Recent Advances in Catalyst and Polymer Related Nanotechnology at UCL/ITRI

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ABSTRACT

The research activities on catalysis and polymer related nanotechnology at UCL, ITRI are focused on the synthesis of nanocatalysts, utilization of catalysts to produce nanotech products, and facilitation of catalysis by using nanotechnology. The potential of these technologies can be realized in environmental protection, energy, textile, polymers, electronics, and biosensors. Integration of several research labs at ITRI and cooperation with universities and industries has accelerated the development of new nanotech applications. This article will illustrate some recent progress of nanotechnology related catalysis at UCL: nano gold catalysts for CO oxidation at room temperature, Pt/Ru electrocatalysts for direct methanol fuel cell, catalytic synthesis and application of carbon nanotubes or carbon nanofibers. Space-confined polymerization technique was developed for the preparation of ultra high crystalline PE, HDPE/aPS and HDPE/sPS with improved properties. Molecularly imprinted polymer film on semiconductor nanoparticles was prepared for analyte detection.

KEYWORDS
gold catalyst, DMFC, CNT-FED, confined-reactor, molecular imprinting

1. INTRODUCTION

Nanotechnology has great impact on all aspects of science and technology. Not only is nanocatalyst an important part of nanotechnology, but also catalysis and nanotechnology could complement each other. For example, catalysts can be used to facilitate the production of some nanotech products such as carbon nanomaterials and high performance polymer. Some recent progress in nanocatalysis and nanopolymers at UCL/ITRI will be described in this paper.

Gold has long been considered as an inert metal until Haruta (1987) discovered in 1987 that it exhibits extraordinary catalytic activities under certain conditions. When nano-sized gold particle is dispersed on oxide carriers (Bond et al., 1999) it becomes an excellent catalyst for the oxidation of carbon monoxide (CO) even under ambient conditions. Although the use of deposition-precipitation (DP) and chemical vapor deposition (CVD) methods are capable of forming gold particles of crystallite size below 10 nm, agglomeration of Au particulate takes place easily which resulted in the rapid deactivation of catalyst. In this study, an active catalyst for CO oxidation was prepared by a precipitation method, in which HAuCl₄ was precipitated onto a suspension of the iron hydroxide or nano-TiO₂ support. In order to suppress the deactivation of supported gold catalyst due to active site agglomeration, UCL has devoted extensive efforts to improve the interaction between gold and the support in order to alleviate the possibilities of active site agglomeration. Detail performance of supported gold catalyst will be presented.

The simplicity in structure and inherent high power density of direct methanol fuel cell (DMFC) make it the most possible candidate as the next generation power source for low to medium portable power applications (Tan et al., 1998) and power density demanding device. The oxidation of fuel
methanol at the anode is the rate-limiting step that affects the performance of the fuel cell. The development of a more active and durable anode catalyst has become one of the most essential issues towards the realization of DMFC. Pt-Ru/C bimetallic catalyst is currently the state of the art anode catalyst for DMFC. Pt and Ru metals located next to each other forms the dual active site, which is responsible for the enhanced activity of methanol conversion. Factors such as particle size, particle size distribution, oxidation states of Pt and Ru, homogeneity of Pt and Ru distribution are the major catalyst properties which affect the performance of the anode catalyst towards the oxidation of fuel methanol. In the present study, preparation method(s) favoring the formation of more homogeneous distribution of Pt and Ru was developed for the preparation of Pt-Ru/C catalysts with much enhanced activity.

MWNTs can be used as field emission display (FED) (de Heer et al., 1995), gas storage and Li-ion battery. SWNTs can be used in hydrogen storage, field emission transistor (FET) and memory storage materials. Field emission by CNTs is hundreds times higher than conventional materials. Compared to conventional field emission materials, CNTs also possess higher aspect ratio, smaller tip diameter, as well as higher chemical and mechanical stability. These superior properties make possible the replacement of Mo as the source of field emission display (FED). Carbon nanotube (CNT) can be prepared by laser ablation (Thess et al., 1996), arc-discharge (Iijima et al., 1993) or chemical vapor deposition (Biro et al., 1997). UCL employed DP method to prepare supported catalysts with different loading and grain size. By applying different catalysts, in conjunction with variation of CVD reaction conditions, it is capable of controlling the growth of SWNTs and MWNTs.

