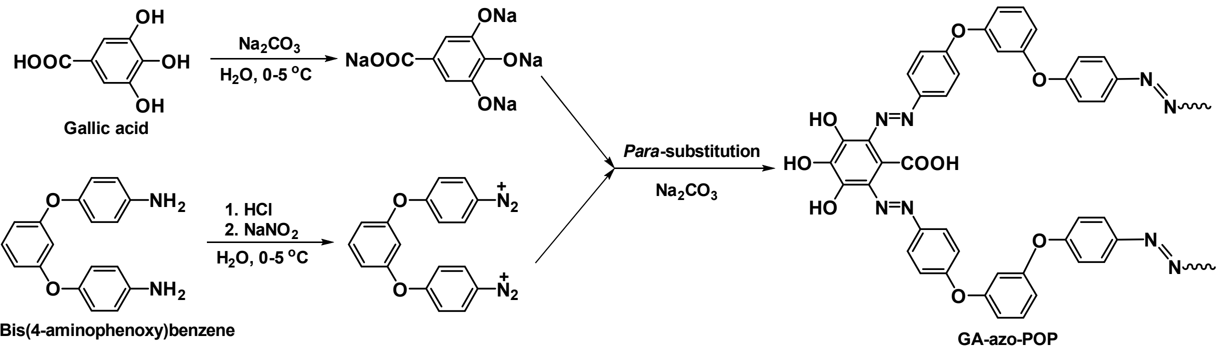
with the results from N_2 sorption and XRD measurements. Additionally, the generated GA-azo-POP was found to be insoluble in water or common organic solvents (DMF, THF, DMSO, Fig. S4), indicating its highly stable and interwoven structure. The thermogravimetry analysis further confirmed the stability of GA-azo-POP (Fig. S5). The prepared GA-azo-POP may have wide-ranging applications in different fields due to the existence of multifunctional groups and its stable property.

Notably, other azo-POPs could also be successful synthesized from the reaction of gallic acid with 4,4'-diamonodiphenyl sulfone, or the reaction of tannic acid (another common polyphenols in plants, Scheme S1) with 4,4'-diamonodiphenyl sulfone or 1,3-bis(4-aminophenoxy)benzene (Fig. S6), indicating that this method was highly flexible and applicable to prepare a variety of azo-POPs by simply adjusting the biomass-derived polyphenols and arylamines.



Scheme 1. Synthetic process of GA-azo-POP through diazo-coupling reaction between gallic acid and 1,3-bis(4-aminophenoxy)benzene.

Carboxylative cyclization of CO_2 and propargyl alcohols over Ag/GA-azo-POP

The carboxylative cyclization of propargyl alcohols with CO_2 is an attractive reaction for CO_2 transformation to synthesize α-alkylidene cyclic carbonates, which are versatile intermediates in organic synthesis.[31,32] Although some homogeneous catalysts showed relative activity for the cyclization of propargyl alcohols with CO_2,[33-36] heterogeneous catalysts are more attractive in separation and recyclability. So far, only several heterogeneous catalysts have been developed for this important transformation, and these catalytic systems generally suffered from low efficiency, high CO_2 pressure, or high loading of transition metals (up to 10 mol%).[37,38] Therefore, it is highly desired to design efficient heterogeneous catalysts for the reaction between CO_2 and propargyl alcohols. It has been reported that metal nanoparticles supported on porous materials show good activity on CO_2 fixation reactions.[39,40] Considering the advantage of the supported metal nanoparticles and the properties of the synthesized GA-azo-POP, *i.e.*, the CO_2-philic property of azo groups and the stabilization ability of phenolic -OH groups on metal nanoparticles,[41,42] the prepared GA-azo-POP showed great potential to be used as a multifunctional porous material to design supported catalysts for the above-mentioned CO_2 transformation. Herein, we prepared GA-azo-POP supported Ag nanoparticles (denoted as Ag/GA-azo-POP) for the reaction of propargyl alcohols with CO_2 by treating GA-azo-POP in the aqueous solution of silver nitrate (detail process shown in Supporting Information). The Ag nanoparticles could be highly dispersed on the GA-azo-POP owing to the reduction role and the stabilization effect on Ag particles of the phenolic -OH groups (Fig. 2A).[43,44] There were two peaks at 368.47 and 374.47 eV in X-ray photoelectron spectroscopy (XPS) spectrum of Ag in Ag/GA-azo-POP, which corresponded to the spin states of Ag, Ag $3d_{5/2}$ and Ag $3d_{3/2}$, respectively, confirming the formation of Ag^0 in the Ag/GA-azo-POP.[30,38] Meanwhile, The area ratio of the two spin states (Ag $3d_{5/2}$/Ag $3d_{3/2}$) was about 3:2, which was consistent with the theoretical value.[45] The average diameter of these Ag particles centered around 1 nm (Fig. 2A) with a Ag content of 0.74 wt% determined by ICP-AES.

