Polypropylene Fibers Modified by Plasma Treatment for Preparation of Ag Nanoparticles

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A novel method for preparing poly(propylene-graft-2-methacrylic acid 3-(bis-carboxymethylamino)-2-hydroxy-propyl ester)-silver fibers (PPG-IAg fibers) by plasma-induced grafting polymerization is presented in this study. The chelating groups, $-N(CH_2COO^-)_2$ (GMA-IDA), on the surface of the PPG-I fibers are the coordination sites for chelating silver ions. At these sites, Ag nanoparticles were grown first by reduction with UV light with a wavelength of 366 nm, and second, through immersion in a 24% formaldehyde solution with pH values set variously at 2, 5, 8, and 11. The characteristics of the PPG-I fibers with differing durations of plasma treatment were monitored by using a Fourier transform infrared (FT-IR) spectroscope. Scanning electronic microscopy (SEM) and elemental analysis show that the percentage of GMA-IDA grafted onto PP fiber reaches a maximum when the plasma treatment time is 3 min. Plasma treatment time beyond a certain length of time results in an abundance of free radicals and causes considerable cross-linking on the fiber surface which thus decreases the extent of grafting. Moreover, the crystalline phase of Ag nanoparticles is identified by using X-ray diffraction (XRD). When the PPG-I fibers are reduced by the UV light method, SEM and TEM microscopes reveal that the size of the Ag nanoparticles on the fiber surface decreases significantly with the increase of pH values in aqueous solutions. Notably, in the reduction of formaldehyde solution, the particle size of Ag nanoparticles reaches a minimum at the lowest pH value. The TEM observations show that Ag nanoparticles are distributed both in the exterior and interior of the grafting layer. In addition, under high pH values the distribution of the Ag nanoparticles permeate more deeply in the GMA-IDA grafting layer due to the swelling effect of the GMA-IDA polymer.

Introduction

Nanoscale materials have attracted a great deal of attention for their interesting chemical and physical properties, which are significantly different from those of bulk solids.[1−3] Numerous methods by which nanoparticulate materials can be fabricated have been reported recently. Among them, using a polymer material as the template to grow nanomaterials which form nanocomposite matrixes has become a popular field of investigation for a number of researchers, due to the versatility of polymer. For example, Zhang et al.[4] used the microgel polymer, poly(N-isopropylacrylamide-acrylic acid-2-hydroxyethyl acrylate), as the template to grow zero-dimensional nanoparticles. Zhang et al.[5] synthesized poly(acrylic acid) and poly(n-butyl acrylate) core−shell cylindrical polymer brushes as a molecule template to grow one-dimensional wirelike CdS nanoparticles. Caruso et al.[6] used polystyrene (PS) latex to adsorb SiO_2−poly-(diallyldimethylammoniumchloride) (PDADMAC) multilayer films, to fabricate two-dimensional hollow inorganic hybrid spheres. Those methods have a similar characteristic in that an ionic functional group, such as carboxylic acid, is used to adsorb metal ions by ionic bonding with the polymer template and in that the inorganic nanocluster is formed in situ on the polymer template. However, the ionic bond between the metal ions and the polymer template is usually unstable in aqueous solution due to the hydration effect, and the metal ions thus will leave

the templates and agglomerate easily. To overcome this problem, high-stability bonding between metal ions and the polymer template is necessary as a replacement for ionic bonding. Fortunately, a chelating polymer, which has chelating groups, is suited to performing this function owing to its high metal stability constant. Ethylenediaminetetraacetic acid (EDTA) is well-known due to its strong chelating ability with metal ions and has been widely used in gas-membrane separation as well as detection of metal ions.[7,8] In fact, EDTA has been successfully introduced into the end of polymer chains and applied in the metal-chelated catalyst, as found in our previous study.[9] However, the number of the EDTA units in the polymer is too low to readily act as the template for generating nanoparticles. Thus, a chelating vinyl monomer, 2-methacrylic acid 3-(bis-carboxymethylamino)-2-hydroxy-propyl ester (GMA-IDA), which has an iminodiacetic acid chelating group, has been successfully synthesized and further copolymerized with the other vinyl monomers to manufacture the chelating copolymer with high adsorption of metal ions. In addition, this kind of metal-chelated copolymer has been utilized in a number of applications, including wastewater treatment,[10,11] gas-membrane separation,[12] organic synthesis catalysts,[13,14] and solid-state electrolytes.[15−17]

In this study, the GMA-IDA chelating monomer is introduced onto the surface of polypropylene fibers by the plasma-induced method[18−20] and then further applied to fabricate the hybrid nanocomposite fibers. The chelating groups of the GMA-IDA are used as the coordination site for chelating silver ions, at which ultrafine Ag particles were grown.

