

Letter to the Editor

Study of Mg Powder as Catalyst Carrier for the Carbon Nanotube Growth by CVD

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The possibility of using magnesium powder as catalyst carrier for carbon nanotube growth by chemical vapor deposition, which may pave a new way to in situ fabricate CNT/Mg composites with high CNT dispersion, was investigated for the first time. The fabrication process of the catalyst supported on Mg powder involves the preparation of colloid by a deposition-precipitation method, followed by calcination and reduction. The results show that the interaction between catalyst and support plays an important role for the catalytic property of the catalyst. Ni alloyed with Mg shows no activity for the decomposition of methane. The introduction of Y in Ni/Mg catalyst can promote the reaction temperature between Ni and Mg and thus enhance the activity of the catalyst. A large amount of carbon nanotubes (CNTs) with an average diameter of 20 nm was obtained using Ni/Y/Mg catalyst at 450°C, while only a few short CNTs were obtained using Ni/Mg catalyst due to the low activity of the catalyst at lower temperature.

1. Introduction

Since the first observation of carbon nanotubes (CNTs) [1], extensive experimental and theoretical researches have been performed to exploit their properties and applications [2, 3]. The experimental and theoretical studies on the mechanical properties of CNTs predict them to be amongst the strongest materials. The elastic modulus of CNTs is comparable to that of diamond, and their tensile strength is about 100 times than that of steel. Therefore, the CNT as reinforcement in the composites is an obvious choice. Although the CNT/polymer composites exhibit a tremendous strengthening effect for the composites [4, 5], the issues of CNT dispersion in metal matrix and nanotube/matrix interaction factors are still very complex and have not been solved for the moment [6, 7]. In order to solve these issues, the authors have attempted to use metal powders as catalyst carrier to in situ obtain CNT/metal composite powders and have successfully performed in Al and Cu composites [8–10], which exhibit a higher advantage

than traditional methods. The key issues for this novel process are to prepare effective catalyst supported on metal powders and synthesize CNTs with controllable conditions.

Mg and its alloys are increasingly used in engineering structures due to their high specific strength. Effort has been made to increase the specific strength further through use of suitable reinforcements such as carbon nanotubes (CNTs), and the CNTs were found to improve the properties of the alloy significantly [11, 12]. In the present work, the possibility of using magnesium powder as catalyst carrier for the carbon nanotube growth by chemical vapor deposition (CVD) was investigated for the first time, which may pave a new way to fabricate CNT/Mg composites. Although it has been reported that nano-intermetallic alloy, MgNi, can be used as catalyst for the CNT growth, a little amount of Mg element is simply used to prevent the catalyst thermal aggregation [13]. The effect of Mg and its interaction with the catalyst (Ni) on the carbon nanotube growth is still unclear. In this paper, the effect of the reaction between the

TABLE 1: The parameters of the CNT growth by CVD.

Catalyst	Reducing temperature (°C)	Reducing time (h)	Growth temperature (°C)	Growth time (h)
10%Ni/Mg	400	5	400	1
	450	2	450	1
	500	2	500	1
16%Ni4%Y/Mg	450	2	450	1
	500	2	500	1
	500	2	600	1

carrier (Mg) and catalyst (Ni or Ni/Y) on the CNT growth was investigated systematically.

2. Experimental

2.1. Preparation of the Catalyst. The magnesium-carried Ni/Y catalyst was prepared by deposition-precipitation. For a typical process, the right amounts of Mg powder (8 g) and NaOH (2.721 g, 98.0% purity) were mixed in 500 mL distilled water. Ni(NO₃)₂·6H₂O (7.926 g, 98.0% purity) and Y(NO₃)₃·6H₂O (1.723 g, 98.0% purity) were dissolved in 300 mL distilled water and added to the previous mixture dropwise with constant stirring. The coprecipitate was then aged, washed several times, and dried at 100°C in Ar (99.9% purity). Then, the ternary colloid was calcined in Ar atmosphere at 250°C and 400°C consecutively for 2 hours each time to form the Ni/Y/Mg catalyst precursor, which would be employed in the following catalytic synthesis experiments. For comparison, 10%Ni/Mg catalyst was prepared using the same process.

