

## IL-assisted synthesis of mesoporous AgCl/MCM-41 microspheres and their photodegradation properties

H. Q. Zhang<sup>1\*</sup>, Q. Wu<sup>1</sup>, J. F. Gao<sup>1</sup>, H. L. Chen<sup>1</sup>, Z. K. Xuan<sup>1</sup>

<sup>1</sup>Department of Chemistry, Hebei Normal University for Nationalities, 067000, Chengde, P.R.China

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Hybrid mesoporous MCM-41 microspheres were prepared using N-(trimethoxysilanepropyl) imidazole hydrochloride ionic liquid, then AgCl materials were *in-situ* deposited on the surface of the mesoporous MCM-41 by inducing Cl<sup>-</sup> in the ionic liquid. AgCl on the mesoporous MCM-41 microspheres was of high dispersion, and the composite displayed an especial pore size distribution with two maximum values centered at 4.0 nm and 7.9 nm. The final loaded amount of AgCl in MCM-41 may be changed by using different amounts of N-(trimethoxysilanepropyl) imidazole hydrochloride. The AgCl materials on MCM-41 possess higher catalytic performance than AgCl bulk materials in the photogradation of dyes such as methyl orange, isatin, methylene blue and congo red.

**Key words:** mesoporous silica, AgCl, photogradation, ionic liquid.

### INTRODUCTION

AgCl materials are used as photosensitive materials in photographic films. It has been found that AgCl supported under UV/Vis illumination can photocatalyze O<sub>2</sub> production from water [1-3]. Recently, AgCl particles with silver NPs were testified as an active and stable photocatalyst under visible light [4]. Further investigations have shown that the morphology of Ag@AgCl nanoparticles has a great influence on their photocatalytic properties, and different morphologies directly determine the photocatalytic activity because of different surface areas [5]. With the exception of the direct preparation of high-surface AgCl materials, the loading method is another efficient way to obtain AgCl nanoparticles with high surface. It has been reported that AgBr dispersed on an Al-MCM-41 support is an effective visible-light photocatalyst for the decomposition of acetaldehyde [6].

Room temperature ionic liquids (RTILs) as special solvents or reactants have been successfully applied in the synthesis of nano- and microstructured inorganic materials [7]. Grafted ionic liquids on solid materials were attracting more attention owing to their special application in catalysis, electrochemistry and adsorption [8-10]. Moreover, the desirable materials can also be introduced by exchanging the anion in the grafted ionic liquid, and the resultant active materials often displayed high dispersion and density. Recently, Pt precursors with negative charge were enriched on

the surface of supporting materials by this method, which resulted in the formation of high-density Pt nanoparticles [11-12]. Wang and coauthors have also developed a facile procedure to synthesize carbon nanotubes/ILs/Pt hybrids using amine-terminated imidazolium ionic liquid as a linker [13].

In the present work, we attempted to obtain AgCl materials in high dispersion on mesoporous MCM-41 by using the N-(trimethoxysilanepropyl) imidazole hydrochloride ionic liquid as an induced reactant. The investigation results confirmed that the hybrid mesoporous MCM-41 synthesized by the direct method showed microspheric morphology after the addition of N-(trimethoxysilanepropyl) imidazole hydrochloride ionic liquid and AgCl nanoparticles in high dispersion were *in-situ* prepared through the reaction of Ag<sup>+</sup> with Cl<sup>-</sup> in the ionic liquid. The catalytic performance of AgCl materials on mesoporous MCM-41 under UV/Vis illumination exceeded that of AgCl bulk materials in the photogradation of dyes.