Recently, the incorporation of nanoparticles into polymer fibers and matrixes has attracted much interest in the textile

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SCHEME 1: Overall Procedure for the Preparation of Hybrid PPG-IAg Nanocomposite Fibers
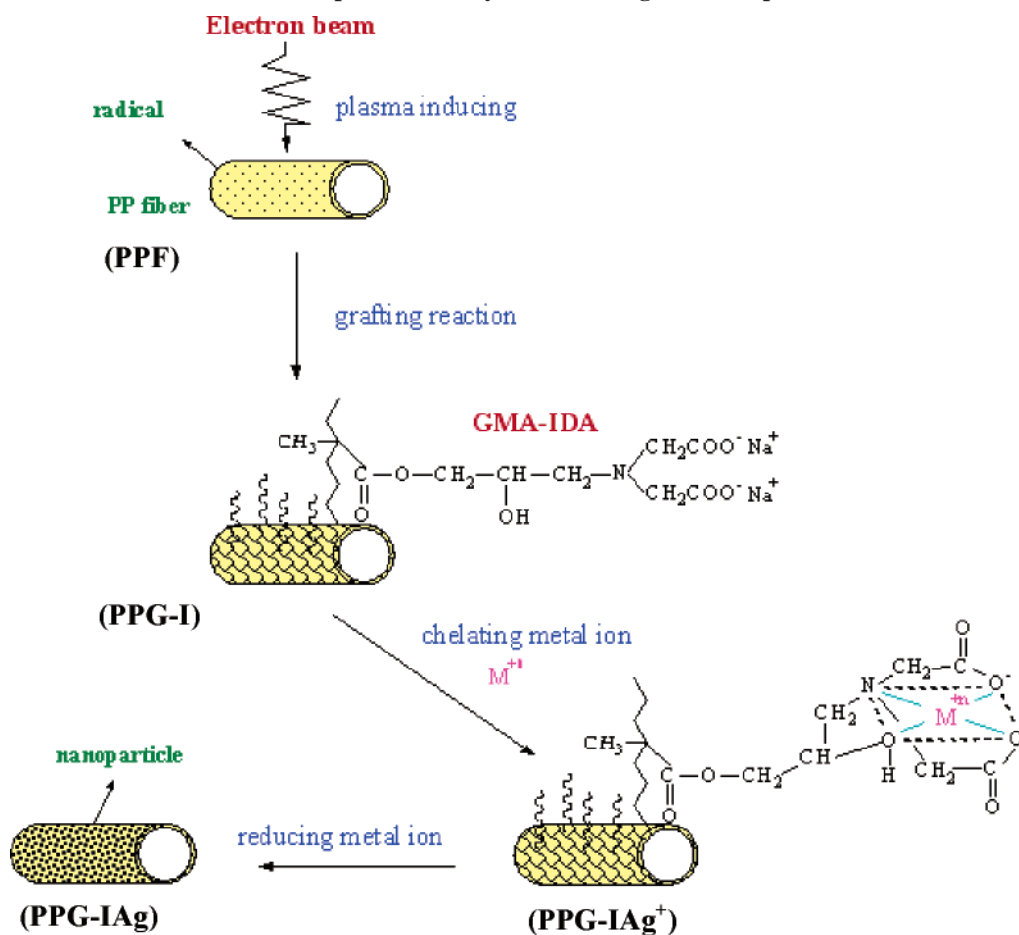
industry. Some researchers[21,22] have claimed that fibers into which Ag nanoparticles are incorporated have antibiotic characteristics. However, the method reported for producing nanocomposite fibers usually involves blending the polymer with nanoparticles before spinning. Since special fibers are sometimes derived from the nanoparticles themselves, one of the major challenges in preparing such materials is to prevent aggregation of clusters in the host matrix. In addition, some of the special functions of a fiber, such as bioactivity, depend on the dispersal of the nanoparticles on the surface of the fiber. The advantage of the in situ technique presented herein is that not only can all the free silver ions in solution be removed simply by washing in order to prevent the aggregation of the Ag nanoparticles during reaction but also that a solution is presented for the problem of redispersion of nanoparticles on the polymer template. Additionally, this approach can be further utilized for preparing various other nanomaterials, such as copper (Cu) and nickel (Ni) metal nanocomposites, as well as cadmium sulfide (CdS) and zinc sulfide (ZnS) semiconductor nanocomposites.

