Bioinspired polydopamine-layered double hydroxide nanocomposites: controlled synthesis and multifunctional performance†

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A biomimetic multifunctional nanocomposite was synthesized, in which a polydopamine (PDA) thin film was deposited on a layered double hydroxide (LDH) through an interlayer polymerization. Kinetic controlled polymerization of dopamine (DA) in a basic buffer solution under a nitrogen atmosphere provided a synthetic pathway for the nanostructured PDA/LDH composites without polymer agglomerates, allowing the crystallinity of the pristine LDH nanoparticles to be maintained. The contraction of the interlayer spacing for the [001] reflection of PDA/LDH nanocomposites demonstrated intercalation of PDA into the LDH interlayer space. The catalytic activity of the PDA/LDH nanocomposites was evaluated by observing the reduction of p-nitrophenol in the presence of NaBH₄, in which the PDA layer acts as a protection layer against surface contamination of the nanocomposites. Electrochemical capacitive performance was also observed due to the strong adhesion of PDA to the Ni foam electrode. The nanostructure of the PDA/LDH nanocomposites induced by interlayer polymerization drove the incorporative organic–inorganic functional materials with blocked surfaces and improved the electrochemical properties, providing a reliable synthetic pathway to prepare multifunctional nanohybrid materials.

Introduction

Surface functionalized materials with enhanced activity and stability have attracted significant interest in both fundamental research and applications in various fields of material science and engineering. Over the past decade, polydopamine (PDA), inspired by an adhesive foot protein of marine mussels, has generated interest in research fields such as biology,1–3 energy materials,4 and functional nanocomposite materials5–7 due to its unique physical and chemical properties which include the strong adhesion ability to various surfaces, strong absorption of light, semiconductor-like behavior, and self-polymerization. Through our recent research in opto-electronic devices, we demonstrated that the PDA has special properties of charge transfer8 and photo-switching,8 as well as semiconducting property. Several challenges at the fundamental level remain for applications in a wide range of research areas, such as understanding structure and solubility control in organic solvents. Our focus on preparation of functional PDA materials was driven by its unique set of advantageous properties which include cost-effectiveness, biocompatibility, and excellent surface functionalization.

Layered double hydroxides (LDHs), known as hydrotalcite-like materials, are a class of two-dimensional anionic clays consisting of positively-charged host layers and exchangeable anions that can incorporate or intercalate into the interlayer galleries of the LDH layer. LDHs can be used as precursors or templates for the formation of nanocatalysts,8,9 and also effective supports for the immobilization of active anionic species through anion exchange10–12 or intercalation procedures in the interlayer space,13–16 facilitating the preparation of new LDH-based functional materials with multifunctional properties. In recent years, polymer/LDH nanocomposites have attracted considerable interest in the field of nanofillers,17 or flame retardants.18 The specific architecture of the layered nanocomposites, consisting of organic and inorganic blocks, promotes a synergistic effect, producing new functional materials with enhanced chemical and physical characteristics when compared with the isolated component. There have been some reports concerning the electrochemical detection of DA using LDHs;19 however, LDH-based nanostructures related to PDA are rarely reported.20

Typically, the morphologies of conventional polymer–LDH composites prepared via the encapsulation of polymer solution into LDH nanoparticles are covered with polymer aggregates of random size. This does not yield an intercalated form between the LDH interlayers, but instead an aggregated one on the LDH
surface. The preparation of the intercalative nanocomposites with conformal surfaces is a challenging issue due to the difficulty of controlling the polymer solution preparation. Recent studies demonstrate that the PDA coating can even be applied to the surface immobilization of proteins or nucleic acids, and the functionalization of nanoparticles, indicating the possibility for use as an active material in functional nanocomposites. However, current PDA coating methods under aqueous aerobic conditions reveal some critical limitations, including the inability to effectively control the solution, the termination of dopamine polymerization, and a slow kinetic process. In addition, PDA prepared via the self-polymerization of DA produces melanin-like aggregates through rapid reaction when it is exposed to an oxygen atmosphere, thus the condition of the PDA is one of the most critical factors for novel multifunctional hybrid nanostructures.