2.2. Synthesis of Carbon Nanotubes. The catalyst of 0.5 g was kept in a quartz boat and placed in a horizontal quartz tube reactor. The quartz tube, mounted in an electrical tube furnace, was heated to reduction temperature in an Ar atmosphere. Then the hydrogen (100 mL/min, 99.9% purity) was introduced to reduce the catalyst. Subsequently, the hydrogen flow was shut off, and the quartz tube was heated again to the reaction temperature in an Ar atmosphere. A mixture of CH₄/Ar (100/300 mL/min, v/v) was introduced into the quartz tube for 60 minutes. The parameter details are listed in Table 1. Finally, the system was cooled to the room temperature under Ar.

2.3. Characterization of the Catalyst and Carbon Nanotubes. The catalysts and products by CVD were characterized by an X-ray diffractometer (XRD, Rigaku D/max 2500 V/pc), scanning electron microscope (SEM, JEOL JSM-T330 and JSM-6700F), and high-resolution transmission electron microscope (HRTEM, PHILIPS TECNAI G2 F20).

3. Results and Discussion

Figure 1 shows the XRD analysis of the 10%Ni/Mg catalyst and reaction products by CVD. It can be seen that there are several weak peaks, apart from that corresponding to Mg in

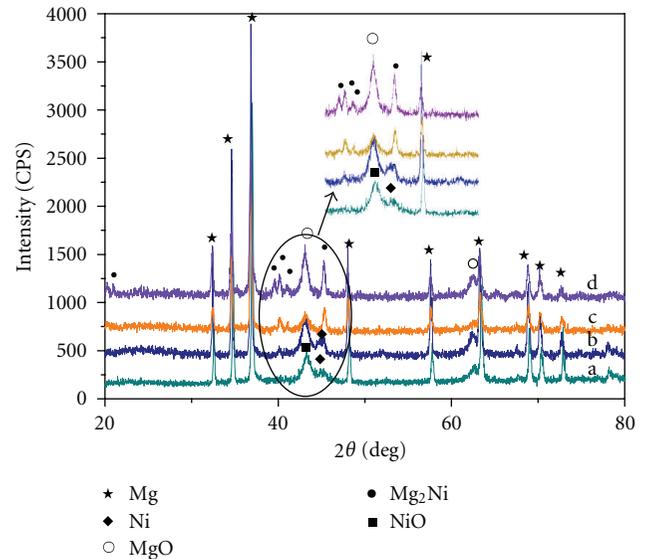
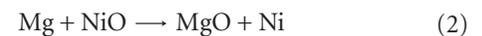
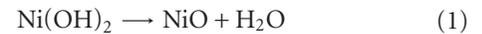


FIGURE 1: XRD analysis of the 10%Ni/Mg catalyst precursor after calcination (a) and reaction products by CVD at 400°C (b), 450°C (c), and 500°C (d).

the XRD pattern of the catalyst precursor after calcination (Figure 1(a)). The peak at 43.335° is very similar to that of Ni. However, there is no reductive gas during the calcination process. The possible reactions during this process are as follows:



Thus, the formation of Ni during calcination process simultaneously produces MgO. It is known that the peaks of NiO (43.095°) and MgO (42.916°) are very close. The broad peak near 43° may be indicated to the existence of MgO or NiO. In order to identify the peak near 43°, the samples were calcined for a longer time or reduced by H₂. The XRD analysis shows that the peak near 43° had no obvious changes (not shown here), proving the existence of MgO, and the reaction equations of (1) and (2) were reasonable. After reduction and reaction at 400°C, the peaks of Ni phase still exist. However, the phases of the samples became more complex when the temperatures were above 450°C. From the binary phase diagram of Ni and Mg, it is known that Ni can react with Mg and result in Mg₂Ni at 506°C. However,

when the sample was reduced and reacted at 450°C, there were no obvious peaks related to Ni, and some other peaks appeared, which should be responsible to Mg₂Ni, apart from that related to Mg and MgO. This may be due to the effect of nanosize level of Ni particles that promote the activity of Ni phase. The peaks between 37°–40° (indicated by black dots in Figure 1) proved the formation of Mg₂Ni. The peak near 45° is corresponding to the (203) peak of Mg₂Ni. In all the 10%Ni/Mg samples, there are almost no obvious C peaks observed.

