A Novel Inorganic-Organic Hybrid Material Based on Monosubstituted Keggin-Type Polyoxometalates by a Metal-Nitrogen of Covalent Bonding

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A new inorganic-organic hybrid material $Na(ANIH)_4ANI[PW_{11}Ni(ANI)O_{39}]\cdot12H_2O$ (ANI = aniline) was prepared based on transition-metal monosubstituted keggin type polyoxometalates $[PW_{11}Ni(H_2O)O_{39}]^{5-}$ as inorganic species and aniline as organic ligand by a covalent bonding of Ni-N. The as-prepared hybrid material was characterized by elemental analysis, IR spectroscopy, TG-DTA analyses, UV-visible spectra and X-ray photoelectron spectroscopy (XPS). Elemental analysis and TG-DTA results confirm the formula of the hybrid material. Experimental results of UV-VIS, IR and XPS approve that the Ni-N covalent bond is formed between the transition-metal in the Keggin-type anion $[PW_{11}Ni(H_2O)O_{39}]^{5-}$ and the nitrogen atom of ANI and the ANIH$^+$ exists as counter ion. Moreover, photocatalytic activity of the as-prepared hybrid material was investigated by photodegradation of dye rhodamine B under UV irradiation and the results showed that the hybrid material exhibited high photocatalytic activity for treatment of dye-containing wastewater.

Key Words: Hybrid material, Keggin type, Polyoxometalates, Photocatalytic activity.

INTRODUCTION

Polyoxometalates (POMs) are a well-known class of structurally well-defined anionic metal oxide clusters that remain a considerable focus, since their fascinating redox character, unique molecular structure and electronic versatility give rise to potential applications in catalysis, photochemistry, electrochromism, magnetism, medicine and biology[1,2]. Recent study has shown that POMs can be viewed as ideal inorganic species to be incorporated into organic complexes for the formation of various POM-based hybrid materials[3]. In addition to their large diversity in chemical and physical properties and shape, hybrid materials also possess the functionalities of POMs and the merits of organic molecules *via* incorporating POMs into organic molecules, thus can be applied in many fields. Preparation of polyoxometalate-based hybrids can mainly be classed into two main approaches: (a) electrostatic interactions between the anionic polyoxometalates and cationic species that can be organic, for example, ammonium salts or metal organics[4]; (b) formation of covalent bonds. This method requires covalent attachment of the organic donor on the polyoxometalate surface and the hybrid materials of this type have better stability and high strength[5]. One of the most notable methods is the reaction of amine with polyoxometalate through the substitution of terminal oxo moieties by organoimine[6,7]. The field of organoimido derivatives of POMs has gained more and more interest after

the outstanding reports of Maatta[8], Errington[9] and Proust[10], in as much as these compounds, the organic π-electrons may extend their conjugation to the inorganic framework, remarkably modifying the electronic structure and redox properties of the parent POM clusters[11]. But examples of covalent bond formed between substituted transition-metal in the Keggin-type polyoxometalates and organic ligand are rarely observed.

In this paper, we firstly report a novel inorganic-organic hybrid material $Na(ANIH)_4ANI[PW_{11}Ni(ANI)O_{39}]\cdot12H_2O$. Aniline (ANI) was selected as organic ligand to interact with transition-metal in the Keggin type anion $[PW_{11}Ni(H_2O)O_{39}]^{5-}$. Our strategy involves incorporating monosubstituted POMs into organic ligand by forming Ni-N covalent bond between the transition-metal in the $[PW_{11}Ni(H_2O)O_{39}]^{5-}$ and the nitrogen atom of ANI. In addition, the photocatalytic activity of the hybrid material was investigated *via* photodegradation of rhodamine B under UV light radiation.

EXPERIMENTAL

All chemicals and solvents in this study are reagent grade and used as received from commercial sources without further purification. $K_5[PW_{11}Ni(H_2O)O_{39}]$ was prepared by the literature method[12]. The contents of Ni, W, Na and P were determined by a Perkin-Elmer Optima 3300DV inductively coupled plasma (ICP) spectrometer. Elemental analyses (C, H and N) were performed on a Perkin-Elmer 2400 CHN elemental analyzer.

