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Deposition of platinum–ruthenium nano-particles on multi-walled carbon nano-tubes studied by gamma-irradiation

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ABSTRACT

Pt/Ru deposited on multi-walled carbon nano-tubes (MWCNTs) was prepared with water/iso-propanol solutions containing Pt(IV) and Ru(III) ions by γ-irradiation. The water/iso-propanol ratio (v/v), additive amount of surfactant, the concentration ratio of Pt(IV)/Ru(III) ions and the total absorbed doses (kGy) were evaluated as synthesis parameters. The sample morphology was characterized by SEM and the Pt/Ru atomic ratio was obtained by EDX. It has been found that multi-walled carbon nano-tubes can be well distributed in the water/iso-propanol solution with additive of surfactant. Pt(IV) and Ru(III) ions can be reduced by both of hydrated electron and radical of iso-propanol produced from hydrogen abstraction reaction. The Pt/Ru atom ratio can be controlled by changing the ratio of Pt(IV)/Ru(III). Small nano-particles of Pt/Ru deposited on MWCNTs can be obtained for possible application of electro-catalysts in the proton exchange membrane fuel cells (PEMFC) under optimum conditions with absorbed doses, amount of surfactant, water/iso-propanol ratio and so on. The reduction of Pt(IV)/Ru(III) ions in the aqueous solution with additive of surfactant was also studied by use of pulse radiolysis and the mechanism involved in the reduction process has been proposed.

1. Introduction

Developing fuel cells is a promising way for energy sustainability, and the search for new electro-catalysts is of great importance in terms of improving performance of fuel cells. It is a common way to produce the catalysts with the colloidal method (Franco et al., 2003; Seger et al., 2008). Platinum–ruthenium (Pt–Ru) catalysts are effective electro-catalysts for CO tolerance and/or methanol oxidation in fuel cell applications, and Pt:Ru ratio has attracted increased research interest. Multi-walled carbon nano-tubes (MWCNTs) deposited with Pt–Ru nano-particle catalysts may be an electrode of fuel cell, because of the excellent conductivity. A number of methods, such as microwave-assisted process (Liu et al., 2004) and ion-exchange (chemical reduction) (Liang et al., 2005), have been reported. Chemical reduction of Pt–Ru nano-particles in alcoholic solutions at elevated temperatures has been widely adopted. Using γ-ray-induced reduction method, Seong-Dae Oh studied the dispersion of Pt–Ru alloys onto carbon materials (Oh et al., 2006) and Dionísio F. Silva prepared the PtRu/C electro-catalysts (Silva et al., 2007). Ming-Chi Tsai succeeded in growing platinum–ruthenium nano-particles directly on carbon nano-tubes by electro-deposition for methanol oxidation (Tsai et al., 2008). In this work to investigate Pt/Ru deposited on MWCNTs, water/iso-propanol mixed solution containing Pt(IV) and Ru(III) ions was irradiated to different doses by ^{60}Co γ-rays, so as to find an optimum condition for preparing Pt/Ru nano-particle catalysts.

2. Experimental

$H_2PtCl_6 \cdot 6H_2O$ (Pt ≥ 37.0, National Chem Co., Ltd.) and $RuCl_3 \cdot nH_2O$ (Ru ≥ 59.5%, Shanghai Jiuyue Co., Ltd.) were used as received. The MWCNTs were from Shenzhen Nanotech Port Co., Ltd. All the agents used in this study are of analytical grade and used as received. Double distilled water was used to prepare aqueous solution. Unless otherwise specified, the experiments were performed at room temperature.

MWCNTs (0.1 g) were dispersed in iso-propanol (20–30 mL) with a beaker of 100 mL using an ultrasonic bath. It was added with 10–20 mL aqueous solution containing $H_2PtCl_6 \cdot 6H_2O$ and $RuCl_3 \cdot nH_2O$ of different ratios and different amounts of $C_{18}H_{29}NaO_3S$ (sodium 2-dodecylbenzenesulfonate) surfactant. After further dispersion using the ultrasonic bath, the solution was transferred into a cuvette and bubbled for 30 min with pure N_2 to remove oxygen. The samples were irradiated by ^{60}Co γ-rays to different doses at a dose rate of 29.4 Gy/min to form the Pt–Ru nano-particles deposited on MWCNTs. The products were filtered

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and washed by distilled water several times, and were dried in a oven until a constant weight was achieved. Morphology of the samples was characterized by scanning electron microscopy (SEM, Hitachi S-4800). Elemental analysis was performed using energy-dispersive X-ray spectroscopy (EDX, attached to Oxford 7426 SEM). The crystal formation was identified using X-ray diffraction (XRD, Philips X'Pert Pro).