Synthesis of polymers in a controlled fashion in both microstructure and morphology is of fundamental interest and practical importance. The use of mesoporous silicates, such as MCM-41 (Kresge et al., 1992) with uniform pore size and regular orientation as supported materials in polymerization reaction have shown to be capable of controlling the morphology as well as the microstructure of the polymer (Tajima, 2000). Other than being the catalyst support, mesoporous carbon can also act as a space-confined reactor for polymerization reaction. Channels of the catalyst coated mesoporous support act as the polymerization nanoreactors. The so-called “tubules-within-a-tubule” (TWT) type of mesoporous support (Lin and Mou, 1996) not only offers space-confined effect during the polymerization, but also provides nanochannels between the walls within the bundle to speed up the mass transfer of the monomers during the reaction. Enhanced activities for the polymerization are expected. The loading of two catalytic systems within the pore of mesoporous support allows the formation of two polymers simultaneously. The significance of this development is to blend two polymers to nano-scale range through direct reaction without the need of a compatibilizer. Much better mixing of the two polymers involved are expected compared with other blending methods such as physical blending or conventional reactor blending technique (Li et al., 2003). This study presents a novel method of preparing two polymers with nano-scaled blending through space-confined polymerization.

Recognition of analyte molecules by utilizing the luminescent chromophoric nature of semiconductor nanoparticles, viz., quantum dots, is a well-established method in biological science (Bruchez-Jr et al., 1998). In principle, this concept can be applied to the detection of specific analytes in competitive assay of analyte molecules in molecular imprinting technology (MIT) (Wulff, 1995). Optical detection is found to be a straightforward methodology especially in sensor applications for the detection of analytes. Organic fluorescent dyes have been used widely for analyte detection in molecular imprinting process (Turkewitsch et al., 1998). But better results can be obtained from inorganic semiconductor nanoparticles. Due to their broad excitation spectra, which is effective to whole spectrum of colors, emission without red tailing and photodegradation stability, quantum dots are very attractive as fluorescent labels.
2. EXPERIMENTAL

2.1 Nanocatalysts

2.1.1 Nano Au catalyst for CO Oxidation

The iron hydroxide support was prepared by a precipitation method using FeCl$_3$·6H$_2$O and 30% ammonia solution. The pH of the solution was controlled to 10 to facilitate the precipitation of Fe(OH)$_x$. The resulting mixture was filtered and washed with de-ionized water to remove the chlorine ions, followed by drying at 110 °C to obtain Fe(OH)$_x$ support. Titanium hydroxide support was prepared by the precipitation of TiCl$_4$ with 30% ammonia solution at pH of 10. The obtained mixture was filtered and washed with de-ionized water to remove the chlorine ions, followed by drying at 110 °C to obtain Ti(OH)$_x$. Nano-TiO$_2$ support was prepared by a hydrothermal treatment at 100 °C in which 70% of nitric acid aqueous solution was used to adjust the pH to 2. The obtained mixture was filtered and dried at 110 °C to obtain nano-TiO$_2$. Supported gold catalyst on either iron hydroxide or nano-TiO$_2$ was prepared by precipitation of an aqueous solution of HAuCl$_4$ onto the corresponding support. Ammonia solution was used to adjust the pH value to 10 to facilitate precipitation. Then, the precipitated catalyst precursor was filtered and washed with de-ionized water to remove the chlorine ions, followed by drying at 110 °C and calcination at 150~350°C.

The catalysts were characterized by N$_2$ sorption (Micromeritics ASAP2000), TEM (Jeol FS2000), ICP-AES (Perkin Elmer OPT 1MA 3000DV), X-ray diffraction (Shimadzu XD-D1). XRD line broadening was used to calculate the average crystallite size using the Scherrer equation. The loading of Au was determined by ICP-AES.

CO oxidation was used to probe the performance of the gold catalysts prepared in this study. Catalyst activity was measured in a quartz fixed-bed reactor (diameter 6 mm). 500 mg of 30-40 mesh catalyst was used for all activity measurements. Catalyst pretreatment was performed in an air stream at 180°C for 4 h before the reactant gas with various CO concentrations was directed to the catalyst bed. The catalyst temperature was monitored with a quartz-tube covered thermocouple in contact with the inlet of the catalyst bed. The composition of the reaction mixture was controlled using mass flow controllers. High concentration of CO in the outlet gas was analyzed by a Rosemount Analytical CO analyzer (Model 880A with the detection range of 0.01~20%). An Industrial Scientific Co. CO detector (the detection range of 0~1999ppm) was used for low concentration analysis. Calibration was performed using a standard gas containing known concentrations of the components.