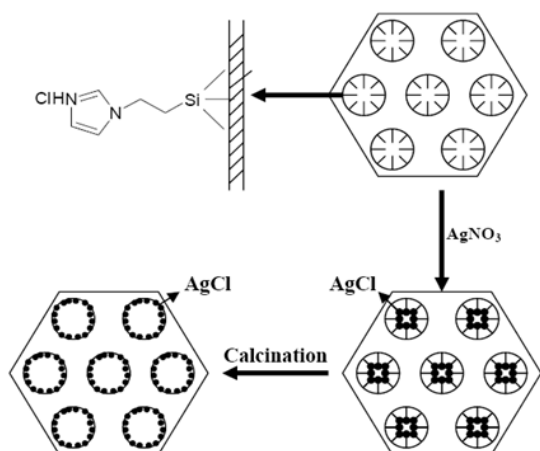
### EXPERIMENTAL SECTION

#### *Synthesis of 3(N-imidazolyl)propyltrimethoxysilane hydrochloride ionic liquid*

3 (N-imidazolyl) propyltrimethoxysilane hydrochloride was prepared as follows [14]: a 6.8 g sample of imidazole was added into a 250 ml three-necked flask containing 100 ml of dried toluene, and then the mixture was heated to 383K in N<sub>2</sub> atmosphere. After that, 18.4 ml of (3-chloropropyl) trimethoxysilane liquid was added, and the resultant solution was further heated at the circumfluent temperature for 12 h. The

\* To whom all correspondence should be sent:  
E-mail: zhang\_hengqiang@163.com

bottom layer liquid was separated, washed with hot toluene, and the final 3(N-imidazolyl) propyltrimethoxysilane hydrochloride product was obtained by removing the toluene.



**Scheme 1.** The synthesis of Ag@AgCl/MCM-41 photo catalyst.

*Synthesis of modified mesoporous MCM-41 microspheres and AgCl/MCM-41 materials*

In a typical synthesis for mesoporous hybrid MCM-41, 0.87 g of cetyltrimethylammonium bromide (CTAB) was added to a solution containing 41 g of deionized water and 10.5 g of 25 wt%  $\text{NH}_3 \cdot \text{H}_2\text{O}$  under vigorous stirring. Then 0.53 g of as-prepared 3 (N-imidazolyl) propyltrimethoxysilane hydrochloride ionic liquid and 3.7 g of tetraethylorthosilicate (TEOS) were added to the above mixture. The ionic liquid:TEOS molar ratio is 0.1:0.9 in this synthesis. The resulting solution was stirred at 353K for two days. The product was filtered, washed with water, and dried overnight at room temperature. The CTAB template was removed by solvent extraction and the resultant sample was referred to as 10wt%-MCM-41. 5wt%-MCM-41 and 20wt%-MCM-41 mesoporous hybrid MCM-41 samples were also prepared using a similar preparation process with a different ionic liquid:TEOS molar ratio (0.05:0.95 and 0.2:0.8).

For the synthesis of the AgCl/MCM-41 material, 1 g of hybrid mesoporous MCM-41 sample was added into 150 ml of alcohol-water (1:1 vol.) solution of 0.075M  $\text{AgNO}_3$  and stirred for 1 h in dark. The AgCl/MCM-41 product was obtained by further calcination at 623K for 4 h, with a heating rate of 1K/min.

*Photodegradation properties of AgCl/MCM-41 materials*

Photodegradation experiments were carried out in a cylindrical Pyrex glass cell, and were

performed at 298 K under constant stirring. In a typical photodegradation experiment, a 0.1 g AgCl/MCM-41 sample was placed in a 150 ml aqueous solution containing dyes (10 mg/L methyl orange, 20 mg/L isatin, 10 mg/L congo red, 5 mg/L methyl blue and 5 mg/L rhodamine B). Before irradiation, the reaction system was equilibrated for 30 min to allow absorption of the dye molecules. The suspended solution was irradiated with a 250W middle-pressure mercury lamp (wavelength >290 nm) surrounded by cooling water circulation, while magnetically stirred. The absorbance of the solution during the photodegradation experiment was determined by visible spectrophotometry. The degradation ratio of dyes was represented as:

$$C_t = 1 - C/C_0 = 1 - A/A_0$$

(t is the irradiation /photodegradation time;  $A_0$  is the absorbance value after the adsorption equilibrium, A is the absorbance value after the photodegradation of dyes).