Experimental Section

Materials. Polypropylene fibers (PPFs) were provided by Fehrer Enterprise Corporation, Republic of China. The diameters of the PPFs were in the range of 10 to $\sim$20 μm. Glycidyl methacrylate (GMA) (Merck Co.) was purified by vacuum distillation method. Iminodiacetic acid (IDA) (Aldrich Co.), silver nitrate (Fluka Co.), and formaldehyde (Fluka Co.) were used as received.

Synthesis of PPG-I Fibers. The plasma treatment was carried out in a parallel plane electrode reactor, and the volume of the

TABLE 1: Abbreviation Names of the Polypropylene Fiber Derivatives

symbols	representation
PPG-I	PP fibers[a] grafted poly(GMA-IDA)[b]
PPG-IAg+	PP fibers grafted poly(GMA-IDA) and chelate Ag+ until saturation
PPG-IAg	PPG-IAg+ are reduced to form hybrid Ag nanocomposite fibers

[a] Polypropylene fiber (PP fiber). [b] Poly(2-methylacrylic acid 3-(bis-carboxymethylamino-2-hydroxy-propyl ester)) (GMA-IDA).

stainless steel vacuum chamber was about 5×10^3 cm^3. The electrodes were made of circular Cu plates (diameter = 5 cm) which were separated at a distance of 5.5 cm. The fiber films were also cut into circle shapes with a diameter of 2 cm and individually subjected to plasma treatment. Prior to starting up the plasma reaction, the pressure was reduced to 10^{-6} torr in the reactor. Then, pure Ar gas was introduced into the reactor via a leak valve at a flow rate of 50 mL/min, and the vacuum pressure of the plasma reactor was controlled well at 0.1 torr by using the throttle valve. The electrical power of plasma was supplied by an RF power generator operating at 50 W and at 13.56 MHz.

Scheme 1 illustrates the procedure of our method. At the beginning, a large number of radicals were generated on the surface of PPFs by plasma treatment, and then the chelating vinyl monomer, 2-methacrylic acid 3-(bis-carboxymethylamino)-2-hydroxy-propyl ester (GMA-IDA), which was synthesized by following our previous study,[23] was injected into the reactor to graft onto the surface of PPFs at 30 °C for 2 h. After the grafting polymerization, the polypropylene grafted GMA-IDA fibers
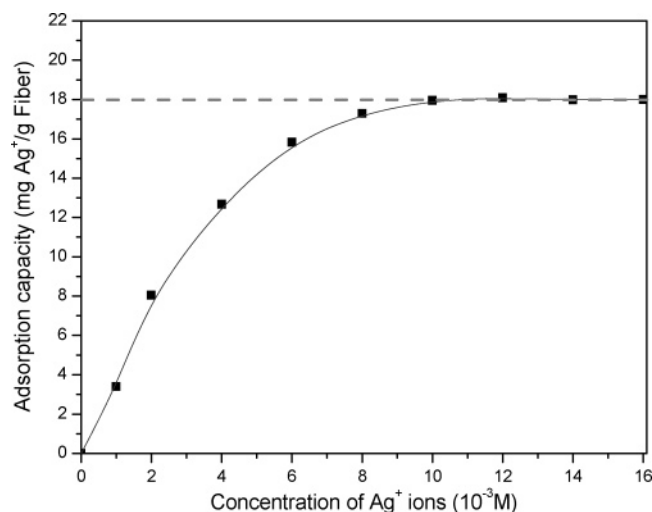
Figure 1. Isothermal absorption curve of the PPG-I fibers at different concentrations of Ag+ solutions at 30 °C for 24 hr.

Figure 2. FT-IR spectra of (a) polypropylene fiber, (b) GMA-IDA polymer, (c) PPG-I fiber, and (d) PPG-IAg+ fiber.

(PPG-I) were purified by distilled water and were immersed in Ag+ solution (1×10^{-2} M) to chelate silver ions until equilibrium (PPG-IAg+). Finally, the PPG-IAg+ fibers were reduced, respectively, by UV light with a wavelength of 366 nm and through immersion in a formaldehyde solution to form PPG-IAg nanocomposite fibers. Table 1 represents the symbols used in this study.