2.1.2 Pt-Ru/C catalyst for use in direct methanol fuel cell (DMFC)

Mesoporous (CMK-1) carbon was prepared using MCM-41 as the template according to Joo et al. (Joo et. al., 2001). Carbon supported Pt-Ru binary metal catalysts (Pt-Ru/C) were prepared using deposition-precipitation (DP) (Arico et al., 2002), impregnation (IM) (Arico et al., 2002) and incipient wetness (IW) methods. Both commercial carbons black (Cabot Vulcan XC-72) and in house CMK-1 carbon were used as the catalyst carriers. In the incipient-wetness method, carbon support in a round-bottom flask was evacuated before an aqueous solution containing both Pt(NO$_3$)$_2$(NH$_3$) and Ru(NO)(NO$_3$)$_3$ were added until wetting of the support is observed. The amount of precursor solution used for catalyst preparation is equivalent to the pore volume of the support employed for the preparation of catalyst. Removal of solvent from the wetted support was facilitated by vacuum drying. Further drying at 120°C resulted in the formation of the catalyst precursor. The catalyst precursor is then reduced in hydrogen before testing. Metal loading of the catalysts was varied while the atomic ratio of Pt/Ru was kept at 1/1. Commercial catalysts were obtained from Johnson Matthey and E-Tek.

Transmission electron microscopy (TEM), XRD, and BET were used for the characterization of
Pt-Ru/C catalyst. A beaker-type electrochemical cell equipped with the working electrode, a platinum mesh counter electrode, and an Ag/AgCl reference electrode was used for all electrochemical measurements according to Takasu et. al. (Takasu et al., 2003). The cell was purged with nitrogen to remove dissolved oxygen from the methanol solution. All potentials throughout this paper are referred to the reference hydrogen electrode (RHE) scale. CO stripping voltammetry and catalyst activity measurements were recorded at ambient temperature and 60°C using an Autolab PGSTAT 30 Potentiostat. The electrochemical oxidation of methanol was characterized by the steady-state current density at 0.5Vin 1.0 M CH₃OH/0.5 M H₂SO₄ solution.

2.2 Carbon Nanomaterials

2.1 Low temperature growth of MWNT for CNT-FED application

A new process to grow CNTs on soda-lime glass substrate at lower temperature was developed in this study. MWNT used for the preparation of CNT-FED was prepared by catalytic CVD method. Deposition-precipitation (DP) method was used to prepare the Ni/Ag (5/100, by weight) catalyst. A 1:3 (wt ratio) mixture of Ni/Ag catalyst and an Ag paste (50% Ag) was then screen-printed on an Ag coated (5~10µm) glass substrate. Vertically aligned CNTs were then grown on the glass substrate by CVD method operated at 500°C.

The same technique was applied to grow CNTs on triode. A Ni/Ag catalyst and conductive paste mixture was coated on a Na-glass substrate; the substrate was heated in air to form a conductive Ag cathode layer; then an insulating layer and a gate anode layer were applied on top of the cathode layer. After sandblasting to make unit gate holes, the triode structure was formed. Finally, CVD method was used to grow CNTs on the Ag cathode layer at low temperatures. Through the control of reaction temperature, reaction time and the concentration of acetylene in the feed gas, CNTs can be directly grown on the triode at low temperatures. In order to prepare CNT on the substrate, the catalyst coated substrate was treated with Ar/H₂ (500/75 ml/min) at 500°C for 5 min, followed by Ar/H₂/C₂H₂ (500/75/25 ml/min) at 500~550°C for 30 min.

2.3 Molecularly designed polymeric materials

2.3.1 Nano-blended Polymers by space-confined polymerization

MCM-41 used in this study was synthesized as described in the literature (Kresge et al., 1992). TWT-MCM-41 was prepared according to the procedure published by Prof. Mou (Lin and Mou, 1995). Supported catalysts were prepared by adding Cp₂ZrCl₂ (0.19g in 10ml of toluene) solution dropwisely to 30 ml of toluene with 1.0 g mesoporous material. After stirring for 24 hrs, MAO solution (1.4 M, 15 ml) was added to the mixture and stirred for another 24 hrs. The final product was filtered and dried by vacuum. Spaced-confined polymerization was conducted in a Parr reactor at 80°C. 250 ml of toluene was loaded into the reactor followed with 1ml of TIBA (triisobutylaluminoxane) as scavenger. The supported catalysts were loaded to the reactor after the reactor was stabilized at a set temperature. The mixture was then pressurized with ethylene with stirring for 1 hr. When the reaction was complete, methanol was used to precipitate out the polymer. This precipitated polymer was washed with MeOH and oven dried at 50°C.