Nanosecond pulsed radiolysis (Ma et al., 2007) was performed on a 10 MeV linac delivering 5 ns electron pulses. The dose per pulse was determined by thiocyanate dosimetry using 10 mM KSCN solution saturated with air and taking $\varepsilon=7600\ M^{-1}\ cm^{-1}$ and $G=2.8$ for $(SCN)_2^-$ at 480 nm. The average pulse dose for the kinetic determination was about 10 Gy. The samples in quartz cell for pulse radiolysis were bubbled with N_2 (99.99%) for 20 min and additive of iso-propanol to scavenge $\cdot OH$ so before use. The time-resolve experiments were carried out at $(15\pm2)\ ^\circ C$.

3. Results and discussion

As shown in Fig. 1, Pt/Ru nano-particles in sizes of 3–12 nm deposited on MWCNTs were synthesized by 40 kGy irradiation of an aqueous solution (in water/iso-propanol ratio of 5:3) containing $H_2PtCl_6\cdot 6H_2O$ and $RuCl_3\cdot nH_2O$. The nano-particles were distributed homogeneously on the surface of the MWCNTs. The nano-particles consist of just Pt and Ru (Fig. 2). It was found that the particle size would increase if the irradiated samples were not treated immediately after irradiation, indicating that the Pt and Ru particles tend to aggregate in the solution, hence the necessity of immediate collection of the samples after irradiation.

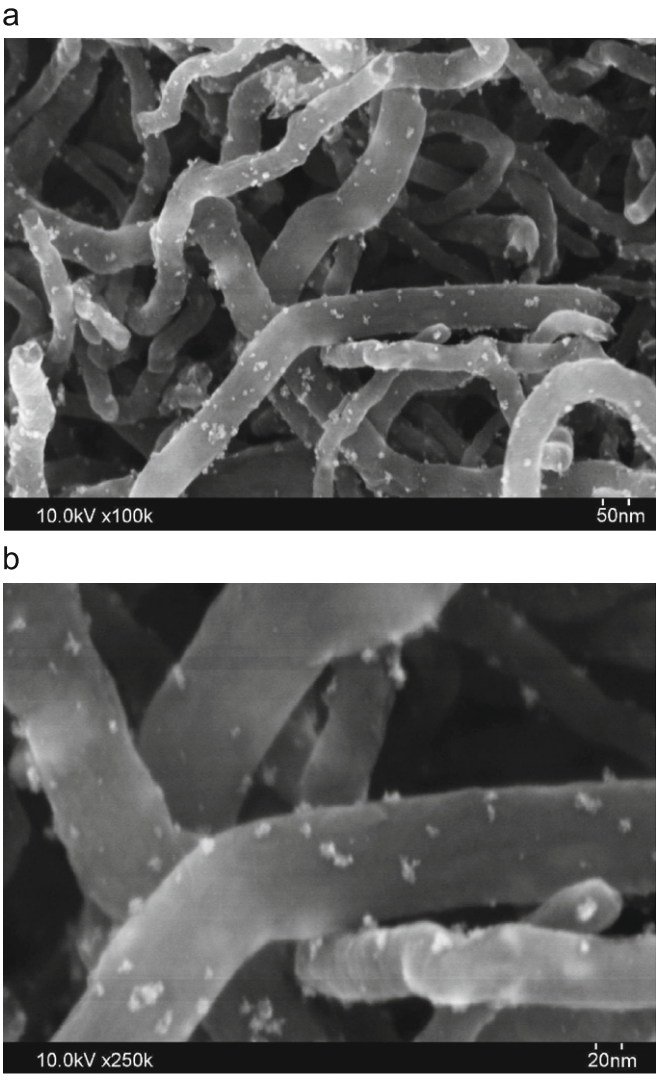

Fig. 1. SEM image of the Pt/Ru nano-particles on MWCNTs prepared in aqueous solution with a water/iso-propanol ratio of 60:40(v/v) irradiated to 40 kGy.