PPG-I fibers, which were modified by plasma treatment for 3 min, were immersed in different concentrations of Ag+ solution at 30 °C for 24 h. Then the PPG-IAg+ fibers were washed by distilled water several times to remove the free (unchelated) Ag+. The amount of the Ag+ chelated on the PPG-IAg+ fiber is extracted by nitric acid and determined by atomic absorption spectrophotometry. Figure 1 is the isothermal absorption curve of PPG-I fibers at different concentrations of Ag+ solutions at 30 °C for 24 h. From the result of the isothermal absorption curve, the amount of the Ag+ chelated increases as the immersion concentration of the Ag+ solution increases. The maximum adsorbed concentration of Ag+ on the PPG-I fiber is 18 mg of Ag+/g of fiber at the concentration of 0.01 M Ag+ solution.

The swelling measurement is carried out as follows: the PPG-I fibers were immersed in the aqueous solutions of pH = 2, 5, 8, and 11 for 5 h until equilibrium, then it was removed from the aqueous solution, wiped with tissue paper to remove excess water, and weighed. The swelling percentage is calculated as shown:

Swelling (%) =
((Swollen mass − Original mass)/Original mass) × 100

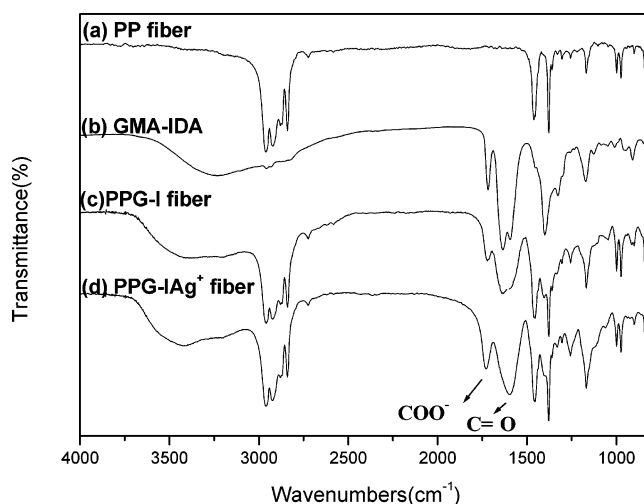**Identification.** The X-ray diffraction (XRD) patterns were recorded on a Rigaku ATX-E diffractometer equipped with graphite monochromated Cu Kα radiation ($\lambda = 0.15405$ nm) operated at 30 mA and 40 kV from $2\theta = 10-90°$. Field emission scanning electron microscopy (SEM; Hitachi S4200) and transmission electron microscopy (TEM; Hitachi model HF-2000) were used to observe the size and morphology of the Ag nanoparticles. The amount of Ag+ chelated is determined by an atomic absorption spectrophotometer (AA; Perkin-Elmer, Analyst 100). Fourier transform infrared (FT-IR; Bio-Rad FT-IR spectrometer,) spectra were recorded from 700 to 4000 cm^{-1} at room temperature. Before the IR measurement, the fiber samples were ground and pressed into a tablet.

Results and Discussion

Surface Modification of the Polypropylene Fibers. FT-IR spectra, as shown in Figure 2, are used to monitor the surface modification of PPFs in the plasma treatment. The absorption peaks of the pristine PPFs (Figure 2a) are respectively assigned as follows; −CH stretching vibrations at 2840 to ∼3000 cm^{-1} and the asymmetric and symmetric stretching of −CH in PP fibers at 1375 and 1450 cm^{-1}. After the grafting of the GMA-IDA polymer, the absorption band at 1725 cm^{-1} is caused by the stretching vibrations of the ester carbonyl groups and the strong band at 1633 and 1399 cm^{-1} is associated with the asymmetric and symmetric stretching of C=O in carboxylate salts (−COO$^-$Na$^+$) (Figure 2b). This result is consistent with the final composition of the PPG-I fibers that includes both polypropylene and GMA-IDA units (Figure 2c). In addition, as the PPG-I fibers chelated with silver ions, PPG-IAg+ fibers, the peak position of carboxylate group (−COO$^-$Na$^+$) at 1633 cm^{-1} shifted to 1594 cm^{-1} (Figure 2d) due to coordination chemistry,[24] which demonstrates that the PPG-I fibers have the ability to chelate with metal ions. The above results present