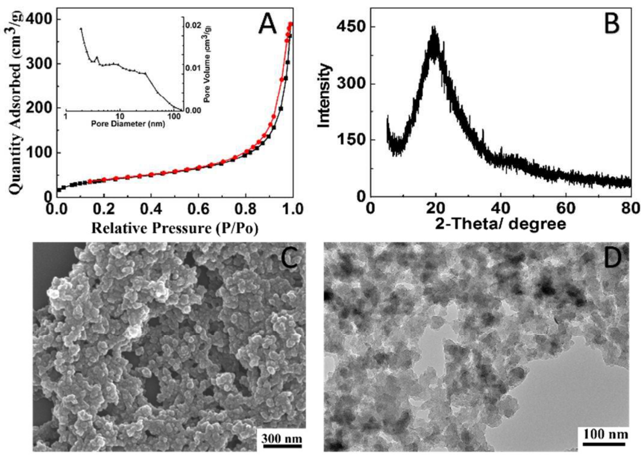


Fig. 1. Characterization of the obtained GA-azo-POP. A) N_2 adsorption-desorption isotherm (The inset is the mesopore-size distribution), B) Powder XRD pattern, C) Scanning electron microscopy (SEM) image, and D) Transmission electron microscopy (TEM) image.

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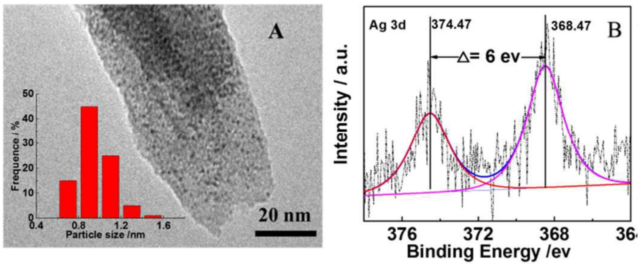
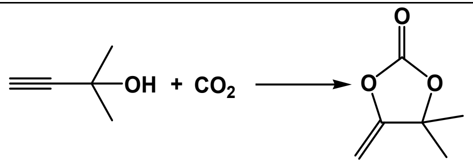


Fig. 2. A) TEM image for Ag/GA-azo-POP. The insert is the Ag particle size distribution. B) XPS spectrum of metallic Ag^0 in Ag/GA-azo-POP.

The cyclization of 2-methyl-3-butyn-2-ol with CO_2 was first investigated as a model reaction to examine the catalytic activity of the prepared Ag/GA-azo-POP (Table 1) at room temperature with a CO_2 pressure of 1 MPa. Control experiments indicated that nearly no product was detected in the presence of DBU or Ag/GA-azo-POP alone (Table 1, entries 1 and 2), indicating the synergistic effect of DBU and Ag/GA-azo-POP for the reaction. Among various bases (Table 1, entries 3-7), DBU showed the best performance (Table 1, entry 3) with a yield of 98% resulting from its stronger basicity. In the reaction cycle, DBU played the key role on the activation of the propargyl alcohol,[38,46,47] which was beneficial for the insertion of CO_2 to generate a carbonate intermediate (Scheme S2), an important step for the synthesis of α-alkylidene cyclic carbonates. Meanwhile, GA-azo-POP/DBU showed very low activity (Table 1, entry 8), suggesting the catalytic effect of Ag nanoparticles. Furthermore, kinetic experiments indicated that the reaction could be completed in 7 h (Fig. S7) in the presence of very low Ag usage (0.14 mol%) at room temperature. A high TOF value of 400 could be achieved in 0.5 h (Table 1, entry 9), and the TOF value (372) was comparable with a prolonging reaction time of 1 h (Table 1, entry 10), indicating the higher reaction rate in the initial stage. Additionally, Ag/GA-azo-POP showed higher activity than the reported heterogeneous catalysts, including (dimethylamino)-methyl-polystyrene-supported CuI (Table 1, entry 11),[37] polystyrene-supported NHC-Ag complexes (Table 1, entry 12),[48] and some supported Ag nanoparticles (Table 1, entry 13).[38] More importantly, the catalytic activity of Ag/GA-azo-POP was higher than some reported homogeneous Ag salts (Table 1, entry 14) under similar conditions.[49] These results indicated that Ag/GA-azo-POP was a superior heterogeneous catalyst for the carboxylative cyclization of propargyl alcohols with CO_2. Control experiments were performed over AgOAc with azobenzene as an additive to explore the reasons of the high performance of Ag/GA-azo-POP. It was clearly that the azobenzene could improve the activity of AgOAc (Table 1, entries 15 and 16), indicating the key role of azo groups in Ag/GA-azo-POP owing to the CO_2-philic property of the azo groups. Therefore, the high catalytic activity of Ag/GA-azo-POP may result from the porous structure with highly dispersed Ag nanoparticles as well as the promotion effect of azo groups.