By radiolysis of the aqueous solution containing iso-propanol, $H_2PtCl_6\cdot 6H_2O$ and $RuCl_3\cdot nH_2O$, we could find that the primary product is only hydrated electron, as $\cdot OH$ is scavenged by iso-propanol, and the quantum yield of H may be involved in the reduction of the salts of Pt(IV) and Ru(III) at the experimental pH (pH=2.5). The reactions can be described as follows:

$$H_2O \rightarrow \cdot OH(H), e_{aq}^-, H_3O^+$$

$$OH(H) + iso{-}PrOH \rightarrow iso{-}PrO\cdot + H_2O$$

$$PtCl_6^{2-} + 2e_{aq}^- \rightarrow PtCl_4^{2-} + 2Cl^-$$

$$PtCl_4^{2-} + 2e^- \rightarrow Pt + 4Cl^-$$

$$RuCl^{3-} + 3e^- \rightarrow Ru + 3Cl^-$$

$$2H + PtCl_6^{2-} \rightarrow PtCl_4^{2-} + 2HCl$$

$$PtCl_6^{2-} + 2iso{-}PrO\cdot \rightarrow PtCl_4^{2-} + products$$

$$PtCl_4^{2-} + 2iso{-}PrO\cdot \rightarrow Pt + products$$

$$RuCl^{3-} + 3iso{-}PrO\cdot \rightarrow Ru + products$$

The reduced Pt and Ru atoms are deposited on surface of the MWCNTs, forming small seed crystals due to the high surface energy of MWCNTs. As the dose increases, the seed crystals grow with more and more Pt and Ru atoms produced in the solution, instead of forming an increased number of seed crystals on the surface of MWCNTs (Oh et al., 2006). Structure of the Pt/Ru nano-particles was investigated by XRD (Fig. 3), and the particles were well mixed/alloyed (Antolini and Cardellini, 2001). This will be further investigated by expanded X-ray fine structure (EXFS) on Shanghai synchrotron radiation facility (SSRF).

The solution containing 0.1 g MWCNTs, suitable amount of $C_{18}H_{29}NaO_3S$ surfactant, 40 mL water/iso-propanol (60:40,V/V), 0.12 g $H_2PtCl_6\cdot 6H_2O$ and 0.06 g $RuCl_3\cdot nH_2O$ was irradiated to different doses. Atomic ratios of the deposited Pt and Ru are listed in Table 1. The weight percentage, given by the EDX results, represents the elemental composition on the detected surface area, and the rest percentage must be attributed to carbon of MWCNTs. The atomic ratio is calculated from the atomic mass of Pt or Ru. It can be seen that quantity of the deposited Pt or Ru increases, and the Pt/Ru nano-particles grows, with the dose, whereas the Ru/Pt atom ratio decreases with increasing dose. However, it was found that at higher doses the Pt or Ru percentage decreased sharply and particle aggregation was so serious that the nano-particles became large enough to fall off from surface of the MWCNTs in the treating process. The optimum dose is 30–40 kGy.

Because iso-propanol is used for scavenging the $\cdot OH$ its radical (iso-PrO·) produced from hydrogen abstraction reduces Pt(IV) and Ru(III) (so the MWCNTs are dispersed in iso-propanol first and then in water/iso-propanol system). But this effect of iso-propanol on Pt/Ru deposition is not serious. As shown in Table 2, the quantity of deposited Pt/Ru does not change significantly with the water/iso-propanol ratio, though Ru is more easily to be reduced than Pt. The Pt/Ru nano-particles in sizes of 5–15 nm deposited homogeneous on MWCNTs when the water/iso-propanol ratio is 5:3 (Fig. 1).

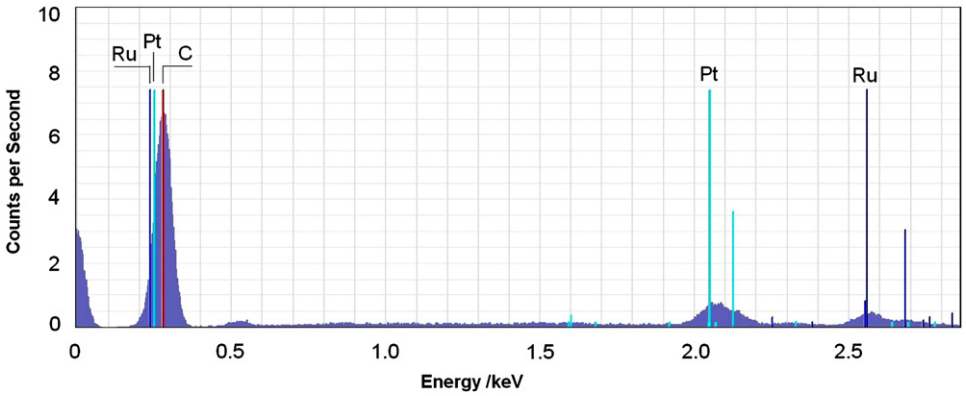

Fig. 2. EDX spectrum of the Pt/Ru nano-particles on MWCNTs.