Figure 2 shows the XRD analysis of the 16%Ni4%Y/Mg catalyst and reaction products by CVD. From the XRD pattern of the catalyst precursor after calcination (Figure 2(a)), we can see that there are no obvious peaks corresponding to Ni, inferring that yttria doped in NiO can stabilize the structure of NiO. Meanwhile, when the reduction and reaction temperatures were performed at 450°C, carbon peaks were obviously observed and no Mg₂Ni peaks appeared (Figure 2(b)). However, the peaks near 43° still existed. This may be due to either incompletely reduction of NiO or the existence of MgO. In order to distinguish this, the same catalyst was reduced at 400°C for different times and reacted at 450°C. As shown in Figure 3, the peak near 43° had almost no change and existed even in the sample that reduced for 5 hours, inferring that this peak was not related to NiO. The existence of MgO peaks indicated that the raw Mg was in some sort oxidized during the process due to the pure Mg with highly active chemical property. The peak intensity of MgO increased with the reaction temperature arose, further indicating that active Mg reacted with oxygen even in Ar at high temperature. When the sample was reduced and reacted at 450°C, the peaks of Mg₂Ni appeared (in Figure 2(c)). With the temperature increasing, there are no C and Ni peaks detected. At 600°C, Mg reacted with Ni almost completely. Another alloy, Mg₆Ni, was detected apart from Mg₂Ni (Figure 2(d)).

The morphologies of the products obtained by CVD were characterized by SEM and TEM. From Figures 4(a) and 4(b), it can be seen that some very short CNTs are obtained by CVD at 400°C using Ni/Mg catalyst, and all catalyst nanoparticles are located on the top of the CNTs (indicated by arrows in Figure 4(b)), inferring that “top-growth mode” is suitable for this experiment. However, the activity of the catalyst is very low due to the lower reaction temperatures (only about 1 wt.% of carbon deposit was obtained, which may be the cause why XRD could not detect the existence of carbon). With the reaction temperature increasing, there is almost no obvious carbon deposit observed by SEM and TEM. Furthermore, the catalyst particles become larger and joint together (Figures 4(c) and 4(d), compared with the catalyst nanoparticles located on the top of CNTs in Figure 4(b)). Combined with the XRD results (Figure 1), it can be concluded that Ni nanoparticles begin to react with Mg and lose their catalytic activity at and above 450°C.

Figure 5(a) shows the low-magnification SEM image of the product obtained at 450°C using Ni/Y/Mg catalyst. Almost all the Mg particles were covered by a dense CNT coating. Figure 5(b) is the high-magnification SEM image of the CNTs at 450°C. It can be seen that the CNTs with an

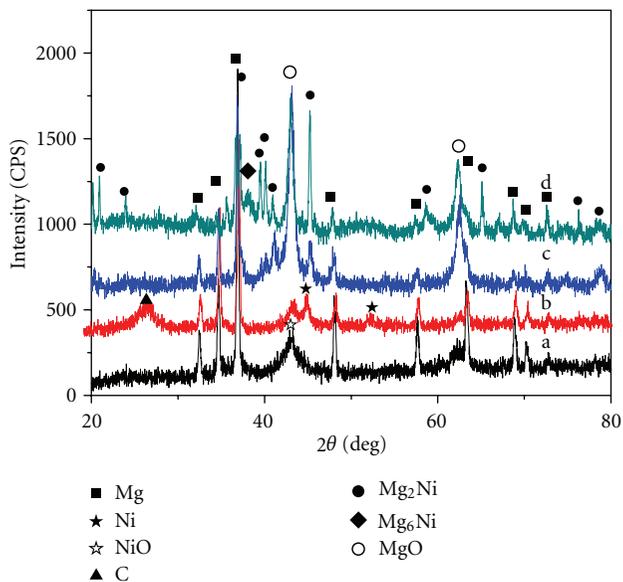


FIGURE 2: XRD images of the 16%Ni4%Y/Mg catalyst precursor after calcination (a) and reaction products by CVD at 450°C (b), 500°C (c), and 600°C (d).