Infrared spectra in the range of 4000-400 cm^{-1} (KBr disks) were measured with a Nicolet-Impact 400 Fourier-transformed infrared (FTIR) spectrometer. Thermogravimetric analysis (TG) and differential thermal analysis (DTA) were conducted on a Netzscn STA 449C thermogravimetric analyzer. Samples were heated under an air atmosphere at 303.2 to 973.2 K and at a heating rate of 10 K/min. XPS spectra were taken on an VG ESCA LAB MKII photoelectronic spectrometer with MgK$_\alpha$ as excitation source and the combination energy criterion was C1s = 284.6 eV. UV-visible spectral measurements were recorded on a Shimadzu UV-1700PC spectrometer.

Preparation of Na(ANIH)$_4$ANI [PW$_{11}$Ni(ANI)O$_{39}$]·12H$_2$O: Na$_2$WO$_4$·2H$_2$O (6.6 g, 20 mmol) and Na$_2$HPO$_4$ (0.26 g, 1.8 mmol) were dissolved in 40 mL H$_2$O. This solution was heated to 80-90 ºC and acidified with conc. HNO$_3$ until pH 4.8. Aqueous Ni(NO$_3$)$_2$·9H$_2$O (0.44 g, 2.4 mmol, 3 mL) was added and the pH was then adjusted to 4.5 by adding small aliquots of NaHCO$_3$. After 0.5 h of stirring, the solution was cooled to 70 ºC and then aniline (1.7 mL) was added slowly. After stirring for 4 h, yellow block solids were obtained. Then the solids were filtered out and washed with acetonitrile and water, followed by air-drying at room temperature.

The yield was 23 %. Elemental anal. (%) calcd. (found) for C$_{36}$H$_{70}$N$_6$O$_{51}$PW$_{11}$NiNa: C, 12.22 (11.7); H, 1.98 (1.93); N, 2.38 (2.32); P, 0.88 (0.83); W, 57.17 (55.41); Na, 0.65 (0.62); Ni, 1.66 (1.55).

Photocatalytic activity: The photocatalytic activity of the as-prepared hybrid material was investigated *via* photo-degradation of rhodamine B under UV light radiation. In a photodegradation experiment 150 mL of fresh aqueous dye solution (10 mg/L) and photocatalyst (containing 40 mg of pure K$_5$[PW$_{11}$Ni(H$_2$O)O$_{39}$], Na(ANIH)$_4$ANI [PW$_{11}$Ni(ANI)O$_{39}$] ·12H$_2$O) were used. The suspension (150 mL) was stirred in the dark for 3 h to obtain a good dispersed reactant and establish adsorption-desorption equilibrium between the dye molecules and the catalyst surface. The solution was irradiated under UV light (125 W high pressure mercury lamp, 312 nm) with continuously stirring during the photocatalytic reaction. After the signal intensity of the high pressure mercury lamp became stable, the solution was irradiated. After appropriate time interval of illumination, the 3 mL of sample was taken out and centrifuged, then the filtrates was analysed by UV spectro-photometer.

RESULTS AND DISCUSSION

IR spectroscopy: IR spectra of the as-prepared hybrid material have been recorded in the range of 4000-400 cm^{-1}. In Fig. 1b, a weak but obvious peak at 687 cm^{-1} is attributed to the Ni-N[13] covalent bond formed between the transition-metal center in the [PW$_{11}$Ni(H$_2$O)O$_{39}$]$^{5-}$ cluster and the nitrogen atom of aniline. In addition, the spectrum of hybrid material shows bands in the range of 1100-700 cm^{-1} corresponding to the characteristic P-O bond in the central PO$_4$ unit, W=O and W-O-W bonds of the clusters, appearing at 1062, 959, 888 and 814 cm^{-1}, respectively, which is similar to the characteristic bands of [PW$_{11}$Ni(H$_2$O)O$_{39}$]$^{5-}$ anion[14] (Fig. 1a). This result shows that the monosubstituted Keggin unit remains intact in the as-prepared hybrid material. Some shifts of the peak positions