Table 1. Carboxylative cyclization of 2-methyl-3-butyn-2-ol with CO_2.[a]



Entry	Catalyst	Base	Time/h	Yield (%)[b]	TOF (h^{-1})[c]
1	Ag/GA-azo-POP	--	7	<1	--
2	--	DBU	7	<1	--
3	Ag/GA-azo-POP	DBU	7	98	100
4	Ag/GA-azo-POP	Cs_2CO_3	7	2	--
5	Ag/GA-azo-POP	DABCO	7	0	--
6	Ag/GA-azo-POP	DMAP	7	2	--
7	Ag/GA-azo-POP	NMP	7	0	--
8	GA-azo-POP	DBU	7	<1	--
9	Ag/GA-azo-POP	DBU	0.5	28	400
10	Ag/GA-azo-POP	DBU	1	52	371
11[d]	DMAM-PS-CuI	--	24	99	0.52
12[e]	PS-NHC-Ag	--	24	96	1
13[f]	AgNPs/SMR	DBU	10	91	0.91
14[g]	AgOAc	DBU	5	85	1.7
15[h]	AgOAc	DBU	1	59	30
16[i]	AgOAc/Azobenzene	DBU	1	94	47

[a] Reaction conditions: substrate, 1 mmol; catalyst, 20 mg; base, 1 mmol; THF, 2 mL; CO_2 pressure, 1 MPa; r.t. [b] The yields were determined by ^1H NMR ($CDCl_3$, 400 MHz) using 1,3,5-trioxacyclohexane as an internal standard. [c] Turnover number (TON) = mol of product per mole of Ag; TOF = TON h^{-1}. [d] Data from Ref. 30. [e] Data from Ref. 34. [f] Data from Ref. 31. [g] Data from Ref. 35. [h] 2 mol% Ag. [i] 2 mol% Ag, 10 mol% azobenzene.

To verify the adaptability of Ag/GA-azo-POP, other propargyl alcohols with typical structures were also examined (Table 2). Ag/GA-azo-POP could also efficiently catalyze the cyclization of CO_2 with all the used terminal propargylic alcohols with both alkyl (Table 2, entries 1-5) and aryl substitutes (Table 2, entry 6) at the propargylic position, further proving the high catalytic activity of Ag/GA-azo-POP. Moreover, the as-prepared Ag/GA-azo-POP showed no obvious decrease in activity for the cyclization of CO_2 with 2-methyl-3-butyn-2-ol after 5 cycles (Fig. S8), and TEM image of the recovered Ag/GA-azo-POP showed no aggregation after five times reuse (Fig. S9), indicating that Ag/GA-azo-POP had good recyclability and stability. Additionally, the heterogeneous nature of Ag/GA-azo-POP for cyclization of 2-methyl-3-butyn-2-ol with CO_2 was evaluated by removing it after the reaction was performed for 2 h, and then the reaction continued to be carried out for another 7 h. No further reaction occurred (Fig. S7), indicating the heterogeneous nature of the Ag/GA-azo-POP. Meanwhile, no Ag was detected in the reaction solutions by ICP-AES method, verifying the negligible leaching of Ag. The results above indicated that the obtained GA-azo-POP could be