Here we report a synthetic strategy to prepare a novel PDA/LDH nanocomposite with multifunctional characteristics. In order to obtain homogeneous, well-dispersed inorganic materials within a polymer in nanocomposites, the inorganic nanoparticles should be dispersed in a stable suspension and blended with the polymer, enabling the formation of the nanoscopically-confined nanocomposites. The coating method using N₂-saturated DA solution produced a homogeneous polymer solution that effectively intercalated into the interlayer space of the LDH nanoparticles, resulting in the preparation of multifunctional nanocomposites with surface protection ability and improved electrochemical properties.

Results and discussion

The reaction scheme in Fig. 1 shows the nanostructured PDA/LDH composites with conformal surfaces synthesized via the intercalative polymerization of DA in a metal hydroxide interlayer. PDA was used as an organic modifier, and the nitrate-form LDHs, CoAl-LDH-NO₃ and MgAl-LDH-NO₃ (denoted as CAN and MAN), were reactive precursors, which facilitated the anion exchange and allowed the formation of PDA/LDH nanocomposites. Typical polymer–LDH composites produced by mixing the LDHs with polymers in a solution or polymer melt are referred to as phase-separated microcomposites. These microcomposites are highly aggregated because the polymer is unable to intercalate between the LDH sheets which results in it being encapsulated into the LDHs. In contrast, the PDA in the present nanocomposites was formed between LDH sheets as well as outside the LDH layer, producing a well-ordered nanocomposite with alternating PDA and LDHs, leading to decreased interlayer spacing in the LDHs via the intercalation of DA. In addition, the covalent bonding of the PDA with the LDH sheets through catechol groups can produce strong adhesion since the OH groups of the catechol moiety can be modified and form a strong bidentate complex with the metal hydroxides.

The preparation of PDA/LDH nanocomposites was carried out by the addition of DA solution into LDH colloidal solutions dispersed in pH 8.5 tris(hydroxymethyl)aminomethane (THAM) buffer. The products were denoted as CAN-PD1 and MAN-PD1 for the reactions of CAN and MAN with 0.2 mL of DA solutions and as CAN-PD2 and MAN-PD2 for the reactions of CAN and MAN with 1.0 mL of DA solutions, respectively. The use of a DA solution higher than 69 mM produced PDA/LDH nanocomposites with nanosized polymer aggregates on the LDH surface. The use of a nitrogen stream was the most important factor for preparing interlayer polymerization. The present coating method using N₂-saturated DA solution produced a homogeneous polymer solution, enabling the successful preparation of nanoscopically-confined PDA/LDH composites through the effective intercalation of the homogeneous PDA into the interlayer spaces of the LDH.

The colour of the solution prepared in the air-exposed THAM buffer solution changed from colourless to light brown within several seconds when the reaction was carried out in atmosphere, indicating the formation of PDA aggregates. The type of...
The solvent used was critical; the use of DI water without THAM buffer resulted in a ragged morphology due to the partial dissolution of cobalt ion in water solvent, as shown in the SEM images of Fig. S1.† In addition, the XRD data demonstrated that the reaction of CAN-PD1 in water produced an anion exchange into carbonate LDH form, in which the basal spacing changed from nitrate to carbonate form. In contrast to this, the THAM buffer solution resulted in the nitrate form being maintained (Fig. S2†).

Fig. 2 shows photographs and SEM images of the PDA/LDH nanocomposites, showing the colours of the colloidal solution and the morphologies of the products. The reaction of PDA with the colloidal suspension of the CAN in THAM buffer under a nitrogen atmosphere produced PDA/LDH nanocomposites. The suspension colours changed from pink for the pristine LDH suspension to dark pink or brown for the nanocomposite suspension depending on the content of PDA. The suspension colours of the PDA/MAN nanocomposites changed from white for the pristine LDH suspension to yellowish brown and light brown as the PDA content increased. The nanocomposites with higher PDA content exhibited darker colours than those with lower PDA content, resulting in dark pink (CAN-PD1), dark brown (CAN-PD2), yellowish brown (MAN-PD1) and a light brown (MAN-PD2) powders. The MAN produced PDA/LDH nanocomposites regardless of PDA content, while the CAN exhibited much greater colour change due to the oxidation of cobalt.