can be attributed to the interaction of the POMs clusters with organic ligand. A broad band at 3453 cm^{-1} is assigned to the O-H stretch band from water molecule and N-H stretch band from aniline. The 1700-1150 cm^{-1} region is indicative of the organic ligand in the hybrid material (Fig. 1b). The bending vibrations of N-H bonds in aniline are observed at 1601 and 1620 cm^{-1}. The peak at 1491 cm^{-1} observed for the hybrid material is due to the stretching vibrations of the C=C group in aniline[15]. The peaks at 1632 and 1574 cm^{-1} are assigned to asymmetric bending mode of the -NH$_3^+$ group in protonated aniline C$_6$H$_5$NH$_3^+$ (ANIH$^+$). In addition, the peaks at 745 and 706 cm^{-1} in the hybrid material attributed to W-O$_{center}$ bonds in POM clusters overlap the out-of-plane benzene ring deformation band around 690 cm^{-1} and C-H deformation or bending bands around 750 cm^{-1} of ANI and ANIH$^{+ 16}$. These results reveal the coexistence of aniline and protonated aniline C$_6$H$_5$NH$_3^+$ in the hybrid material. The IR results illuminate that the Ni-N covalent bond is successfully formed between [PW$_{11}$Ni(H$_2$O)O$_{39}$]$^{5-}$ and aniline and the protonated aniline ANIH$^+$ exists as counter ions.
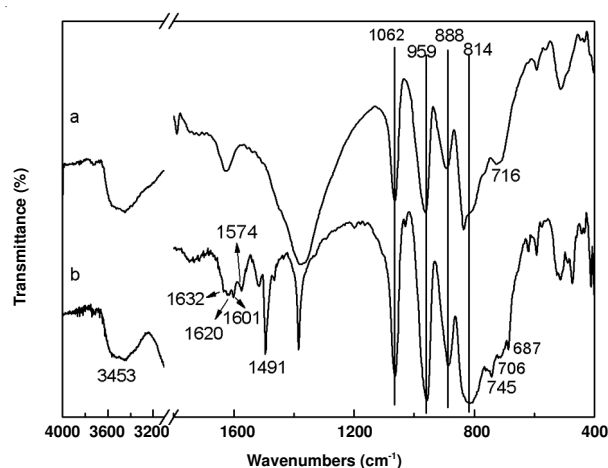
Fig. 1. FT-IR spectra of (a) K$_5$[PW$_{11}$Ni(H$_2$O)O$_{39}$] and (b) Na(ANIH)$_4$ANI [PW$_{11}$Ni(ANI)O$_{39}$]·12H$_2$O

UV-visible spectra: UV-visible spectra of the hybrid material are shown in Fig. 2. For the hybrid material, the absorptions at 201 and 253 nm are assigned to O→W charge-transfer of W=O and W-O-W bonds[17], respectively, which are consistent with the Keggin-type anion [PW$_{11}$Ni(H$_2$O)O$_{39}$]$^{5-}$ (Fig. 2a), suggesting that the primary Keggin unit in the as-prepared hybrid material doesn't change after interacting with organic ligand. In addition, from the insert spectrum of the hybrid material in Fig. 2, a new and broad absorption peak appears at 423 nm after interaction between [PW$_{11}$Ni(H$_2$O)O$_{39}$]$^{5-}$ anion and aniline, which is attributed to a charge-transfer transition of aniline molecule to Ni^{2+}, indicating that the as-prepared hybrid material is formed by a covalent bonding of Ni-N due to the interaction between transition metal center in the [PW$_{11}$Ni(H$_2$O)O$_{39}$]$^{5-}$ cluster and the nitrogen atom of aniline.