*Characterizations*

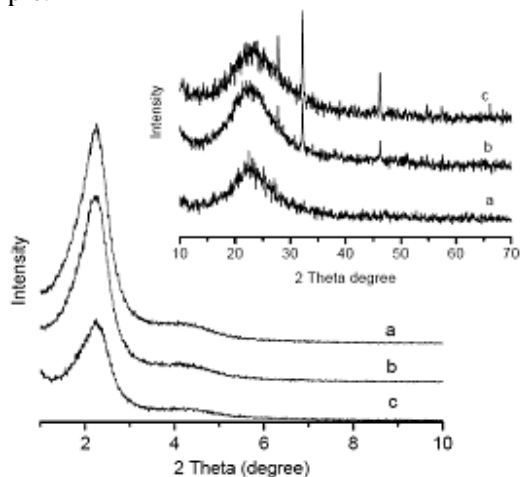
The X-ray diffraction patterns of all samples were collected in  $\theta$ -2 $\theta$  mode using a Rigaku Corporation D/MAX 2200PC diffractometer (Cu  $K\alpha$  radiation;  $\lambda = 0.154$  nm). The porous textures of the mesoporous materials were evaluated from nitrogen adsorption-desorption isotherms at 77 K using a Micromeritics ASAP 2000 system. Surface areas were determined according to the BET method, while the pore size distributions were calculated from the desorption isotherm using the BJH model. Transmission electron microscopy (TEM) was performed with JEM-2010 electron microscope operated at 200 kV. Infrared spectra (FT-IR) were recorded on a Nexus-870 Fourier-transform spectrophotometer from KBr pellets in the range 400–4000  $\text{cm}^{-1}$ . The amount of Ag in the synthesized samples was determined by ICP-AES analysis on a Thermo Elemental PERKIN ELMER PLASMA-2000 spectrometer. UV-VIS diffuse reflectance spectra were measured with a JASCO UV550 UV-VIS absorption spectrometer.

**RESULTS AND DISCUSSION**

*X-ray diffraction*

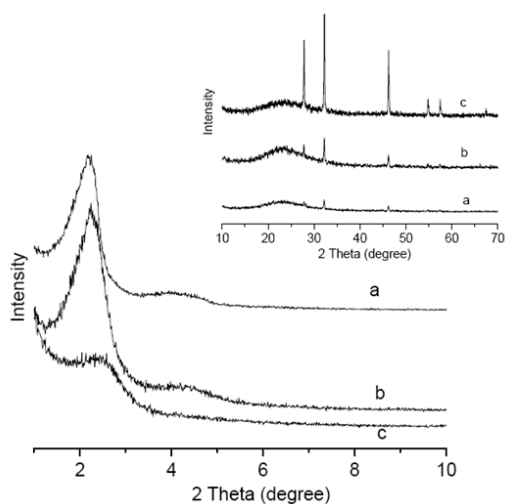
The powder X-ray diffraction pattern of the hybrid mesoporous silica from 1° to 10° (2 $\theta$ ) exhibited similar reflections to siliceous MCM-41 with hexagonal structure (Figure 1 a), and the low-angle XRD patterns of AgCl modified 10wt%-MCM-41 sample did not reveal remarkable changes (Figure 1 b and c). The diffraction peaks assigned to AgCl were also observed in the high-angle patterns of as-prepared

AgCl/10wt%-MCM-41. These peaks had slightly increasing intensity after heat treatment in air owing to the growing-up of AgCl crystals. However, there are no diffraction peaks ascribed to Ag metal in the high-angle XRD, while a darkening color was observed for the AgCl modified sample which indicates trace amounts of Ag metal in the sample.



**Fig. 1.** Low-angle and high-angle (inset) XRD patterns of 10wt%-MCM-41(a), as-prepared AgCl/10wt%-MCM-41(b) and calcined AgCl/10wt%-MCM-41(c)

The X-ray diffraction patterns of AgCl modified 5wt%-MCM-41 and 20wt%-MCM-41 were also recorded (Fig. 2).



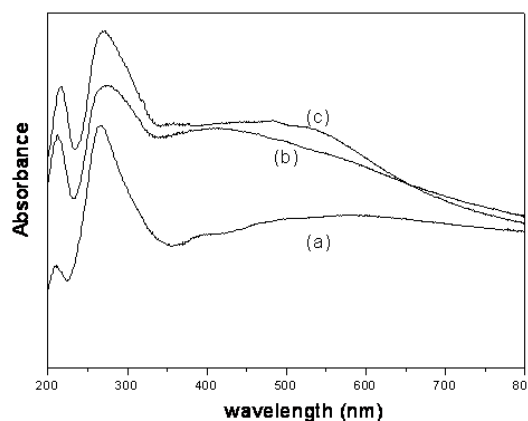
**Fig. 2.** Low-angle and high-angle (inset) XRD patterns of the calcined AgCl/5wt%-MCM-41(a), AgCl/10wt%-MCM-41(b) and AgCl/20wt%-MCM-41(c).