Fig. 2 Photographs and SEM images of the PDA/LDH nanocomposites showing the colors of the colloidal suspensions in THAM buffer and the morphological features of the nanocomposites collected by centrifugation: (a) CAN, (b) CAN-PD1, (c) CAN-PD2, (d) MAN, (e) MAN-PD1 and (f) MAN-PD2.

The pristine CAN and MAN have diameters ranging from 100 to 500 nm and thicknesses of approximately 100 nm, as shown in Fig. 2a and d. Interestingly, the morphological features of the PDA/LDH nanocomposites were not changed regardless of the PDA content, indicating that the PDA was effectively adsorbed on the surface and the interlayers of the CAN and MAN nanocrystals. The nanocomposites demonstrated conformal surfaces via the intercalation of PDA into the interlayer spacing of the LDHs. The morphological changes of the nanocomposites were investigated through SEM images. The nanocomposites exhibited the same morphologies as those of the pristine CAN and MAN in terms of particle size, shape, and conformal surfaces without aggregates of PDA. The SEM images of CAN-PD2 and MAN-PD2 show PDA, five times more concentrated than what was used for CAN-PD1 and MAN-PD1, which resulted in successful thin-layer PDA coating on LDH particles which was not viable using conventional polymer-based nanocomposites with aggregates on the surface ranging in size from several nanometers to micrometers.

The intercalation of the self-polymerized PDA into LDH layers was confirmed by XRD data. Fig. 3 shows the changes in the basal spacing of the nanocomposites via the intercalation of PDA into the LDH layers while maintaining the nitrate anions in the composite structures, with a comparison to those of the pristine CAN and MAN. The CoAl-LDH-CO$_3$ resulted in 7.61 and 3.80 Å corresponding to (003) and (006) reflections, respectively, which increased to 9.28 and 4.54 Å through decarbonation and subsequent anion exchange to a nitrate form. The nanocomposites exhibited d-spacing values smaller than those of the pristine CAN due to the addition of PDA. The basal spacing of 9.28 Å for (003) reflection of CAN decreased to 9.17 Å for CAN-PD1 and 9.13 Å for CAN-PD2 depending on the PDA contents, demonstrating the structural deformation by the intercalation.
of the PDA polymer into the interlayer gallery of the LDHs. The π-stacked structure of the PDA with average interlayer spacing of approximately 3.4–3.8 Å enabled the PDA to intercalate into the empty space of the LDHs. The small peaks of the CoAl-LDH-CO$_3$ can also be observed as impurities. Similarly, the basal spacing values of the MgAl-LDH-CO$_3$ series changed from 7.56 and 3.76 Å to 9.30 and 4.55 Å by anion exchange to a nitrate form, as shown in Fig. 3f. The reaction of the MAN with the PDA polymer also led to a decrease in basal spacing values for (003) and (006) planes to 9.26 and 4.55 Å for MAN-PD1 and 9.21 and 4.54 Å for MAN-PD2. The PDA–LDH compounds exhibited shoulder peaks at approximately 8.77 and 4.24 Å, ascribed to the disordered stacking of the intercalated PDA within the LDH interlayer.

Fig. 4 shows high resolution transmission electron microscopic (HRTEM) images of the nanocomposites, demonstrating a well-defined hybrid nanostructure without nanosized PDA agglomerates. These high-resolution images showed the lattice fringes of the crystalline LDHs and the PDA layers deposited on the LDHs. The PDA was deposited on both the inside and the outside of the LDHs. Since the cobalt has greater oxidation ability than the magnesium, the CAN series showed larger PDA layer thicknesses in the range of 1–3 nm than the MAN series with layer thickness of 0.8–1.4 nm, consistent with the colour changes of the nanocomposites shown in Fig. 2. The fast Fourier transform (FFT) images of the top insets shown in Fig. 4 exhibited hexagonally arranged spots, indicative of the maintenance of the pristine LDH structure even after the intercalation of PDA. The measured lattice distances of the nanocomposites were 0.45, 0.42, 0.26, and 0.25 nm corresponded to the (006) and (012) planes of the LDH phase, which include the d values induced by intercalation of PDA. These results are consistent with the XRD analysis, demonstrating the interlayer polymerization of DA. The clarity of the hexagonal lattice spots decreased gradually as the PDA content increased. The elemental mapping data shown in Fig. S3† indicated that the PDA was well dispersed in the LDH layers.