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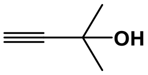
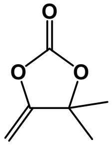
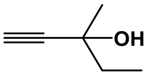
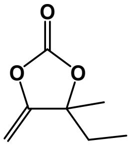
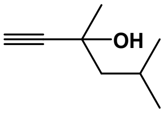
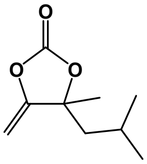
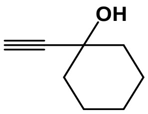
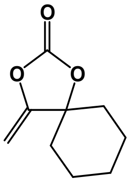
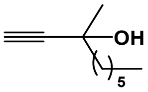
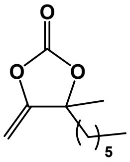
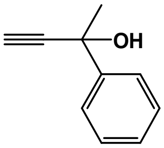
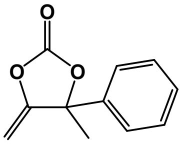
used as a superior material for CO_2 fixation.

Table 2. Cyclization of various propargyl alcohols with CO_2 over Ag/GA-azo-POP.[a]

Entry	Substrate	Product	Time (h)	Yield (%)[b]
1			8	>99 (94)[c]
2			12	>99(93)[c]
3			12	>99(95)[c]
4			12	>99(94)[c]
5			12	96(92)[c]
6			36	92(87)[c]

[a] Reaction conditions: substrate, 1 mmol; Ag/GA-azo-POP, 20 mg; DBU, 1 mmol; THF, 2 mL; CO_2 pressure, 1 MPa; r.t. [b] The yields were determined by ^1H NMR ($CDCl_3$, 400 MHz) using 1,3,5-trioxacyclohexane as an internal standard. [c] Values in parentheses were isolated yields.

I_2 capture by GA-azo-POP

Except for the utilization of GA-azo-POP in CO_2 fixation, considering that GA-azo-POP possesses plenty of aromatic, azo, and phenolic -OH groups, we attempted to use the GA-azo-POP as a solid adsorbent for radiological I_2 capture, which is an unavoidable environmental issue associated with nuclear energy. The I_2 capture ability of GA-azo-POP was examined in the cyclohexane solution of I_2 (2.07 mg/ml) at room temperature, and UV-vis spectroscopy was used to monitor the I_2 capture process by GA-azo-POP (Fig. 3A). The I_2 adsorption capacity of GA-azo-POP increased quickly during the first 24 h, and then the adsorption rate decreased until the equilibrium was reached (Fig. 3A). The I_2 capture capacity of GA-azo-POP calculated based on UV-vis spectroscopy (Fig. S10) could be reached up to 287 mg/g, which was higher than that of the reported solid adsorbents (Table S1) under similar I_2 concentration. XPS spectrum of the GA-azo-POP after soaking in I_2 cyclohexane solution indicated that the I_2 adsorbed by GA-azo-POP existed in the form of I_2 and I_3^- (Fig. 3B).[50] This examination suggested that the adsorbed I_2 on the GA-azo-POP could be readily transformed into various polyiodide states, especially I_3^-, which was generated by the formation of charge-transfer complexes (Scheme S3) between the absorbed I_2 and the azo groups (good electron donors) on the GA-azo-POP via charge-transfer interaction.[28,51-53] The change of I_2 valence state suggested the chemisorption taking place together with the physical absorption, such as the hydrogen-halogen bond between I_2 and phenolic -OH,[50,52,53] and thus a high amount of I_2 uptake (up to 287 mg/g) was achieved.

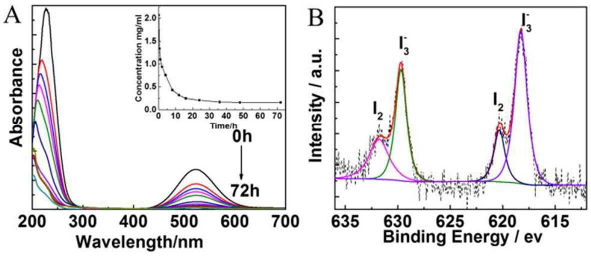


Fig. 3. A) Time-dependent UV-vis absorption spectra of I_2 uptake. The insert was the related I_2 concentration calculated by UV-vis absorbance at 525 nm. Adsorption conditions: GA-azo-POP, 10 mg; cyclohexane solution of I_2 (2.07 mg/mL), 1.5 mL; room temperature. B) XPS spectrum of I_2 adsorbed on GA-azo-POP.