SBA-15 with pore size ~6.0 nm coated with the designated catalyst (and co-catalyst) was used as the mesoporous confined reactor for the nano-blending reactions (Luken et al., 1992). Azobisobutyronitrile (AIBN) was used as the free radical initiator in the preparation of atactic polystyrene (aPS). Syndiotactic polystyrene (sPS) was prepared using pentamethylyclopentadienyl titanium trimethoxide [Cp*Ti(OMe)$_3$] (Ishihara, et al., 1986) and methylaluminoxane (MAO) as the
catalyst and co-catalyst, respectively. Ethylene homopolymer is made from a catalyst prepared by pretreating the mesoporous support with cocatalyst, MAO, prior to adding metallocene precursor, zirconocene dichloride (Cp₂ZrCl₂ where Cp stands for the cyclopentadienyl ligand).

Molecularly blended HDPE/sPS and HDPE/aPS were prepared using mesoporous confined reactor containing the proper catalysts pre-deposited in the cavity of the pores. Suitable catalysts/initiators are sequentially supported onto surface of mesoporous silicate. This dual catalytic system is then exposed to the two monomers of interest simultaneously to generate polymer blends.

2.3.2 Molecularly imprinted polymeric film on semiconductor nanoparticles

Polymeric host materials were synthesized based on molecular imprinting process. The preparation of CdSe coated with ZnS was described elsewhere (Cordero, 2000). CdSe/ZnS nanocrystals were functionalized with polymerizable organic moieties by simply exchanging the surfactant, trioctylphosphine, with 4-vinylpyridine in a repeated precipitation procedure. Small to medium sized analyte molecules were imprinted using afore-mentioned CdSe/ZnS derived hosts. A variety of templates including caffeine were successfully imprinted and detected by quenching of photoluminescence emission, without the use of a transducer.

3. RESULT AND DISCUSSION

3.1 Nanocatalysts
3.1.1 Nano Au catalyst for CO Oxidation

XRD diffraction patterns revealed that the nano-TiO₂ support prepared in this study has an anatase crystallite phase with metal crystallite size ~8nm and BET surface area of 160 m²/g. TEM and BET results revealed that the iron hydroxide support has a particle size of less than 20 nm and surface area of 250 m²/g, respectively. Both the pH and the calcination temperature are key parameters that affect the size of iron hydroxide support. Iron hydroxide of nanosize is needed to facilitate the homogeneous dispersion of nanosized gold. Larger particle size of iron hydroxide is unfavorable in which catalyst with inferior performance is resulted. Calcination converts the iron precursor into either Fe(OH)₃ or iron oxide while calcination converts the gold precursor into both gold oxides and metallic gold. The BET surface area of the Au/Fe(OH)₃ catalyst was found to be 250 m²/g which is similar to the original Fe(OH)₃ support (surface area=250 m²/g). This result suggested that the nano-sized gold particles did not block the pore channel of the support.

XRD diffraction patterns of the gold catalysts revealed the co-existence of both iron hydroxide and α-Fe₂O₃ at calcination temperatures higher than 250°C. Amorphous catalyst support was observed when the calcination temperature was below 200°C. Calcination of the catalysts at high temperature should be avoided as it could lead to the formation of crystalline iron oxide and loss of surface area. No characteristic XRD peaks for gold were observed, which suggested that the crystallite sizes of gold were too small to be detectable by XRD. However, TEM photograph showed that gold particle are finely dispersed on the iron hydroxide support. The particle size of gold metal was about 2 nm.