X-Ray photoelectron spectroscopy: Confirmatory evidence for the formation of the polyoxometalate-aniline adduct Na(ANIH)$_4$ANI[PW$_{11}$Ni(ANI)O$_{39}$]·12H$_2$O is further supported by XPS spectra. The N1s XPS spectrum of the hybrid material is shown in Fig. 3 and the corresponding data of the binding energies are shown in Table-1. For K$_5$[PW$_{11}$Ni(H$_2$O)O$_{39}$],
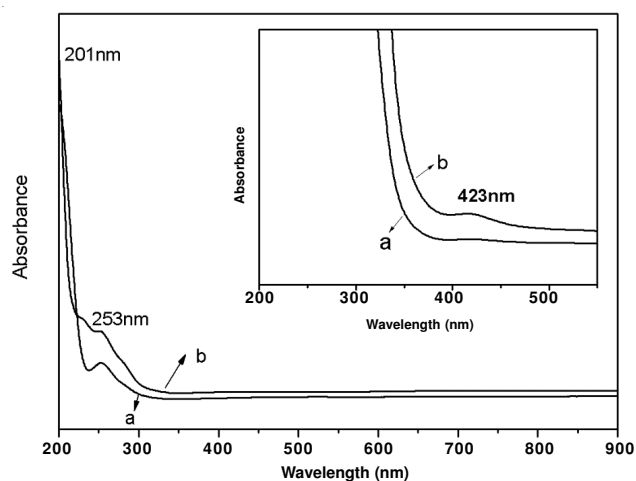
Fig. 2. UV-Visible spectra of (a) $K_5[PW_{11}Ni(H_2O)O_{39}]$ and (b) $Na(ANIH)_4ANI[PW_{11}Ni(ANI)O_{39}]\cdot 12H_2O$ $(0.3 \times 10^{-6}$ M). Insert: UV-visible spectra of (a) and (b) $(1.2 \times 10^{-4}$ M)
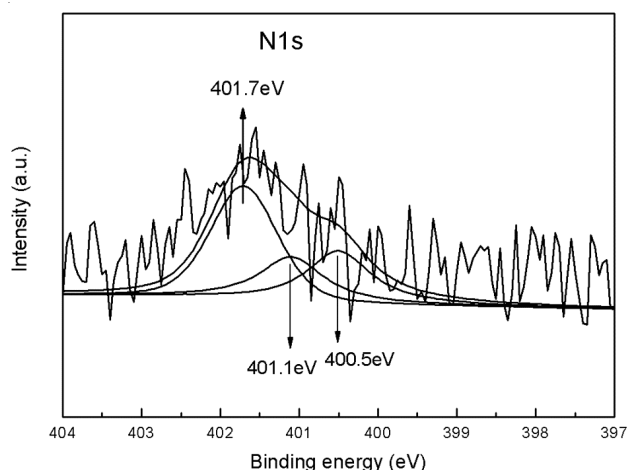

Fig. 3. XPS spectrum of the N 1s of $Na(ANIH)_4ANI [PW_{11}Ni(ANI)O_{39}]\cdot 12H_2O$

two peaks at 856.1 and 873.7 eV are attributed to Ni^{2+} $(2p_{3/2})$ and Ni^{2+} $(2p_{1/2})$[18], respectively. For the as-prepared hybrid material, two peaks at 855.5 and 873.5 eV are attributed to Ni^{2+} $(2p_{3/2})$ and Ni^{2+} $(2p_{1/2})$, respectively. The position of N core-level peak of the as-prepared hybrid material is observed at 401.6 eV, which is consistent with N1s. The N1s core level can be deconvoluted into three peaks with the binding energy centered at ca. 401.7, 401.1 and 400.5 eV, respectively, indicating that there are three different states of nitrogen atom on the surface of the hybrid material. The highest energy contribution of the peak at 401.7 eV is attributed to ANIH[+] in the hybrid material[19], which accords with the results of IR

spectra. Compared with the peak at 399.8 eV of pure aniline nitrogen[20], the increased binding energy at ca. 400.5 eV can be assigned to Ni-N covalent bond. It is well-known that the binding energy of N1s increases to higher value when nitrogen is bound to metals[21]. The other weak N1s peak at 401.1 eV means the presence of the N atom from the noncoordinated ANI molecule[22]. The binding energy of nickel on the surface of the hybrid material is decreased by 0.2-0.6 eV versus nickel in $K_5[PW_{11}Ni(H_2O)O_{39}]$ (Table-1), while the binding energy of N1s from Ni-N covalent bond on the surface of the hybrid material is increased by 0.7 eV versus N1s on the surface of aniline. The shift of the binding energies of Ni and N core level is possibly due to the change in the coordination environment of Ni and N atom on the surface of the hybrid material. The above results reflect that the density of electrons on nitrogen decrease and that on nickel increases, indicating that the electrons transfer from the nitrogen atom of aniline to the transition-metal center (Ni) in the Keggin-type anion $[PW_{11}Ni(H_2O)O_{39}]^{5-}$, resulting in the formation of Ni-N covalent bond. The XPS result proves that Ni-N covalent bond is formed and $[PW_{11}Ni(ANI)O_{39}]^{5-}$ anion is surrounded by five aniline containing species: four of them are protonated ANIH[+] and one is noncoordinated ANI molecule.