Raman spectra shown in Fig. S4† provided evidence for the intercalation of PDA into LDH. The Raman spectra of the nanocomposites exhibited a strong band at 1065 cm$^{-1}$ that is assigned to the symmetry vibration peak of the nitrate ions. Band broadening for nitrate ions was observed in the nanocomposites, providing an additional evidence for the PDA, enhanced disorder of LDH molecules via the intercalation of as mentioned in the XRD data analysis. The nanocomposites exhibited two broad peaks in the region between 1300 and 1700 cm$^{-1}$, in which the bands centered at 1390 and 1590 cm$^{-1}$ correspond to the aromatic C=C and C–N stretching mode of the basic indole structure and also related to the vibrational modes of the carbon atoms arranged in graphitic-like domains. The small shoulder peaks at 1215 and 1510 cm$^{-1}$ correspond to phenolic C–O stretching and N–H bending, respectively.

The time-dependent catalytic activities of the PDA/LDH nanocomposites were evaluated by employing the reduction of p-nitrophenol into p-aminophenol by NaBH$_4$, and were monitored using UV/Vis spectroscopy as shown in Fig. 5. As the reduction proceeded, the 400 nm peak associated with the p-nitrophenol was reduced as a function of time while the peak at 290 nm was gradually increased, indicating the formation of the p-aminophenol ions (Fig. 5a–c). The alkaline NaBH$_4$ solution can reduce cobalt chloride, resulting in nanosized Co$_2$B nanoparticles with excellent catalytic activity. The CAN nanoparticles can also produce Co$_2$B nanoparticles via the partial dissolution of the cobalt ions in an aqueous solution. We employed the PDA as a protection material for preventing an exposure of the active cobalt sites. The UV/Vis spectra compared to p-nitrophenol demonstrated high catalytic activity in the CAN with a conversion efficiency greater than 97%, even close to the catalytic activity of the Pt nanoparticles for 6 min of reaction time, while the CAN-PD1 exhibited an 87% conversion efficiency for the same reaction time (Fig. 5d). Considering the linear relationship between $\ln(C/C_0)$ and reaction time, the CAN-PD2 exhibited the slowest reduction rate among the three catalysts, demonstrating the successful formation of a blocked surface by PDA against the reduction of cobalt ions (Fig. 5e). In contrast, the stable MgAl-LDH-PD1 and MgAl-LDH-PD2 nanocomposites did not show any catalytic activities as shown in Fig. S5.†
Cyclic voltammetry (CV) was carried out to study the electrochemical capacitive performance of the pristine CAN and PDA/LDH nanocomposites using a three electrode system and 1 M KOH aqueous solution as electrolyte. Fig. 6 shows CV curves of the nanocomposites deposited on Ni foam electrode by dip-coating for 3 min. The amounts of the nanocomposites deposited on the Ni foam electrode via dip-coating are comparable to those of CoAl-LDH-based supercapacitors with high loading amounts created using a slurry coating with binder materials or direct growth. To our surprise, the loading amounts of the nanocomposites deposited on the Ni foam electrode via rapid dip-coating increased remarkably to 150% for CAN-PD1 and 182% for CAN-PD2 when compared to that of the pristine CAN depending on the PDA content without the use of any binder materials. This confirms the strong adhesion ability of the PDA on solid substrates. The faradaic reaction of nanocomposites containing two pairs of anodic and cathodic peaks during the potential sweep was observed, and can be attributed to the reaction of $\text{Co}^{2+}/\text{Co}^{3+}$ (0.11 V) and $\text{Co}^{3+}/\text{Co}^{4+}$ (0.52 V). The integral area of the CV curve for CAN-PD2 was the largest, suggesting the highest electrochemical capacitance. The specific capacitances for the CAN-PD1 and CAN-PD2 electrodes calculated based on CV curve at a scan rate of 10 mV s$^{-1}$ were 9.13 and 12.6 F g$^{-1}$, larger than that of the pristine CAN with a value of 6.98. Interestingly, the PDA-modified electrodes maintained the pristine morphological characteristics after repeated CV cyclization processes (Fig. S6†). The modified and collapsed shapes of the nanoparticle were observed for the CAN electrode, indicating that the PDA played an important role in prohibiting the surface modification of the nanocomposites via electro-chemical reaction.

