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Communication

Smart synthesis of silver nanoparticles supported in porous polybenzoxazine nanocomposites *via* a main-chain type benzoxazine resin

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ABSTRACT

In this article, novel silver nanoparticles immobilized on macroporous polybenzoxazine nanocomposites (Ag-poly(BA-ddm)^x_{main}) were prepared as catalysts for catalytic reduction reaction. For this purpose, a main-chain type benzoxazine was cured in dimethyl sulfoxide by thermally activated ring-opening polymerization at 180 °C for 2 days followed by the reduction of silver nitrate in homogeneous polybenzoxazine solution. The porous structure of the resin was confirmed by scanning electron microscope (SEM) analysis and N₂ adsorption/desorption studies. Besides, transmission electron microscopy images showed that spherical particles (around 3–10 nm in sized) are dispersed in Ag-poly (BA-ddm)^x_{main} network. The catalytic activity of the as-prepared nanocomposite has been investigated by photometrically monitoring the reduction of methylene blue by an excess of NaBH₄. The kinetic data of the reduction reaction was explained by the assumption of a *pseudo*-first-order reaction with regard to methylene blue (MB). As evidence by Ultraviolet (UV) spectral analysis, the Ag-poly(BA-ddm)^x_{main} catalyst possesses excellent catalytic reduction of MB, and no deactivation or poisoning of the catalyst was observed. The results demonstrate that porous polybenzoxazine supported silver nanoparticles can be applied as reusable catalysts with satisfied catalytic activity.

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Noble metal nanoparticles (such as Pt, Ag, Au and Pd) have been extensively studied because of their potential applications in the fields of catalysis, fuel cells, sensors, optical devices and biomedicine [1–6]. In General, nanoparticles in nanoscales are typically able to perform highly active centers that are closely resulting their superior catalytic activities [7,8]. However, the high surface energy of nanoparticle bring the problem of aggregation, remarkably decreasing their surface area [9]. One impactful method for developing catalysts with highly dispersion at certain small particle size is to immobilize metal nanoparticles on solid support with high surface area, high chemical stability, good thermal stability, as well as preventing the aggregation of nanoparticles and indefinitely maintaining the catalytic performances [10]. In spite of the enhanced useful performances at a nanoscale level, when nanoparticles are immobilized onto a support matrix, they

possess unique excellent physical properties originated from quantum size effects [11].

Various materials have been demonstrated as suitable candidates for noble metal catalyst supports, such as mesoporous silica, carbon-based materials (graphene, reduced graphene oxide, carbon nanotubes, carbon nanofibers and mesoporous carbon), polymers, metal oxides, etc. [12–18]. Nanocomposites with metal nanoparticles embedded in a polymeric network are highly promising for a number of industrial applications because of the synergistic properties of their constituents. The synthesis strategy of metal nanoparticles is generally carried out by the reduction reaction from metal ions, which is stabilized in polymeric network through complexation. In this way the polymer supports efficiently prevent the aggregation of nanoparticles and serve as carriers. Ordinarily, polymers bear nitrogen-, oxygen- and sulfur-containing functionalities as complexing sites for metal ions are effective for nanoparticle supports [19].

Polybenzoxazine is a recent developed high-performance material that has been attracting substantial attention due to its outstanding properties, such as high thermal stability, high modulus, resistance against flame, chemical resistance, low water