Activity data in Table 1 revealed the performance of Fe(OH)₃ and TiO₂ supported Au catalyst. When mesoporous and anatase TiO₂ support with surface area higher than 200m²/g was used, one gram of this catalyst (3%Au/nano-TiO₂) is capable of completely oxidizing 5L/min of 2,500-10,000 ppm CO in air under ambient conditions and gas hourly space velocity (GHSV) lower than 500,000 h⁻¹. In addition, 3%Au/Fe(OH)₃ catalyst is capable of completely oxidizing CO in the
concentration range of 1,000 and 10,000 ppm at GHSV below 377,000 h⁻¹. These results clearly demonstrated that both 3% Au/Fe(OH)$_x$ and 3% Au/nano-TiO$_2$ catalysts are very effective for the oxidation of CO at ambient temperature. Furthermore, performances of these catalysts are not affected by the presence of water vapor and CO$_2$ (20%). Durability study also revealed that no apparent catalyst deactivation was observed during 100 hours on-stream.

Table 1. Characteristics of supported gold catalysts.

<table>
<thead>
<tr>
<th>Support</th>
<th>Crystallite phase</th>
<th>Surface area (m$^2$/g)</th>
<th>Pore size (nm (BJH))</th>
<th>Catalytic activity* (SV ml/g/h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe(OH)$_x$</td>
<td>amorphous</td>
<td>250</td>
<td>3~4</td>
<td>377,000</td>
</tr>
<tr>
<td>Nano-TiO$_2$</td>
<td>anatase</td>
<td>160</td>
<td>~6</td>
<td>500,000</td>
</tr>
</tbody>
</table>

Catalyst: 500mg, CO in Air 10,000ppm(Air: dew point in 273K) at 23~25°C

* The maximum SV at 100% CO conversion.

3.1.2 Pt-Ru/C catalyst for use in direct methanol fuel cell (DMFC)

By using MCM-41 as the template, mesoporous carbons (CMK-1) with BET surface area (S.A.) of 1,643 m$^2$/g was obtained, which is more than six times higher than the commercial Vulcan XC-72 carbon black (S.A.= 254 m$^2$/g). TEM results showed Pt-Ru catalysts (prepared by the IW method) over CMK-1 has a much smaller crystallite sizes (2.1 nm) than XC-72 supported catalyst (2.7 nm). In addition, better dispersion of metal particles was obtained over CMK-1 support. These results demonstrated that supported catalyst with higher dispersion and smaller particle size could be obtained over support with higher surface area.

Figure 1 shows the Pt-L$^{111}$ edge EXAFS Fourier transforms spectra for the Pt-Ru/C catalysts prepared by the DP and IW methods (metal loading 30%, Pt/Ru atomic ratio =1/1). Two distinct peaks corresponding to the Pt-Ru and Pt-Pt active sites are observed. Comparing the ratio of Pt-Ru to Pt-Pt peak areas revealed that the IW catalyst has a higher Pt-Ru/Pt-Pt ratio than the DP catalyst. These results suggested that the IW method is a better method for the preparation of more homogeneously mixed metal particles and is better than the commonly employed DP method for the preparation of Pt-Ru/C electrocatalyst. Higher catalyst activity towards the electrooxidation of methanol over the IW catalyst was observed (Table 2). The higher activity of the IW catalyst can be related to its higher amount of Pt-Ru active site as revealed by the EXAFS data. These results clearly demonstrated that more homogeneous mixing of Pt and Ru metals is needed for the higher activity of the catalyst. These results also suggest that Pt-Ru dual active site is needed for the effective anodic electrooxidation of methanol. For the dual site mechanism, Pt active site is responsible for the activation of methanol to form CO intermediate, Ru active site is responsible for the activation of water to form active hydroxyl group for the subsequent conversion of adsorbed CO to form CO$_2$ and the regeneration of the dual active site. Despite the IW catalyst has a larger crystallite size (2.7 nm) than the DP catalyst (2.1 nm), it is more active than the DP catalyst because it has more Pt-Ru active sites. More Pt-Ru active sites can be formed by the proper selection of preparation method. The IW method is suitable for the preparation of DMFC catalyst.
Table 2. Activity of Conventional DP and UCL IW Catalysts (ambient temperature)

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Support</th>
<th>Method</th>
<th>Loading (wt %)</th>
<th>Ru/Pt</th>
<th>Particle Size (nm)</th>
<th>Current Density mA/Pt-Ru (mg)</th>
<th>Ru-Pt Pt-Pt</th>
</tr>
</thead>
<tbody>
<tr>
<td>UCL-L47</td>
<td>XC-72</td>
<td>DP</td>
<td>21.85</td>
<td>9.08</td>
<td>2.1</td>
<td>61.9</td>
<td>0.58</td>
</tr>
<tr>
<td>UCL-P20</td>
<td>XC-72</td>
<td>IW</td>
<td>20.97</td>
<td>10.88</td>
<td>2.7</td>
<td>83.4</td>
<td>1.14</td>
</tr>
</tbody>
</table>