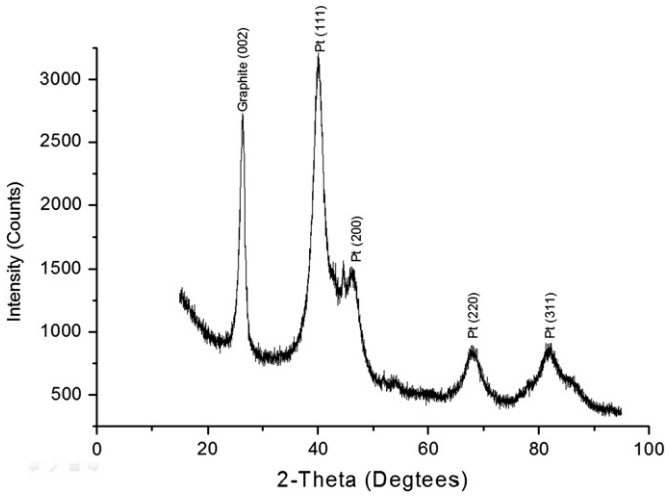

Fig. 3. XRD patterns of radiation synthesized PtRu/CNT catalysts.

Table 1
Deposition of Pt/Ru nano-particles on MWCNTs under γ-ray irradiation.

Absorbed doses (kGy)	Pt (wt%)	Ru (wt%)	Atomic ratio of Pt/Ru
30	1.26	2.16	1:3.38
40	4.21	4.58	1:2.07
48	27.70	10.83	1:0.76

Table 2
Pt/Ru deposition on MWCNTs in solutions of different water/iso-propanol ratios.

Water:iso-propanol (V/V)	Pt (wt%)	Ru (wt%)	Atomic ratio of Pt/Ru
5:2	23.31	11.49	1:0.95
5:3	13.14	8.58	1:1.26
5:4	12.40	7.26	1:1.13
1:1	16.70	9.68	1:1.12

Table 3 shows the effect of the amount of surfactant additive on deposition of Pt/Ru nano-particles on MWCNTs. It can be seen that the Pt/Ru deposition needs the $C_{18}H_{29}NaO_3S$ surfactant, which is of help for the Pt and Ru atoms to interact with MWCNTs. Also the MWCNTs are dispersed better in surfactant-added solution. However, excessive amount of the surfactant would result in severe aggregation of the Pt/Ru nano-particles, and the optimum amount of $C_{18}H_{29}NaO_3S$ is about 0.6%.

It has been known that optimum atomic ratio of the Pt/Ru catalysts is 1:1 for fuel cells with H_2 as fuel source. However, a fuel cell with methanol as fuel source differs in the optimum ratio. Gasteiger et al. (1993) found that the optimum ratio on polycrystalline surfaces was 90:10, due to methanol adsorption on Pt particles and further electro-oxidation of dehydrogenated methanol. Lizcano-Valbuena et al. (2002) found that a Pt/Ru ratio of 75:25 gave the largest activity for methanol oxidation.

In order to optimize the Pt/Ru ratio on surface of MWCNTs, the reduction of $H_2PtCl_6 \cdot 6H_2O$ and $RuCl_3 \cdot nH_2O$ using γ-irradiation was performed with different Pt(IV)/Ru(III) ratios under water/iso-propanol ratio of 5:3, additive surfactant of 0.5% and 40 kGy irradiation. As shown in Table 4, the Pt/Ru atomic ratio on surface of the MWCNTs seems to increase with Pt(IV)/Ru(III) ratio. However, due to complicacy of the reduction process of Pt(IV)/Ru(III) ions in this experimental system, it would be difficult to optimize experimental conditions by adjusting the Pt(IV)/Ru(III) ratio alone. The Pt(IV) and Ru(III) ions compete for capturing hydrated electron in the irradiation process because of their different reaction rate constants. A two-step reduction process was then proposed, and $H_2PtCl_6 \cdot 6H_2O$ or $RuCl_3 \cdot nH_2O$ was added at a certain reduction stage. For example, at 10 h of the sample irradiation (25 kGy), another part of $H_2PtCl_6 \cdot 6H_2O$ was added, and with its higher concentration than that of $RuCl_3 \cdot nH_2O$, and the subsequent irradiation made more Pt deposit on the surface of the MWCNTs. Thus, the surface Pt/Ru ratio can be controlled.