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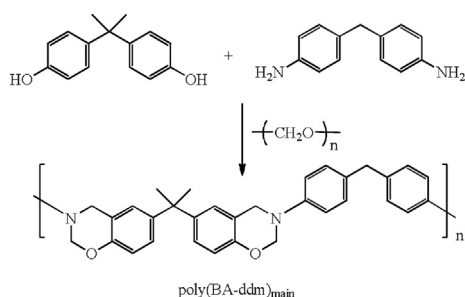
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absorption and very limited volumetric change upon thermally activated polymerization [20–27]. Polybenzoxazines are in general produced via cationic ring-opening polymerization by heating benzoxazine monomers or other polymeric precursors containing benzoxazine moieties with or without added initiators and/or catalysts. There has been much work on designing new benzoxazine structures to further explore their potential applications by considering advantages of molecular design flexibility. The most features of benzoxazine resins are mainly due to the Mannich-base bridges ($-\text{CH}_2-\text{N}(\text{R})-\text{CH}_2-$) and the inter- or intra-molecular hydrogen-bonds among nitrogen and phenolic OH groups. The existence of phenolic O and N atoms in polybenzoxazine networks leads the possibility to bind mercury salts [28]. From this point of view, polybenzoxazine, which contains both N and O atoms, is a potential alternative for metal nanocatalyst supports though the coordination between metal ions and O and N atoms.

In this article, we report a simple strategy to prepare novel nanocomposites ($\text{Ag-poly}(\text{BA-ddm})_{\text{main}}$) with highly dispersed silver nanoparticles supported in porous polybenzoxazine. The surface area of polybenzoxazine has been obviously increased via performing the thermally activated polymerization in a solvent with high temperature of boiling point. Furthermore, the reduction of methylene blue (MB) with NaBH_4 was studied to evaluate the catalytic activity of $\text{Ag-poly}(\text{BA-ddm})_{\text{main}}$.

Initially, the main-chain type benzoxazine was synthesized by reacting bisphenol-A, 4,4'-diaminodipheylmethane (ddm) and paraformaldehyde as shown in Scheme 1. The product was abbreviated to be $\text{poly}(\text{BA-ddm})_{\text{main}}$ from the abbreviations of the starting materials. The molecular weight of $\text{poly}(\text{BA-ddm})_{\text{main}}$ was evaluated by GPC. $\text{poly}(\text{BA-ddm})_{\text{main}}$ shows the number average molecular weight (M_n) of 8604 with a high polydispersity index (PDI) equals to 3.36. The GPC results indicate that the molecular weight of the main-chain benzoxazine directly synthesized from Mannich condensation is not so high. However, the low molecular weight as well as the high PDI of this polybenzoxazine precursor could result generating more phenolic hydroxyl groups in the chain-end functionalities, which has been determined as a powerful catalyst for decreasing the ring-opening temperature of benzoxazine ring [29]. The lower polymerization temperature is highly desired in this study since the polymerization process along with the porous generation was conducted in DMSO.

The structures of $\text{poly}(\text{BA-ddm})_{\text{main}}$ were examined by ^1H NMR and FT-IR spectroscopy. Fig. S1 in Supporting information shows the ^1H NMR spectrum of $\text{poly}(\text{BA-ddm})_{\text{main}}$. The characteristic chemical resonances for methylenes of $\text{O}-\text{CH}_2-\text{N}-$ and $\text{Ar}-\text{CH}_2-\text{N}$ in oxazine ring are observed at 5.28 and 4.52 ppm, respectively. The methyl proton from bisphenol-A and the methylene proton of ddm are located at 1.56 and 3.78 ppm, respectively. FT-IR was also used to further confirm the structure of $\text{poly}(\text{BA-ddm})_{\text{main}}$. In Fig. S2 in Supporting information, the presence of the benzoxazine ring aromatic ether in $\text{poly}(\text{BA-ddm})_{\text{main}}$ is indicated by the band at 1229 cm^{-1} , which is assigned to the C–O–C asymmetric stretching



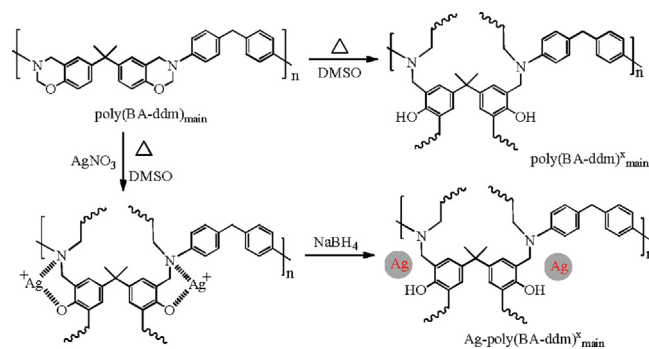
Scheme 1. Synthesis of the main-chain type benzoxazine.