Table 3 shows the activity data obtained from commercial catalysts as well as catalysts prepared in this study using IW method and conventional carbon black (XC-72) as the supports. The prepared catalysts were activated at 200°C before activity test. Higher current densities were obtained from IW catalyst than commercial catalysts. The higher activity of the IW catalyst can be attributed to the incipient wetness method employed in the catalyst preparation. Homogeneous mixing of Pt and Ru resulted in the formation of enhanced Pt-Ru dual active sites, which contributes to the high activity of the IW catalyst.

Table 3. Activity data of UCL catalysts compared to commercial catalysts (60°C)

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Loading (wt %)</th>
<th>Ru/Pt</th>
<th>Current Density mA/Pt-Ru (mg)</th>
<th>Particle Size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Total</td>
<td>Pt</td>
<td>Ru</td>
<td></td>
</tr>
<tr>
<td>Vendor A</td>
<td>39.80</td>
<td>26.30</td>
<td>13.50</td>
<td>1.0</td>
</tr>
<tr>
<td>Vendor B</td>
<td>45.00</td>
<td>30.00</td>
<td>15.00</td>
<td>1.0</td>
</tr>
<tr>
<td>C5</td>
<td>29.97</td>
<td>19.75</td>
<td>10.23</td>
<td>1.0</td>
</tr>
<tr>
<td>C3</td>
<td>45.0</td>
<td>30.00</td>
<td>15.00</td>
<td>1.0</td>
</tr>
</tbody>
</table>
3.2 Carbon Nanomaterials

3.2.1 Low temperature growth of MWNT for CNT-FED application

SEM picture revealed that CNTs grown on the glass substrate exist as radial dispersion. The diameter of CNTs is between 40-50 nm with length of about 2 µm. Fig. 2 shows the field emission data of CNT performed under vacuum (10⁻⁶ Torr). Current densities of 10 µA/cm² and 5 mA/cm² were obtained at 2.8 V/µm and 5 V/µm, respectively. These results are better than the published results (0.1 µA/cm² at 8 V/µm and 75 µA/cm² at 16 V/µm) (Lee et al., 2001). In addition, the emission of our CNT/glass substrate follows the Fowler-Nordheim equation. The field enhancement factor (β value) at high and low electrical field is 3700 and 1800, respectively. These data showed that the field emission property of CNT formed at low temperature on Na-glass is comparable to that of MWNT formed at high temperature.

Better growth of CNTs was observed at higher reaction temperature. CNTs remained straight and tubular in shape at temperature as high as 525°C. Individual CNTs with length between 1-2 µm were formed on the surface of the cathode in which very dense CNTs were formed on the cathode with estimated density of 10⁸ tube/cm². When the reaction temperature was raised to 550°C, more CNTs were formed. Most of the CNTs remained straight and tubular except for those located at the exterior of the triode substrate were bent (Fig. 3). The length of CNTs at reaction time of 30 and 60 minutes were 1-2 and 7-8 µm, respectively. Initial test of this triode by ITRI’s ERSO (Electronic Research & Service Organization) showed very good electron emission.

![Fig. 2 Field emission data of CNT grown on glass substrate at 500°C](image1)

![Fig. 3 CNTs grown on the triode substrate at 550°C.](image2)

3.3.1 Nano blended polymers by Space-Confined Polymerization

When aPS and sPS polymer blends were made by the space-confined polymerization method, polarizing optical microscope (POM) with cross polarized light showed a evenly blended polymers in contrast to reactor blend of two polymers by two unsupported catalysts in one reactor. The reactor blend method under normal reaction conditions does not solve the problem such as phase separation. Space-confined approach demonstrates a much more satisfactory outcome. As well known, aPS is soluble in methyl ethyl ketone (MEK) even at room temperature. Solvent extraction is performed on aPS/sPS from space-confined polymerization. Technique such as physical aging by DSC (Zhao and Fan, 2001) is used to monitor the amount of amorphous phase remained after MEK extraction.
Significant amount of aPS still remained even after 72 hours of MEK extractions while no aPS remained from the reactor blend sample after one-hour extraction under the same conditions. This finding strongly suggests that aPS and sPS polymer chains are highly dispersed and entangled so that spatial confinement imposed on aPS may prohibit its removal by solvent extraction. PE and PS nano-blends further demonstrate the blending effectiveness of two incompatible polymers when using this technology. When PE and sPS were made simultaneously by dual catalysts within mesoporous channels, the crystallinity of PE is suppressed dramatically as shown by both DSC and XRD (Fig. 4A and 4B) while the physical blends usually merely show crystallinity reduction in proportion.