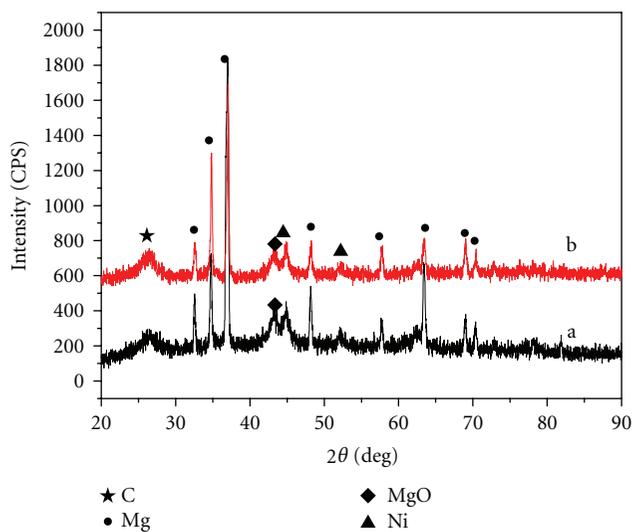


FIGURE 3: XRD images of and reaction products by CVD using the 16%Ni4%Y/Mg catalyst reduced for 3 hours (a), 5 hours (b).

average diameter of 20 nm were also grown based on “top-growth mode” (indicated by arrows). TEM images of the CNTs indicate that the structure of the CNT is herringbone or bamboo-shaped (Figures 5(c) and 5(d)). At 500°C, there were no CNTs formed instead of big particles (Figure 5(e)), similar to that obtained at 450°C using 10%Ni/Mg. When the reaction temperature increased to 600°C, Ni reacted with Mg completely and formed two phases: Mg₂Ni and Mg₆Ni. SEM images of the products show that the surface morphologies of the product obtained become petaline nanosheets (Figure 5(f)).