TABLE 2: Percentage of the GMA-IDA Grafted onto the PP Fibers Measured by Elemental Analysis and the Change of Fiber Weight[a]

plasma modification treatment times (min)	elemental analysis				variations of fiber weight		
	C (wt %)	H (wt %)	N (wt %)	GMA-IDA grafting percentage (wt %)	W_0 (g)	W_1 (g)	GMA-IDA grafting percentage (wt %)
1	77.68	12.86	1.02	30.3	0.080	0.106	32.5
2	76.87	12.43	1.57	55.6	0.080	0.126	58.3
3	76.52	11.95	1.93	79.8	0.080	0.146	82.9
4	77.31	12.78	1.19	37.5	0.080	0.113	41.2
5	78.64	13.01	0.07	19.4	0.080	0.099	24.7

[a] Grafting percentage (wt %) by the change of fiber weight = $100(W_1 - W_0)/W_0$. W_0 = fiber weight before the GMA-IDA is grafted; W_1 = total weight after the GMA-IDA is grafted.

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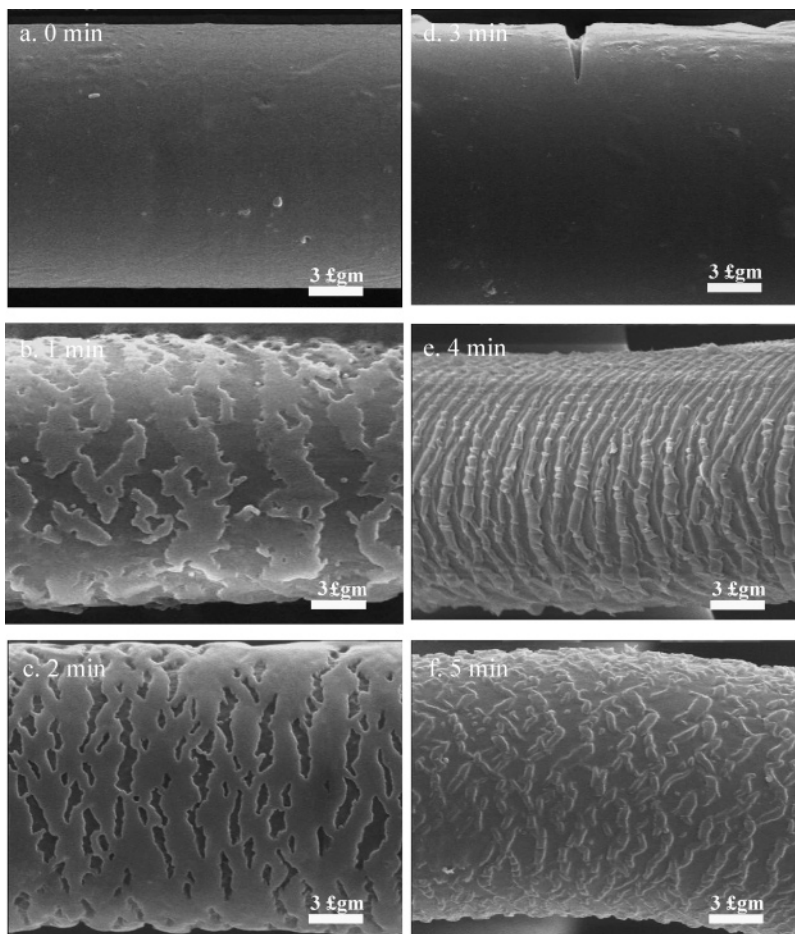*J. Phys. Chem. B, Vol. 110, No. 9, 2006* **4023**

Figure 3. SEM images of the PPG-I fibers; plasma treating times are (a) 0 min, (b) 1 min, (c) 2 min, (d) 3 min, (e) 4 min, and (f) 5 min.

that the chelating group, GMA-IDA, is successfully grafted onto the surface of PPFs.

The degree of grafting of the GMA-IDA polymer on PPFs is measured by two methods: elemental analysis and the changes in fiber weight recorded before and after the grafting polymerization, as shown in Table 2. From the results of the elemental analysis as well as the changes of fiber weight, the percentage of the GMA-IDA grafted onto the PPFs increases as the time of plasma treatment increases from 1 to 3 min. However, this percentage starts to decrease as the treatment time is over 3 min. It has been reported that plasma treatment of polymer past a certain time generates a large number of free radicals and results in considerable cross-linking[25] on the surface of PP fibers which decreases the percentage of grafting of the GMA-IDA polymer.