Conclusions

We have demonstrated a novel multifunctional nanocomposite of PDA/LDH through the interlayer polymerization of DA in the gallery space of the LDH nanoparticles. The homogeneous DA solution prepared under N$_2$-saturated THAM buffer and the effective penetration of the solution into the LDH interlayer were a critical factor in obtaining well-defined PDA/LDH nanocomposites without the exfoliation of the LDH layer by the intercalation of PDA. The intercalation of PDA into LDH was confirmed by the XRD data, in which the decrease and splitting of the d-spacing values for the (00l) reflections demonstrated variation in the coherent domain sizes of crystallites in the stacking and lateral direction. The homogeneous dispersion and strong adhesion ability of PDA polymer with nanocrystalline LDH played a decisive role in stabilizing and preventing the reduction of cobalt ions. The PDA/LDH nanocomposite containing the higher PDA content exhibited the best specific capacitance value and maintained structural stability without a collapse during the capacitance measurement. The synthetic advantages of PDA such as dispersion stability, spontaneous polymerization, and effective penetration into the interlayer space of the layered nanostructures are beneficial for the preparation of multifunctional hybrid nanostructures.

Experimental

Syntheses of LDH nanoparticles

The carbonate form of CoAl-LDH nanoparticles, [Co$_3$Al$_2$(OH)$_{12}$] CO$_3$·nH$_2$O, denoted as CoAl-LDH-CO$_3$, were prepared using
a hydrolysis method under a hydrothermal condition. First, 0.1 M CoCl$_2$$\cdot$6H$_2$O and 0.05 M AlCl$_3$$\cdot$6H$_2$O with the Co/Al ratio of 2 : 1 were dissolved in deionized water to give 100 mL of solution and then 0.175 M hexamethylenetetramine was added to the solution. The aqueous mixture was placed in a 10 mL Teflon inner vessel within a stainless steel outer vessel and allowed to react at 140 °C for 24 h in air-tight conditions. After cooling to room temperature, the resulting pink products were collected by centrifugation at 13 000 rpm, subsequently washed with deionized water and anhydrous ethanol several times, and finally dried in a vacuum.

The anion exchange of the CoAl-LDH from a carbonate to a nitrate form was carried out by treating with a salt-acid mixed solution. Typically, 0.5 g of the as-prepared CoAl-LDH-CO$_3$ was dispersed in 1 L of an aqueous solution containing 1 M NaCl and 3.3 mM HCl in a nitrogen stream. The aqueous mixture was stirred for 12 h to complete the decarbonation of CoAl-LDH-CO$_3$ and thus obtained the Cl-intercalated CoAl-LDH-Cl. For anion exchange from chloride to nitrate, 0.5 g of the CoAl-LDH-Cl was dispersed into 500 mL of an aqueous solution containing 0.1 M NaNO$_3$. The nitrate form of the solid products (CoAl-LDH-NO$_3$, denoted as CAN) were collected by centrifugation at 13 000 rpm, subsequently washed with deionized water and anhydrous ethanol several times, and finally dried in a vacuum.

The carbonate form of MgAl-LDH, [Mg$_4$Al$_2$(OH)$_{12}$]CO$_3$$\cdot$nH$_2$O, denoted as MgAl-LDH-CO$_3$, was prepared using the co-precipitation method. A mixed solution of 2.0 M NaOH and 0.2 M Na$_2$CO$_3$ was slowly added to an aqueous solution containing 1.0 M MgCl$_2$$\cdot$6H$_2$O and 0.5 M AlCl$_3$$\cdot$6H$_2$O under vigorous stirring, during which time the pH was maintained at 10.0 (±0.2). The resulting precipitates were collected by centrifugation and thoroughly washed with deionized water. The products were then dried and resuspended in deionized water for hydrothermal treatment. Hydrothermal treatment was carried out at 180 °C for 24 h to obtain larger crystals and improve the crystallinity of MgAl-LDH-CO$_3$, followed by drying in a vacuum oven. The nitrate form of MgAl-LDH (MgAl-LDH-NO$_3$, denoted as MAN) was prepared by anion exchange in a salt-acid buffer treatment using the same procedures as those described above.