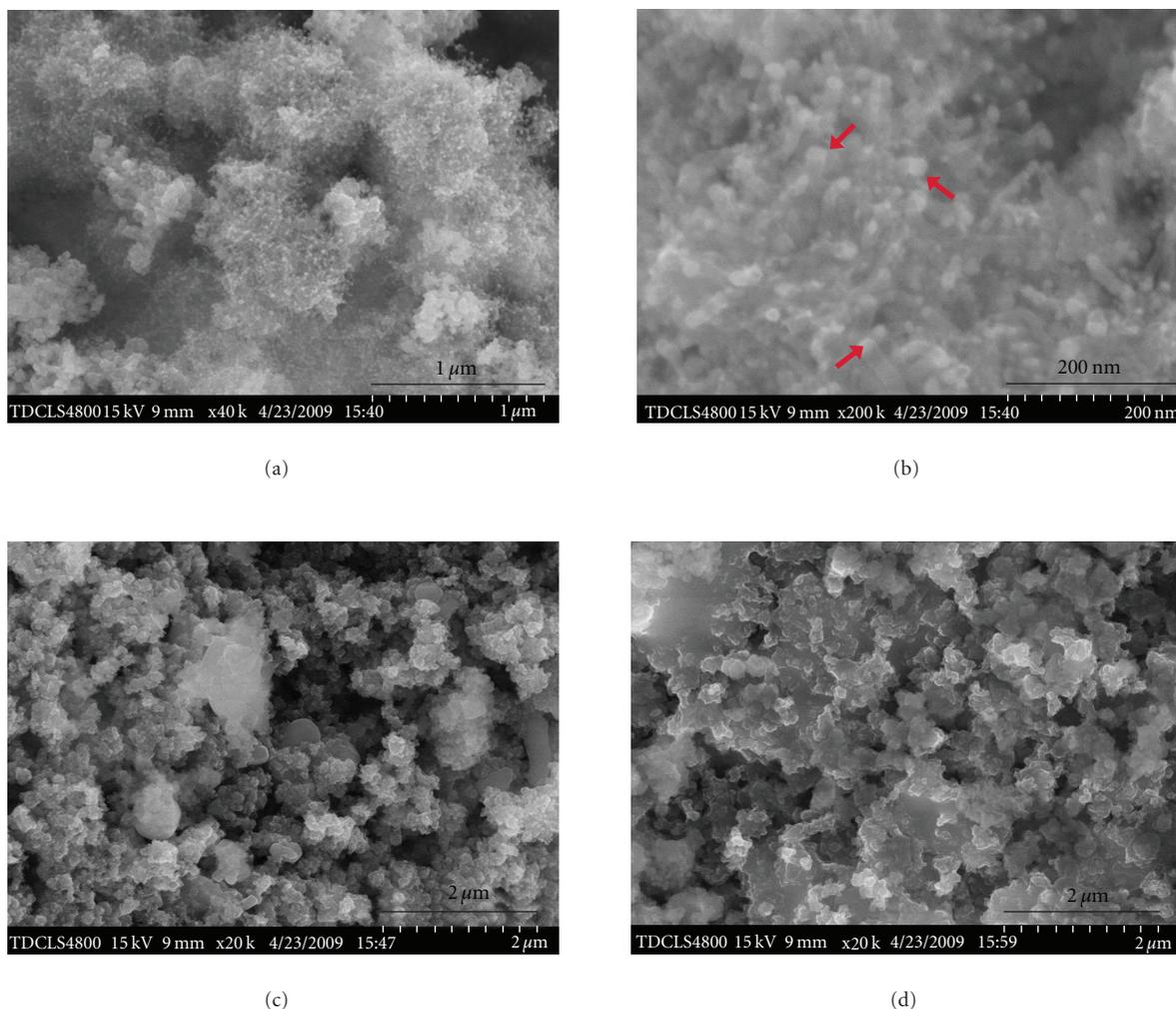


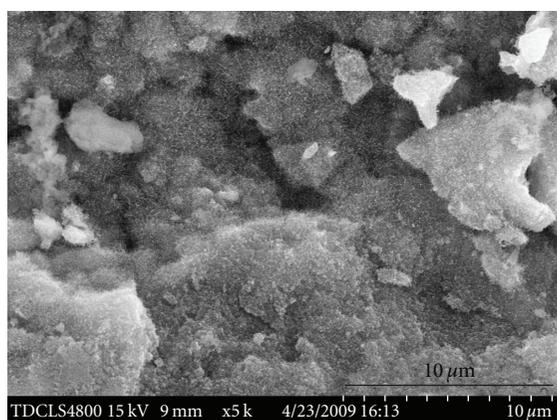
FIGURE 4: SEM images of the products obtained by CVD at different conditions using 10%Ni/Mg catalyst (a, b) at 400°C (c) at 450°C (d) at 500°C.

Based on the above analysis, it is obvious that the reaction between catalyst and support play an important role for the activity of the catalyst. Ni alloyed with Mg has no activity for the decomposition of methane. Thus, the key issue to use Mg as catalyst support is to prevent the reaction between Ni and Mg. Although Ni can be used as catalyst directly, the low activity of the catalyst will limit its further application in composite fabrication process. Preliminary results show that Y doped in Ni can elevate the reaction temperature between Ni and Mg0020 and promote the activity of the catalyst (52.3 wt.% carbon deposit obtained using Ni/Y catalyst compared to the mass of the raw catalyst, while only about 1 wt.% carbon deposit obtained using Ni catalyst). Thus, it is possible to obtain dispersed CNTs with higher quantity and quality using less Ni/Y catalyst supported on Mg powder by optimizing the process parameters. Mg oxidation can be reduced to a minimum content, which has little influence on the property of Mg composites, by using inert gas with higher purity and other solutions instead of water (to avoid the possible reaction between water and Mg). Thus, it is

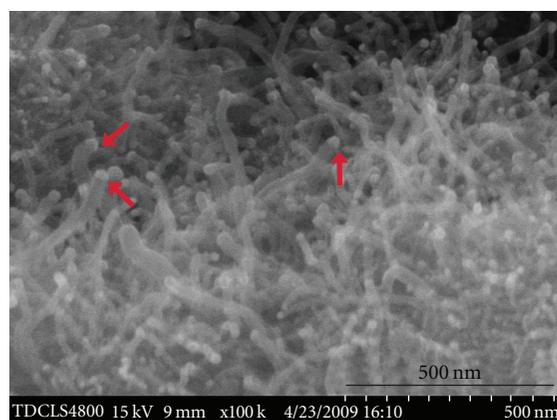
reasonable to prepare CNT/Mg composites with high CNT dispersion using the in situ synthesized CNT-Mg composite powders. Such work is in process.