The calcined AgCl/5wt%-MCM-41 has the same low-angle diffraction pattern as that of AgCl/10wt%-MCM-41, and high angle peaks assigned to AgCl showed lower intensity. Moreover, the low-angle XRD (100) peak of AgCl/20wt%-MCM-41 testified a shift to larger

degrees and the peaks at 4-6° disappeared, suggesting a decreasing order in the mesostructure of AgCl/20wt%-MCM-41 because of the increasing use of 3(N-imidazolyl) propyltrimethoxysilane hydrochloride ionic liquid. The increasing amount and particle size of AgCl in the AgCl/20wt%-MCM-41 samples resulted in a stronger XRD reflection of AgCl in the intensity.

#### UV-vis DRS and the loaded amount

The UV/Vis diffuse-reflectance spectra of the prepared AgCl loaded mesoporous MCM-41 are shown in Figure 3.



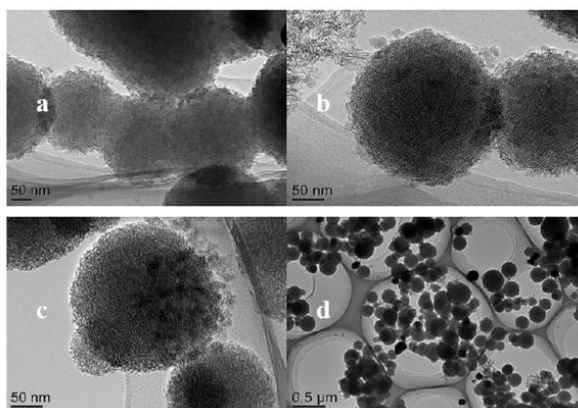
**Fig. 3.** UV-vis DRS of the calcined AgCl/5wt%-MCM-41(a), AgCl/10wt%-MCM-41(b), AgCl/20wt%-MCM-41(c).

As pure MCM-41 mesoporous silica material is almost transparent in the range of 200–800 nm, the absorption at 290 nm in the UV spectrum of as-prepared AgCl/10wt%-MCM-41 may mainly come from AgCl. On calcination, the ionic liquid molecule grafted on the MCM-41 surface is eventually removed, and well-dispersed AgCl on MCM-41 is obtained. The Ag<sup>0</sup> could be formed during carbonization and removal of ionic liquid molecule since a reducing environment could be present in the pores under these conditions. A strong absorption in the visible region was observed in the calcined AgCl/10wt%-MCM-41 sample, which was attributed to the plasmon resonance of silver nanoparticles deposited on AgCl particles [4]. Furthermore, the absorption intensity in the UV and visible region increased with increasing of the added amount of ionic liquid. The loaded amount of elemental Ag in the AgCl modified silica materials is 1.27wt% (for 5wt%-MCM-41), 4.69% (for 10wt%-MCM-41) and 12.02wt% (for 20wt%-MCM-41), according to the ICP-AES analysis.

#### TEM images

TEM images of AgCl/10wt%-MCM-41 and

AgCl/20wt%-MCM-41 (Figure 4) reveal the typical hexagonal mesostructure of MCM-41 over a large area, in agreement with the low-angle XRD of these samples.