**Syntheses of PDA/LDH nanocomposites**

The PDA/LDH nanocomposites were prepared by deposition of PDA on LDH. PDA was prepared via the oxidative self-polymerization of DA in basic conditions. The 0.01 M tris(hydroxymethyl)aminomethane (THAM) buffer solution with a pH of 8.5 was prepared using a stock solution of 1 M THAM solution. The 0.065 g of DA (69 mM) was dissolved in 5 mL of 0.01 M THAM buffer with a pH of 8.5 in a nitrogen stream, and was stirred at room temperature for 24 h. To prepare the PDA/LDH nanocomposites, the 0.05 g of CAN and MAN were dispersed into 10 mL of 0.01 M THAM buffer with a pH of 8.5 in a nitrogen atmosphere. The 0.2 mL and 1.0 mL of DA solutions were added dropwise to the CAN and MAN colloidal suspensions in THAM buffer and allowed to react for 2 h under vigorous stirring. The resulting precipitates were collected by centrifugation at 13 000 rpm and washed with deionized water three times, followed by drying in a vacuum oven. The products were denoted as CAN-PD1 and MAN-PD1 for the reactions of CAN and MAN with 0.2 mL of DA solutions and as CAN-PD2 and MAN-PD2 for the reactions of CAN and MAN with 1.0 mL of DA solutions, respectively.

**Kinetic study of catalytic activity**

The catalytic reduction of the PDA/LDH nanocomposites was carried out in a 10 mL vial. The aqueous solutions of 1.7 mM p-nitrophenol and 0.8 M NaBH$_4$ were freshly prepared. In this study, an excess amount of NaBH$_4$ was added to exclude the influence of NaBH$_4$ concentration on the reduction rate. In a typical reaction procedure, 1.0 mL of NaBH$_4$ solution was added to the vial containing 3.0 mL of p-nitrophenol solution. Subsequently, 0.2 mL of as-prepared nanocomposites (0.011 g, 2 mL H$_2$O) was added. 0.1 mL of the reaction mixture was immediately transferred to an UV/Vis cell containing 2.0 mL of deionized water to record the UV/Vis absorption spectra at room temperature.

**Electrochemical measurements**

All electrochemical measurements were carried out in a conventional three-electrode system consisting of a working electrode, a platinum wire counter electrode, and Ag/AgCl reference electrode at room temperature. To measure the capacitance, 0.85 mg (4.2 wt%) of samples of CAN, CAN-PD1 and CAN-PD2 were dispersed in THAM buffer, respectively. Three samples were then prepared by dip-coating the Ni foam electrodes into the three colloidal solutions for 3 min. Finally, the nanocomposites deposited on the Ni foams were washed and dried under vacuum.

**Characterization**

X-ray diffraction (XRD) patterns of the LDH nanoparticles and PDA/LDH nanocomposites were measured with a Rigaku X-ray diffractometer, D/MAX-2000 Ultima, in the $\theta$–$2\theta$ scanning mode at 30 kV and 40 mA using Cu-K$_\alpha$ radiation ($\lambda = 1.5405$ Å). Raman spectra were measured using a Micro-Raman spectrometer (Renishaw) with a 514.4 nm line of argon laser as an excitation source. Phase contrast TEM images of the PDA/LDH nanocomposites were obtained using a side-entry JEOL High Resolution TEM operating at 300 kV. UV/Vis spectra were measured using a UV/Vis spectrophotometer (Schimadzu UV-3600). Cyclic voltammetry was carried out to measure capacitance in 1 M KOH solution as the electrolyte using a computer-controlled PGSTAT128N Autolab (EcoChemie, Utrecht, The Netherlands) potentiostat. The conventional three-electrode configuration was employed, which consists of a platinum counter electrode and an Ag/AgCl (3 M NaCl) reference electrode at a scan rate of 10 mV s$^{-1}$. 

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