In addition, an SEM is used to observe the surface morphology of the PPG-I fibers. Figure 3 shows the SEM images of the PPG-I fibers as the time of plasma treatment is increased from 1 to 5 min. Figure 3a shows an SEM image of pristine PPFs which shows a smooth surface; Figure 3b illustrates the change in the PPG-I fibers after a 1 min plasma treatment, clearly showing that a layer of grafted GMA-IDA polymer has partially covered the pristine PPFs. Notably, the GMA-IDA polymer layer spreads extensively with the increase of the time of plasma treatment until a complete coverage on the PP fibers is reached at the time of 3 min (Figure 3b−d). The grafting percentage of the GMA-IDA polymer, however, starts to decrease as the plasma treatment time exceeds 3 min (Figure 3, parts e and f) which, corresponds to the results of elemental analysis. To summarize the EA and SEM results, the 3 min plasma treatment time produces a uniform and full coverage of
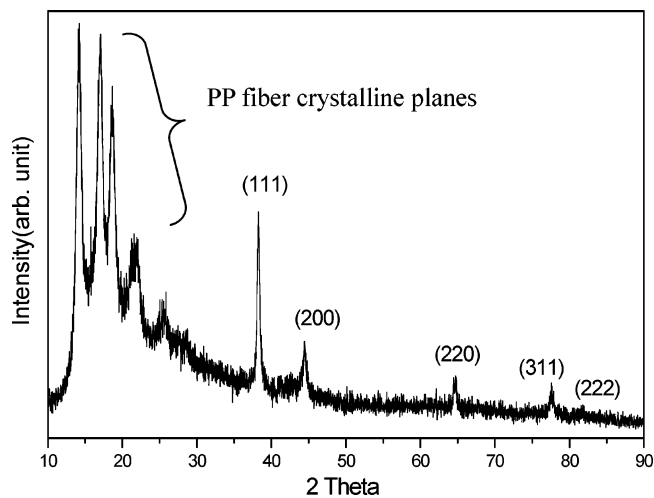

Figure 4. XRD diffraction pattern of the PPG-IAg fibers.

GMA-IDA polymer; the fully covered PPG-I fibers were chosen as the template for the subsequent formation of Ag nanocrystals in this study.