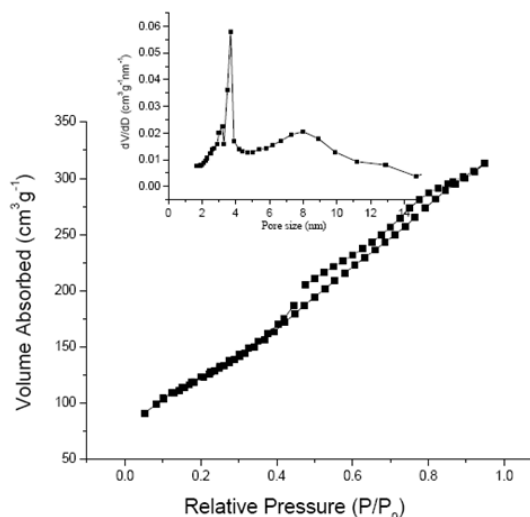


**Fig. 4.** TEM images of AgCl/10wt%-MCM-41 (a and b) and AgCl/20wt%-MCM-41(c and d).

These AgCl loaded MCM-41 samples show a special microsphere morphology with a diameter about 200 nm. The self-assembling behavior of inorganic and organic specie in the formation of MCM-41 may be affected by the addition of 3(N-imidazolyl) propyltrimethoxysilane hydrochloride ionic liquid. Moreover, the filling phenomenon of AgCl can be observed in all these images because of their more dark contrast grade in the silica particles. Few AgCl particles on the external surface of mesoporous silica can be found in the observed TEM images of AgCl loaded 10wt%-MCM-41, suggesting that most of AgCl species are well-dispersed on the internal surface of MCM-41 materials. However, few AgCl particles are observed in the samples of AgCl/20wt%-MCM-41, which is in good agreement with the sharper diffraction peaks of AgCl/ 20wt%-MCM-41.

#### *N<sub>2</sub> adsorption–desorption analysis*

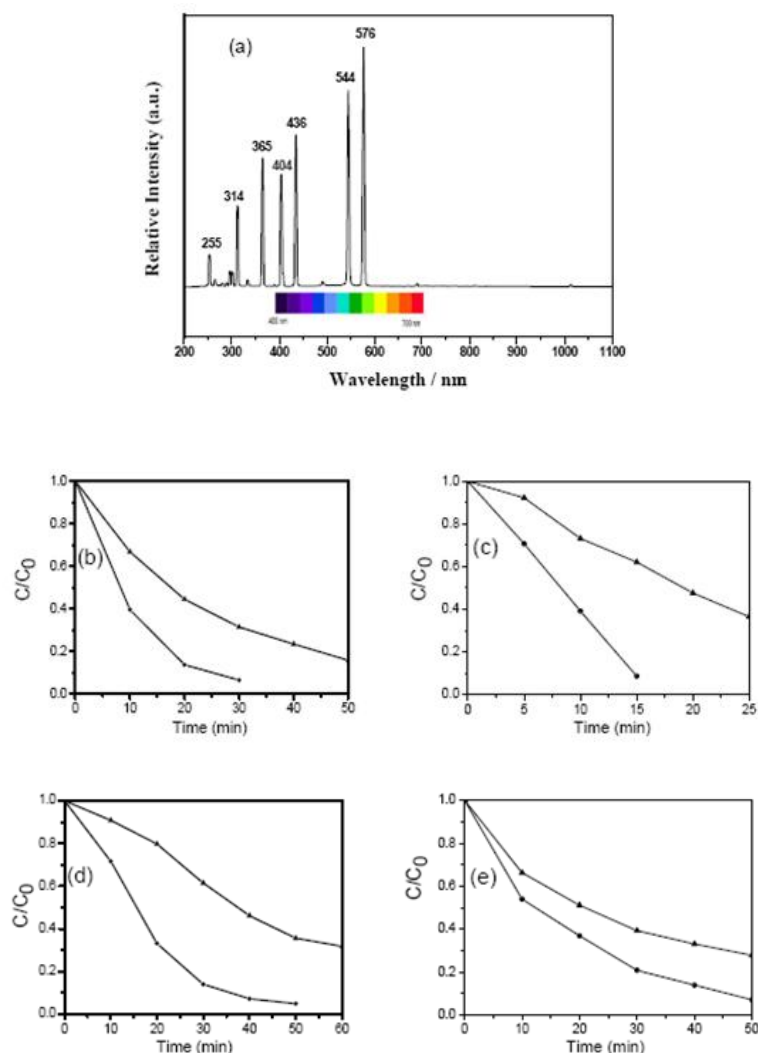
Fig. 5 shows the N<sub>2</sub> adsorption–desorption isotherms and the corresponding pore size distribution curves for AgCl/10wt%-MCM-41. The mesoporous materials exhibit type-IV isotherms with a clear hysteresis loop. In particular, there seem to be two H<sub>1</sub> hysteresis loops in the relative pressure region between 0.4-0.9, and the corresponding pore size distribution curve testified two maximum values at 4.0 nm and 7.9 nm. The former is assigned to the mesopore size. The latter may be due to the intergranular pores between the 10wt%-MCM-41 particles or another mesopores resulting from the addition of 3(N-imidazolyl) propyltrimethoxysilane hydrochloride. The AgCl/10wt%-MCM-41 sample shows a 438m<sup>2</sup>/g BET surface area and a 0.51 cc/g pore volume.