Cycloaddition of CO_2 with epoxides over I_2/GA-azo-POP

Generally, efficient utilization of the captured I_2 is an interesting topic. As well-known, I^- and phenolic -OH could promote the cycloaddition of CO_2 with epoxides to produce cyclic carbonates,[54,55] which is a very important reaction for CO_2 fixation.[56-60] On the basis of the above analysis, there were many I_3^- ions formed from I_2 adsorbed on GA-azo-POP and plenty of phenolic -OH existed in GA-azo-POP. Therefore, this provided the possibility that I_2 adsorbed on GA-azo-POP (denoted as I_2/GA-azo-POP) could catalyze the cycloaddition of CO_2 with epoxides. Herein, we attempted to apply I_2/GA-azo-POP as a metal-free heterogeneous catalyst for this transformation (Table 3). To our delight, various epoxides could be converted with CO_2 into cyclic carbonates with high yields, suggesting I_2/GA-azo-POP was suitable for cycloaddition of various epoxides with CO_2 into cyclic carbonates, and this was a new application for the adsorbed I_2. In addition, the GA-azo-POP without adsorbing I_2 could not catalyze the cycloaddition, indicating the catalytic role of the adsorbed I_2 species. In the catalytic cycle, the epoxide was firstly activated by the hydrogen bonding formed between the oxygen atom in the epoxy ring and the phenolic -OH on GA-azo-POP, and then the I_x^- anion generated from the absorbed I_2 attacked the less

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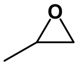
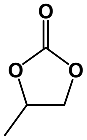
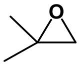
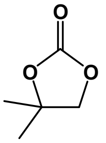
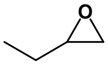
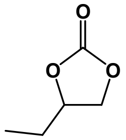
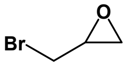
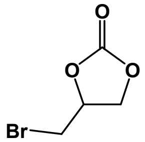
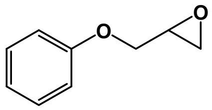
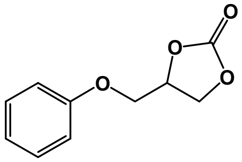
hindered carbon atom of the activated ring, followed by ring opening reaction step. Subsequently, CO_2 was reacted with the opened epoxy ring to form an alkylcarbonate anion, which was stablilized *via* the hydrogen bonding. Finally, the intramolecular cyclic step was happened to generate the corresponding cyclic carbonates (Scheme S3).

Table 3. Cycloaddition of various epoxides with CO_2 over I_2/GA-azo-POP.[a]

Entry	Epoxide	Product	Yield (%)[b]
1			97
2			94
3			96
4			97
5			>99

[a]Reaction conditions: substrate, 10 mmol; I_2/GA-azo-POP, 50 mg; CO_2 pressure, 3 MPa; temperature, 150 °C; time, 10 h. [b]The yields were determined by GC analysis using n-butanol as the internal standard.

Conclusions

In summary, a biomass-derived multifunctional porous organic polymer (GA-azo-POP) can be synthesized using naturally occurring gallic acid. Because of the porous structure and the co-existence of several functional groups, including aromatic, azo, and phenolic -OH groups, the prepared GA-azo-POP could be used as a multifunctional material to support Ag nanoparticles (Ag/GA-azo-POP) for CO_2 fixation, and as a solid adsorbent for I_2 adsorption. The Ag/GA-azo-POP showed excellent performance for the carboxylative cyclization of propargyl alcohols to CO_2 under room temperature with very small amount of Ag (0.14 mol%). Moreover, GA-azo-POP as a solid adsorbent could adsorb I_2 with very high adsorption capacity up to 287 mg/g. Moreover, as a new application, the GA-azo-POP after adsorbing I_2 could effeciently catalyze cycloaddition of CO_2 with epoxides without any additional cocatalyst. We believe that more functional porous polymers could be prepared using naturally occurring polyphenols for different applications.

Conflicts of interest

There are no conflicts to declare.

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