Preparation of PPG-IAg Hybrid Fibers. Here we proposed two methods, the UV light exposure and the formaldehyde reduction, that are employed to prepare the Ag nanoclusters on the surface of the PPG-I fibers, PPG-IAg fibers. The PPG-I fibers were immersed in different pH aqueous solutions (pH = 2, 5, 8, and 11) until equilibrium, and then the Ag^+/polymer complex was first reduced by the UV light exposure method, and second, through immersion in a 24% formaldehyde solution with pH values set variously at 2, 5, 8, and 11.
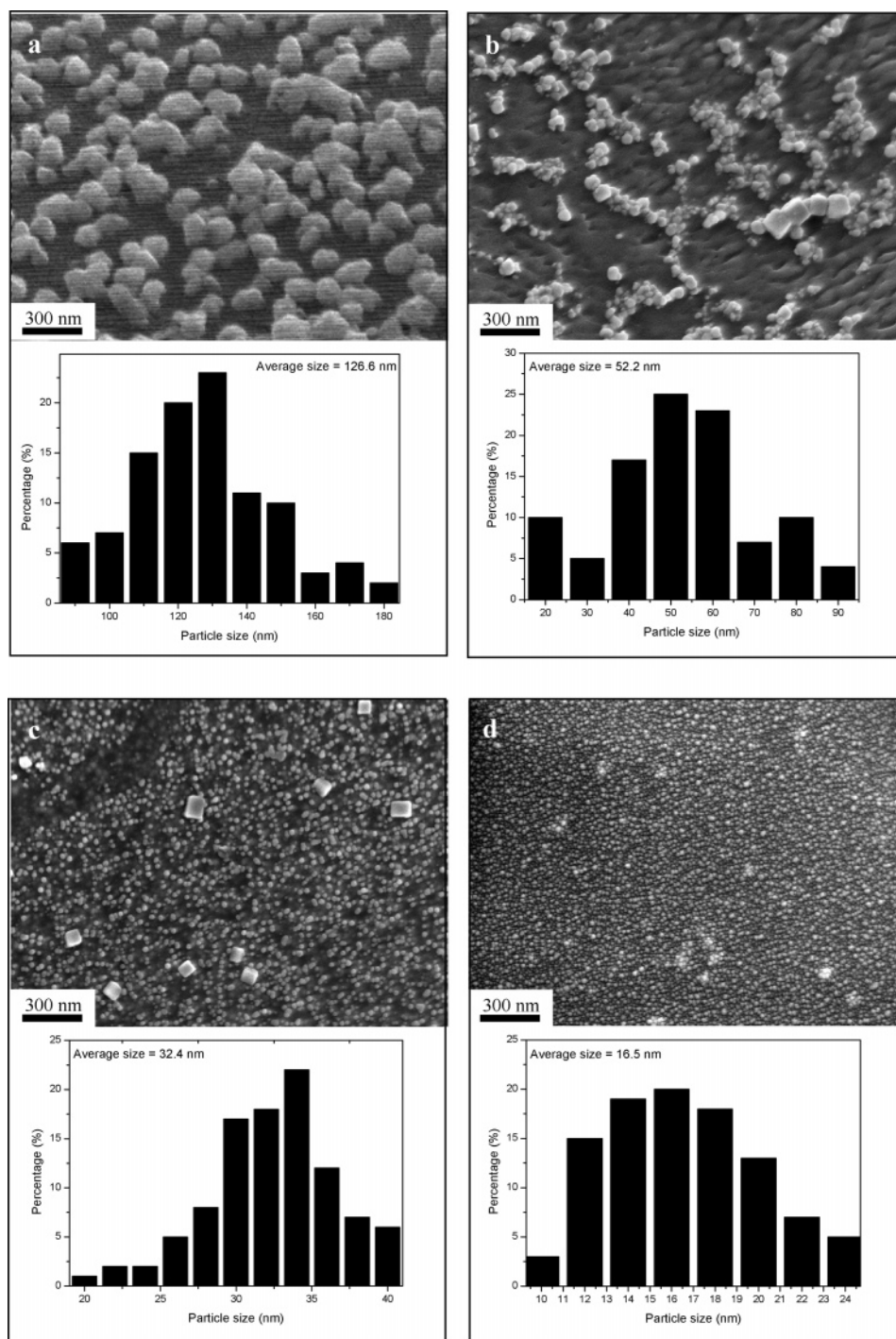
Figure 5. SEM images of the PPG-IAg fibers reduced by UV light with a wavelength of 366 nm under different pH conditions: (a) pH = 2, (b) pH = 5, (c) pH = 8, (d) pH = 11.

The XRD diffraction pattern of the PPG-IAg hybrid fibers are shown in Figure 4. The broad peak in the spectrum at $2\theta =$ 13° to ~22° corresponds to a crystalline phase of polypropylene. The other five peaks at 2θ values of 38.2°, 44.3°, 64.5°, 77.0°, and 81.8° are corresponding to the (111), (200), (220), (311), and (222) crystalline planes of silver, respectively. All the peak positions are consistent with those of bulk silver. Restated, no peaks resulted from impurities suggest that the Ag nanoparticles are highly pure silver which is very important in preparing silver nanocrystals, since silver nanoparticles are prone to oxidation during the preparation. Moreover, the peaks of the crystalline silver obtained here are much broader than those corresponding

to bulk silver. Generally, smaller particles yield broader XRD peaks revealing nanosized silver particles are formed in this study.[26]