Pulsed radiolysis was carried out with the solution in a water/iso-propanol ratio of 25:16 and containing $H_2PtCl_6 \cdot 6H_2O$ in different concentrations. Since the transient absorption of Pt atom or $PtCl_4^{2-}$ cannot be observed in the detected wavelength range, the rate constant for reaction of hydrated electron with $PtCl_6^{2-}$ or $PtCl_4^{2-}$ could be obtained by using the decay of e_{aq}^- at 640 nm. As shown in Fig. 4, with increase in $H_2PtCl_6 \cdot 6H_2O$ concentrations the decay of e_{aq}^- becomes faster. The rate constants for e_{aq}^--Pt(IV) and e_{aq}^--Ru(III) reactions were determined at $k_{Pt}=5.7\times10^9$ and $k_{Rut}=6.2\times10^{10}\,dm^3\,mol^{-1}\,s^{-1}$, respectively. The reduction of metal ions depends on their reduction potential

$$PtCl_6^{2-}+2e_{aq}^- = PtCl_4^{2-}+2Cl^- \quad E^\circ = 0.68VSHE \tag{1}$$

$$PtCl_4^{2-}+2e_{aq}^- = Pt+4Cl^- \quad E^\circ = 0.755VSHE \tag{2}$$

$$RuCl^{3-}+3e_{aq}^- = Ru+3Cl^- \quad E^\circ = 0.68VSHE \tag{3}$$

From the rate constants of Pt(IV) and Ru(III), Ru(III) can be easily reduced than Pt(IV). The radiolysis results agree with the result of deposition experiment. Ru is deposited firstly on MWCNTs and then Pt is deposited, suggesting enriched Pt on the surface of platinum–ruthenium nano-particles and meanwhile enriched Ru in the interjacent part of platinum–ruthenium nano-particles on multi-walled carbon nano-tubes.

Table 3
Deposition of Pt/Ru nano-particles on MWCNTs in systems of different amounts of surfactant additive.

Systems	Pt (wt%)	Ru (wt%)	Atomic ratio of Pt/Ru	Description of the products
Without surfactant	21.01	12.04	1:1.11	Fewer Pt/Ru nano-particles
Additive 0.5% (0.2 g)	3.44	2.30	1:1.26	Homogeneous distribution
Additive 0.75% (0.3 g)	4.78	3.26	1:1.34	Homogeneous distribution
Additive 1% (0.4 g)	6.88	4.64	1:1.31	15–20 nm, aggregation

Table 4
Deposited Pt/Ru under different Pt(IV)/Ru(III) ratios.

Pt/Ru ratio	Pt (wt%)	Ru (wt%)	Pt/Ru atomic ratio
1:1	20.19	13.39	1:1.28
2:3	31.47	11.27	1:1
1:2	18.75	15.94	1:1.64
2:5	21.08	17.62	1:1.61