TG-DTA analysis: Elemental analysis and TG-DTA results confirm the formula of the hybrid material. The TG-DTA profiles of the as-prepared hybrid material are shown in Fig. 4. A two-step weight loss is shown: the weight loss of 6.04 % during the first step from 30-177 °C corresponds to the loss of all water molecules (calcd. 6.11 %). The second weight loss is 16.3 % between 178 and 700 °C, which accords with the loss of four protonated ANIH[+] ions, one noncoordinated ANI molecule and one coordinated ANI molecule (calcd. 15.89 %).
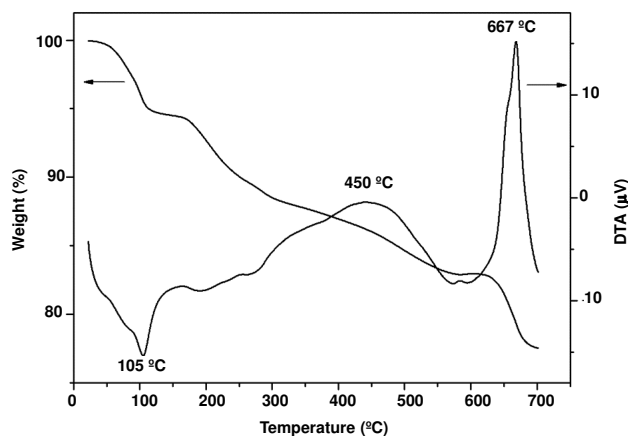

Fig. 4. TG-DTA curves of $Na(ANIH)_4ANI [PW_{11}Ni(ANI)O_{39}]\cdot 12H_2O$

TABLE-1
BINDING ENERGIES (eV) OF Ni2p$_{3/2}$, Ni2p$_{1/2}$, AND N1s ON THE SURFACE OF $K_5[PW_{11}Ni(H_2O)O_{39}]$,
ANI (ANILINE) AND $Na(ANIH)_4ANI [PW_{11}Ni(ANI)O_{39}]\cdot 12H_2O$ COMPOUND

XPS peaks	Binding energy (eV)			ΔE_b (eV)
	$K_5[PW_{11}Ni(H_2O)O_{39}]$	$Na(ANIH)_4ANI [PW_{11}Ni(ANI)O_{39}]\cdot 12H_2O$	ANI	
Ni^{2+}$_{2p3/2}$	856.1	855.5	–	–0.6
Ni^{2+}$_{2p1/2}$	873.7	873.5	–	–0.2
N$_{1s}$	–	401.7[a]	–	–
–	–	401.1[b]	–	–
–	–	400.5[c]	399.8	0.7

[a]ANIH[+]. [b]Noncoordinated ANI. [c]Ni-ANI.

In the DTA curve of the hybrid material, there is one endothermal peak and two exothermic peaks corresponding to the weight losses of the TG curve. The strong endothermal peak is observed at 105 ºC, which should be related to the release of the water molecules. Meanwhile, the two exothermic peaks appearing at 450 and 667 ºC are attributed to the loss of $ANIH^+$ cation and ANI molecules. From the results above, the formula of the hybrid material can be deduced to be $Na(ANIH)_4ANI[PW_{11}Ni(ANI)O_{39}] \cdot 12H_2O$.