[30,31]. Besides, the characteristic benzoxazine related mode is centered at 932 cm^{-1} .

In the subsequent step, $\text{Ag-poly}(\text{BA-ddm})_{\text{main}}^x$ was prepared by polymerization of $\text{poly}(\text{BA-ddm})_{\text{main}}$ with AgNO_3 in DMSO at 180°C for two days, later by reduction of the silver ion via NaBH_4 to form the silver nanoparticles immobilized on porous polybenzoxazine nanocomposites (Scheme 2). During the polymerization, both O and N atoms from the free phenolic hydroxyl group and an adjacent tertiary amino group in polybenzoxazine result a coordination system with silver ion. In addition, the polymerization of the pristine $\text{poly}(\text{BA-ddm})_{\text{main}}$ was also performed to form a porous resin ($\text{poly}(\text{BA-ddm})_{\text{main}}^x$) for comparison. Fig. S2 also depicts some of highlighted infrared bands, which can be used to verify the ring-opening reaction of benzoxazine ring. The characteristic absorption bands at 1229 cm^{-1} (C–O–C asymmetric stretching modes) and 932 cm^{-1} (benzoxazine related mode) disappear in both $\text{poly}(\text{BA-ddm})_{\text{main}}^x$ and $\text{Ag-poly}(\text{BA-ddm})_{\text{main}}^x$, suggesting the completion of ring-opening polymerization of oxazine after heating in DMSO.

The completion of polymerization of $\text{poly}(\text{BA-ddm})_{\text{main}}$ was also monitored by DSC. It is known that benzoxazine resins can undergo a thermally activated ring-opening polymerization, which is able to be detected by DSC due to the ring-opening of oxazine ring is an exothermic behavior. Fig. 1 shows the thermographs of $\text{poly}(\text{BA-ddm})_{\text{main}}$, $\text{poly}(\text{BA-ddm})_{\text{main}}^x$ and $\text{Ag-poly}(\text{BA-ddm})_{\text{main}}^x$. Different from the traditional benzoxazine monomers, the DSC thermogram of $\text{poly}(\text{BA-ddm})_{\text{main}}$ exhibits multiple thermal events in the form of several exotherms. These three exothermic peaks were observed with the maxima around at 110, 163 and 247°C , attributing to the reaction between the chain-ends and the end groups along with the ring-opening polymerization at higher temperature [32,33]. The second exothermic peak, which is caused by the ring-opening polymerization of oxazine ring promoted by the phenolic chain end groups, clearly suggesting the possibility of the polymerization of $\text{poly}(\text{BA-ddm})_{\text{main}}$ in DMSO at a lower temperature. Furthermore, both $\text{poly}(\text{BA-ddm})_{\text{main}}^x$ and $\text{Ag-poly}(\text{BA-ddm})_{\text{main}}^x$ did not show any exothermic peak, indicating the completion the consumption of benzoxazine rings after the designed thermal treating process.

In general, benzoxazine resin can undergo a thermally activated ring-opening polymerization without any solvent to form polybenzoxazine. However, the specific surface area of the polybenzoxazine generated from solvent free polymerization is generally not more than $1\text{ m}^2/\text{g}$ [28]. Polybenzoxazines with such low porosity is unfit to applied as metal nanocatalyst supports. In this study, $\text{poly}(\text{BA-ddm})_{\text{main}}$ was thermally treated via polymerization in DMSO at 180°C for two days to form porous polybenzoxazine resin. Also the Ag nanoparticles supported in porous polybenzoxazine was obtained by the reduction of silver ion from the



Scheme 2. Preparation of silver nanoparticles immobilized on porous polybenzoxazine nanocomposite.

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