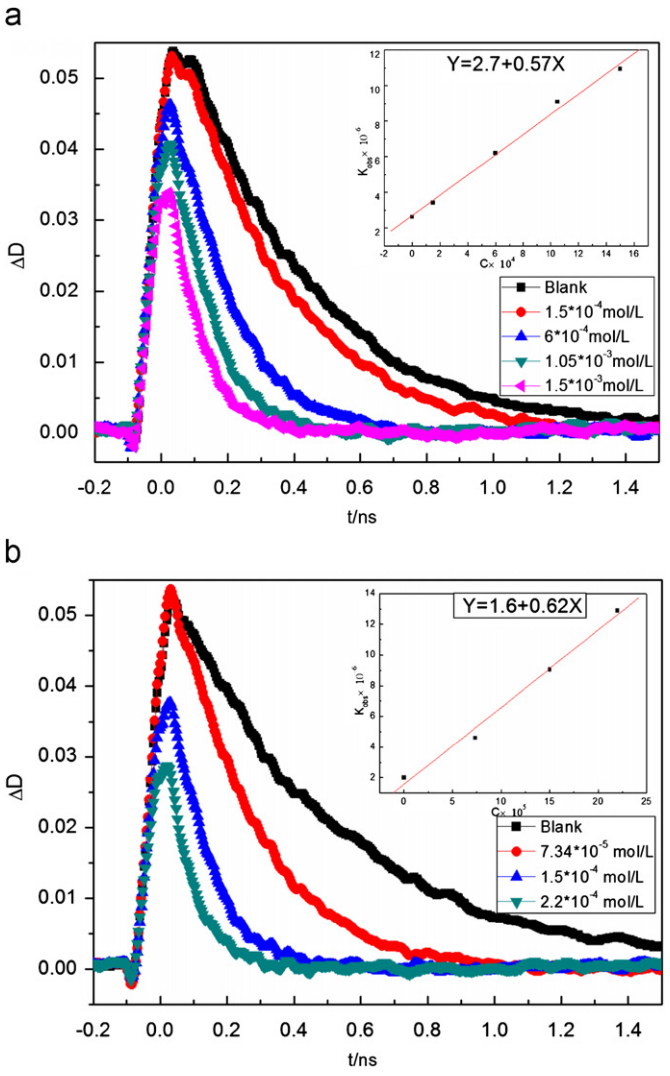

Fig. 4. Decay curves of hydrated electron for solutions with different concentrations of (a) Pt(IV) and (b) Ru(III). The insets: the observed rate constants vs concentrations.

When the solution was added with the surfactant 0.5% (Fig. 5), the decay of hydrated electron becomes slower than that of the surfactant-free system. The rate constant for e^-_{aq}-Pt(IV) reaction was determined at $9\times10^8\,dm^3\,mol^{-1}\,s^{-1}$, indicating that the

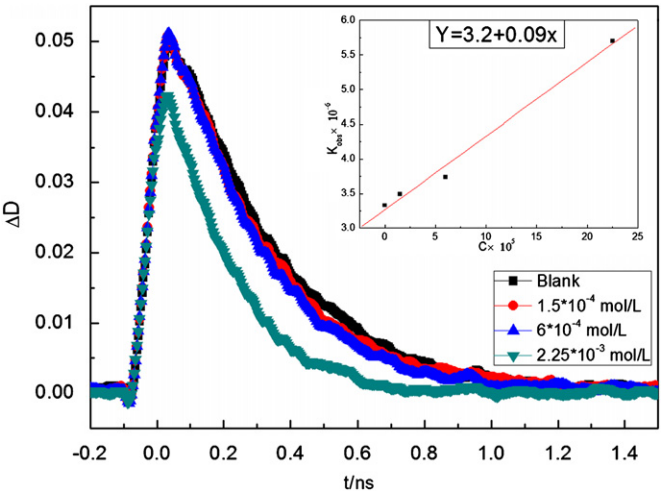

Fig. 5. Decay curves of hydrated electron for solutions with different concentrations of Pt(IV) added with surfactant of 0.5%. The inset: the rate constants vs concentrations.

surfactant additive leads to mild reduction of Pt(IV), and homogeneous smaller nano-particles may be deposited on the surface of the MWCNTs.

Both structural and electrochemical characterizations of the Pt/Ru nano-particles on MWCNTs should be performed for understanding the effect of sample structure on electro-catalytic activity in fuel cell systems. Nevertheless, an electro-catalyst assembly for fuel cell systems requests a sufficient amount of MWCNTs deposited with Pt/Ru nano-particles. This work, in which each irradiation produced just about 0.1 g sample, is part of a systematic research on the fuel cell, and further studies on performance of the catalysts will be carried out.

4. Conclusion

In order to investigate the possibility of preparing the MWCNTs deposited with Pt/Ru nano-particles as electro-catalyst for fuel cells, γ-ray irradiation has been used with a solution of water/iso-propanol containing $H_2PtCl_6\cdot6H_2O$ and $RuCl_3\cdot nH_2O$. Effects of the water/iso-propanol ratio (V/V), amount of surfactant additive, atomic ratio of the Pt(IV)/ Ru(III) ions and irradiation dose on deposition of the Pt/Ru nano-particles have been investigated. It was found that the water/iso-propanol ratio has no significant effect on the amount of deposited Pt/Ru nano-particles, while the surfactant additive makes the deposition more homogeneous. Instead of changing the Pt(IV):Ru(III) ratio, a new reduction process of multiple-steps may be useful to control the surface composition of Pt/Ru on MWCNTs. The optimum dose is 40 kGy. Pulsed radiolysis was used to investigate the mechanism in reduction of Pt(IV) and Ru ions and the rate constants for e^-_{aq}-Pt(IV) and e^-_{aq}-Ru(III) reactions with or without the absence of surfactant were obtained.

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