4. Conclusions

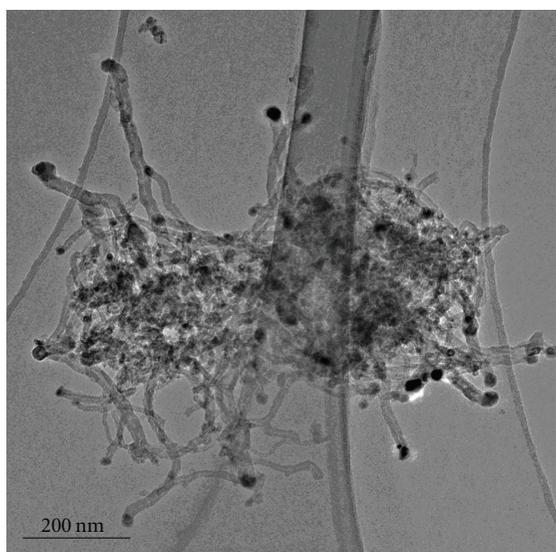
The present paper demonstrates that Mg powder can be used as a suitable catalyst carrier for the CNT growth by CVD. However, the chemical interactions between the catalyst and substrate should be avoided, because any Ni alloy with Mg demonstrates no activity for the decomposition of methane. The introduction of Y in Ni/Mg catalyst can promote the reaction temperature between Ni and Mg and thus enhance the activity of the catalyst. A large amount of CNTs with an average diameter of 20 nm was obtained by CVD using Ni/Y/Mg catalyst at 450°C, while only a few short CNTs were obtained using Ni/Mg catalyst due to the too low activity of the catalyst at lower temperature.



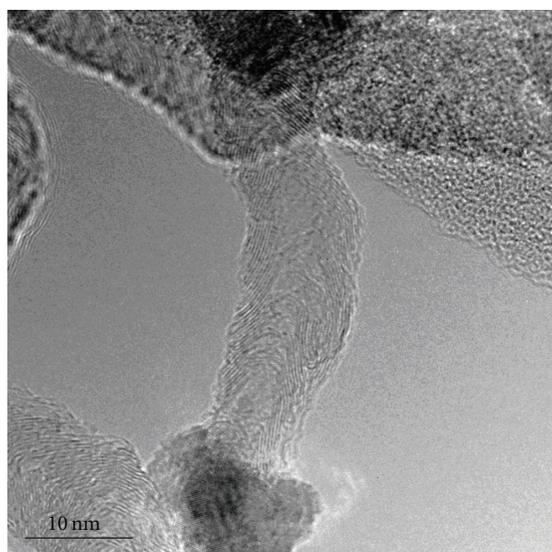
(a)



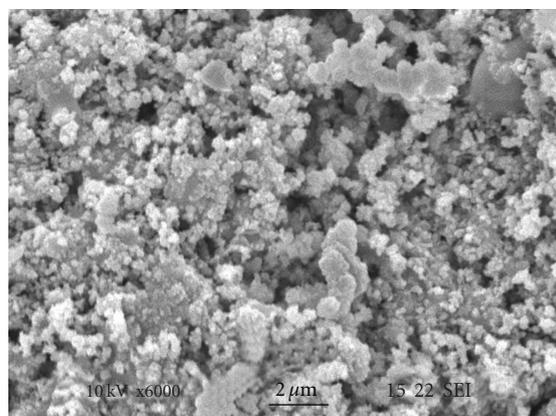
(b)



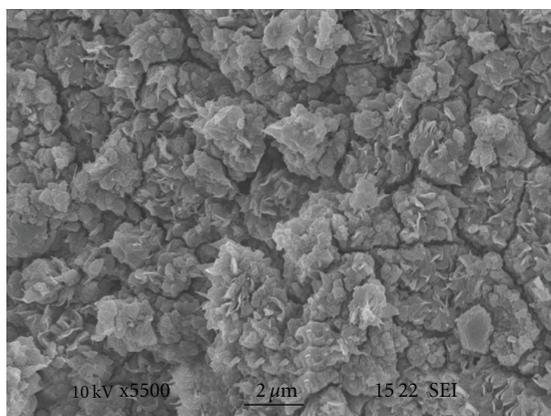
(c)



(d)



(e)



(f)

FIGURE 5: SEM and TEM images of the products obtained by CVD at different conditions using 16%Ni4%Y/Mg catalyst (a, b, c, d) at 450°C, (e) at 500°C, and (f) at 600°C.

Acknowledgments

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