**Fig. 5.** N<sub>2</sub> adsorption–desorption isotherms and the corresponding pore size distribution curves for AgCl loaded 10wt%-MCM-41.

#### *Photocatalytic performance of AgCl /10wt%-MCM-41*

The photocatalytic degradation of dyes in solution was accomplished by visible light irradiation with only slight ultraviolet contribution. From the full wavelength spectra of the used light source (Fig. 6 a), it is seen that its irradiation is mainly concentrated in the visible range with little ultraviolet. The degradation experiment results of different dyes under irradiation are shown in Fig. 6 b-c. There is weak degradation of the dyes within the test time without irradiation or without the photocatalyst. Methyl orange is hardly detected after irradiating the solution over AgCl/10-wt%-MCM-41 for 30 min. For comparison, blank experiment of methyl orange decomposition over AgCl was also carried out under the same conditions, and about 80wt% of methyl orange was found to be degraded during irradiation for 50 min. Furthermore, the decomposition of 20 mg/L isatin over AgCl/10-wt%-MCM-41 materials was completed in 15 min. For methylene blue and congo red, decomposition was completed for about 50 min. Bulk AgCl revealed a decomposition property under irradiation which is obviously lower than that of AgCl/10-wt%-MCM-41. These results exhibit that the AgCl supported on MCM-41 has an enhanced photocatalytic performance probably resulting from the better dispersion of AgCl materials and the different size and morphology of the loaded particles.



**Fig. 6.** The full wavelength spectra of the used light sources (a); The photodegradation performance of AgCl, AgCl/10wt%-MCM-41 for dyes: (b) 10mg/L methyl orange, (c) 20mg/L isatin, (d) 10mg/L methylene blue, (e) 5mg/L Congo red

## CONCLUSIONS

We have synthesized a novel hybrid mesoporous microspheric AgCl/MCM-41 using N-(trimethoxysilanepropyl) imidazole hydrochloride ionic liquid. The AgCl/MCM-41 material reveals higher catalytic performance than AgCl bulk material in the photodegradation of dyes such as methyl orange, isatin, methylene blue and congo red.

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## СИНТЕЗА НА МЕЗОПОРЕСТИ МИКРОСФЕРИ ОТ AgCl/MCM-41 С ПОМОЩТА НА ЙОННИ ТЕЧНОСТИ И ФОТО-ДЕГРАДАЦИОННИТЕ ИМ СВОЙСТВА

Х. К. Жанг<sup>1\*</sup>, К. У<sup>1</sup>, Ж. Ф. Гао<sup>1</sup>, Х. Л. Чен<sup>1</sup>, Ж. К. Ксюан<sup>1</sup>

<sup>1</sup>Департамент по химия, Многонационален университет в Хебей, Ченгде, Китай

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(Резюме)

Приготвени са мезопорестимикросфери МСМ-41 с помощта на N-(триметоксисиланпропил) имидазолхидрохлорид като йонна течност, след което върху тях се отлага AgCl чрез индуциране на Cl<sup>-</sup> в йонната течност. Частиците от AgCl върху мезопорестимикросфери МСМ-41 са с голям дисперзитет, а разпространението на порите е би-модално с максимуму при 4.0 nm и 7.9 nm. Количеството на вложения AgCl може да бъде променено използвайки различни количества от йонната течност при приготвянето на МСМ-41. Така приготвените микросфери със AgCl върху МСМ-41 показват по-висока каталитична активност от обемен материал от AgCl за фото-деградацията на багрила като метил оранж, изатин, метиленово синьо и конго червено.