![Fig. 4. (A) Comparison of DSC scans of nano-blended HDPE and sPS with PE/sPS mole ratio of 1.33 (by 13C NMR) with unblended samples. (B) Crystallinity of (a) HDPE and (b) Nano-blended PE with sPS with PE/sPS mole ratio of 1.33 by XRD.](image)

The crystallinity of PE was reduced by a significant amount (ΔH of DSC for PE at 123°C reduces from 190 J/g to 10.38 J/g) despite the fact that the mole ratio of sPS/PE in this sample is only 3/4 by NMR. Meanwhile, the crystallinity of sPS in the same sample is reduced less significantly (ΔH reduces from 32 J/g for pure sPS to 11 J/g in this blend). The 13C NMR spectrum of this sample rules out the possibility of copolymer formation of the crystallinity suppression of PE can only be attributed to the lack of homogeneous nucleation due to the existing sPS crystal structures while cooling down. The sPS spherulites having higher Tm and Tc would be present during melting and crystallizing of PE. The evenly distributed sPS domains would hinder the PE spherulite growth, thus lowering the heat of crystallization (ΔH) for PE; meanwhile, the reverse situation is not as serious. The TEM image of nano-blended PE/sPS is given in Fig. 5.
3.3.2 Molecularly imprinted polymeric film on semiconductor nanoparticles

Scheme 1 illustrates the general scheme for the preparation of imprinted polymers with CdSe/ZnS core-shell functionalized with 4-vinyl pyridine as the quantum dots, methacrylic acid (MAA) as the functional monomer and ethyleneglycol dimethacrylate (EGDMA) as the cross-linker. Toluene was chosen as the porogen. The analyte detection was done by the PL emissions from CdSe/ZnS core-shell nanoparticles with attached MIP. The PL emission intensities of MIP with template were drastically reduced from the values of which the templates were removed from MIP. The photoluminescence emission from CdSe/ZnS core-shell nanoparticles was quenched upon analyte binding to the receptor site. The re-binding experiment of quantum dot-MIPs with the printing molecule showed a four to five-fold reduction in emission intensity when caffeine was used as the printing molecule. Selectivity of the recognition sites was demonstrated for caffeine-imprinted polymers. The as made MIPs exhibited no response to caffeine analogues such as theophylline and theobromine, in terms of PL quenching emission. The emission intensity of quantum dot-MIP is unaffected with these molecules. All the imprinted polymers exhibited much higher template recognition toward the corresponding printing molecule than its analogous structures, while a control polymer did not show any change in photoluminescence emission derived from the quantum dots.

The results indicate that the template can be selectively bound to receptor sites of the host polymer. The binding significantly affects the intensity of photoluminescence emission from quantum dots which may be attributed to the fluorescence resonance energy transfer (FRET). It involves radiation-less energy transfer that occurs between CdSe/ZnS and bound guest molecule (Cordero et al., 2002). This phenomenon can be exploited in ELISA (enzyme-linked immunosorbent assay) type assay applications. These observations of quenching of fluorescence using the solid structure of MIPs are qualitatively similar to the homogeneous soluble cases of biomolecules explored elsewhere.

Fig. 5. TEM images of nano-blended PE/sPS. The dark phases are the PS phase stained with diluted RuO₄ solution for 17 minutes.
4. CONCLUSIONS

Nanotechnology is a crucial research topic at UCL. Besides developing nanocatalysts and nonomaterials for catalysis, UCL utilizes nanocatalyst to develop the precise growth of carbon nanotube on substrates at low temperatures. UCL are cooperating with other laboratories at ITRI to develop products that require multidiscipline such as DMFC system and CNT-FED. Space-confined polymerization technique was also developed which allows the homogeneous micro blending of polymer mixtures. Furthermore, Molecularly imprinted polymer film coated on semiconductor nanoparticles was prepared for analyte detection with very good specificity.
5. REFERENCES