Photocatalytic activity: Rhodamine B was selected as the target to investigate the photocatalytic activity of the as-prepared hybrid material $Na(ANIH)_4ANI[PW_{11}Ni(ANI)O_{39}] \cdot 12H_2O$. As shown in Fig. 5 disappearance of rhodamine B (10 mg L^{-1}, 150 mL) was monitored by a UV-visible spectrometry at wavelength of 554 nm. In the absence of the catalyst, direct photolysis of rhodamine B under UV irradiation for 180 min does not cause obvious degradation. When suspension of aqueous rhodamine B solution (10 mg L^{-1}) and the catalyst powder (including 40 mg of hybrid material $Na(ANIH)_4ANI[PW_{11}Ni(ANI)O_{39}] \cdot 12H_2O$ or $K_5[PW_{11}Ni(H_2O)O_{39}]$) were mixed and stirred in the dark for 180 min, a good dispersion occurred and an adsorption-desorption equilibrium established. In the homogeneous system of an aqueous rhodamine B solution and $K_5[PW_{11}Ni(H_2O)O_{39}]$, the photocatalytic activity of $K_5[PW_{11}Ni(H_2O)O_{39}]$ for photodegradation of rhodamine B is low and the conversion of rhodamine B is 10.66 %. However, the conversion of rhodamine B is 59.73 % over the as-prepared hybrid material. The photocatalytic activity of $Na(ANIH)_4ANI[PW_{11}Ni(ANI)O_{39}] \cdot 12H_2O$ is much higher than that of $K_5[PW_{11}Ni(H_2O)O_{39}]$. This result indicates that the as-prepared hybrid material exhibits favorable photocatalytic activity for degradation of rhodamine B and can be used for treating the dye-containing wastewater.
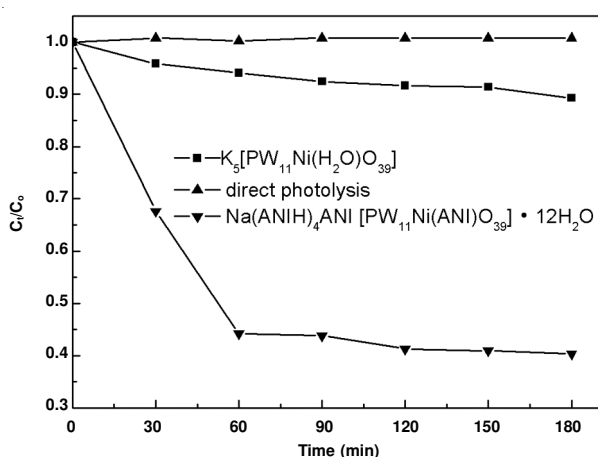

Fig. 5. Photocatalytic degradation of rhodamine B (10 mg L^{-1}) in aqueous dispersions of different catalytic materials under UV irradiation

Conclusion

A novel inorganic-organic hybrid material $Na(ANIH)_4ANI[PW_{11}Ni(ANI)O_{39}] \cdot 12H_2O$ was successfully synthesized. The hybrid material was prepared based on transition-metal mono-substituted Keggin-type anion $[PW_{11}Ni(H_2O)O_{39}]^{5-}$ and organic ligand aniline by covalent bonding of Ni-N. Characterization

of the as-prepared hybrid material illuminated that the Ni-N covalent bond was formed between transition-metal in the Keggin-type anion $[PW_{11}Ni(H_2O)O_{39}]^{5-}$ and the nitrogen atom of ANI molecule, indicating that polyoxometalate anions reacted chemically with organic ligand and electrons transferred from the nitrogen atom to the transition metal center. Also the anion $[PW_{11}Ni(ANI)O_{39}]^{5-}$ was surrounded by five aniline containing species: four of them were protonated $ANIH^+$ as counter-ions and one was noncoordinated ANI molecule. Photocatalytic degradation of dye rhodamine B indicated that the as-prepared hybrid material $Na(ANIH)_4ANI[PW_{11}Ni(ANI)O_{39}] \cdot 12H_2O$ showed higher photocatalytic activity than $K_5[PW_{11}Ni(H_2O)O_{39}]$. Therefore, the hybrid material has great potential for application in practical photodegradation. The interaction of the organic ligand with the transition-metal center of the polyoxometalates results in the formation of covalent bond. Based on this mechanism a variety of hybrid materials can be designed, prepared and applied in many fields.

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