Figure 5 presents the SEM images of the PPG-IAg nanocomposite fibers reduced by the method of UV light. From the SEM images, the mean diameters of the nanoparticles in Figure 5a–d are 126.6 nm, 52.2, 32.4, and 16.5 nm, respectively, which correspond to the reduction condition pH values of 2, 5, 8, and 11. The particle size of Ag nanoparticles on the fiber surface clearly decreases with an increase in pH value. Moreover, the TEM images of the cross section of the PPG-IAg fibers which were prepared by using microtome also show that the mean
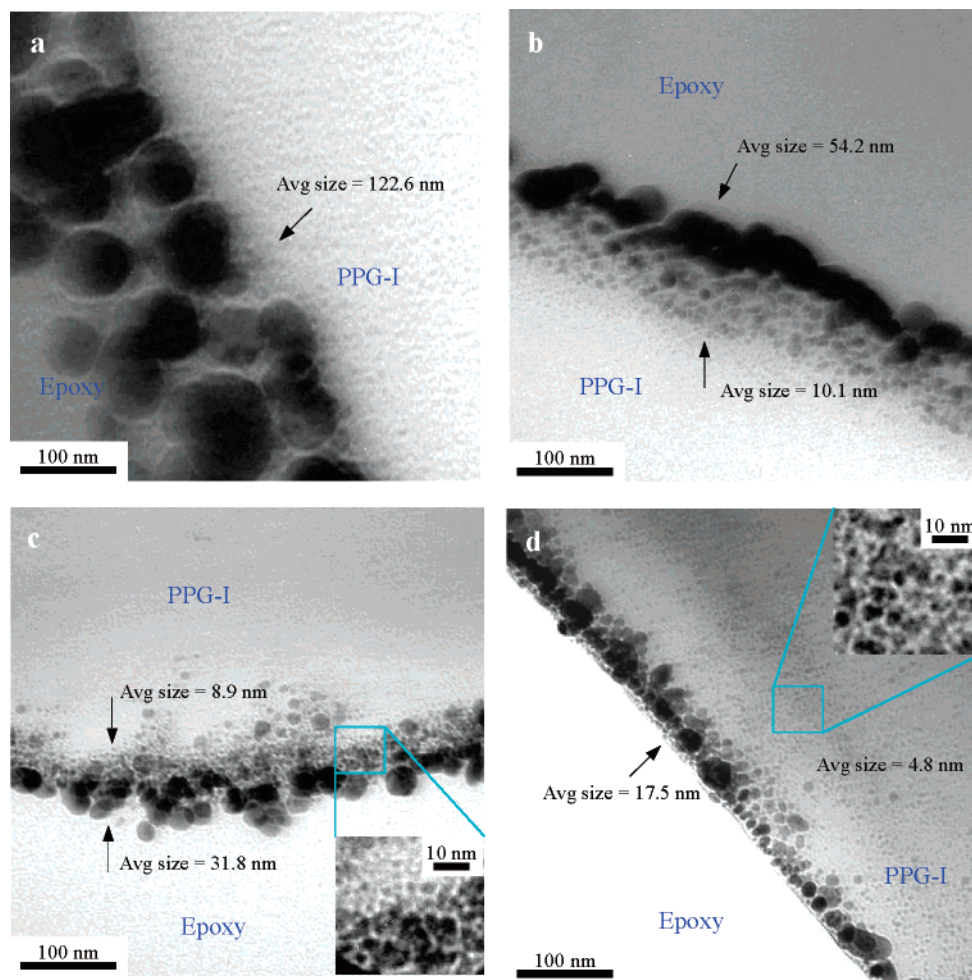
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Figure 6. TEM images of the PPG-IAg fibers reduced by UV light with a wavelength of 366 nm under different pH conditions: (a) pH = 2, (b) pH = 5, (c) pH = 8, (d) pH = 11.

diameter of the Ag nanoparticles decreases with the pH value. Both the SEM and TEM images illustrate that the Ag nano-clusters are not only formed on the surface of the PPG-I fibers but also formed within their interior. Significantly, the results of the pH values of 5 and 8 reveal bimodal size distribution of Ag nanoparticles. With a pH value of 5, the mean diameters of the outer and interior particles are 54.2 and 10.1 nm, respectively. For a pH value of 8, the respective outer/inner measures are 31.8 and 8.9 nm. We can derive this result from the following condition: the Ag nanoparticles formed in the interior of the PPG-IAg$^+$ fibers are protected by the GMA-IDA polymer chains, which inhibit the aggregation of Ag nanoparticles and lead to a smaller particle size. This result demonstrates that the GMA-IDA polymer performs the same function as surfactant in preventing the aggregation of nanoclusters. In contrast, the Ag nanoparticles which have been reduced on the surface of the PPG-I fibers agglomerate easily due to the thermodynamic unstability of nanoclusters and the lack of that protection of the polymer. However, as the pH value increases, one can observe that the mean size of the Ag nanoparticles formed on the PPG-I fibers will become smaller. This result can be attributed to the propensity of the carboxylate groups (−COO$^-$-Na$^+$) of the GMA-IDA polymer to form a −COO$^-$ structure in aqueous solutions; thus, the GMA-IDA polymer chains become more hydrophilic from the result of swelling effect which varies with different pH solutions, as shown in Figure 7. Figure 7 displays that the GMA-IDA polymer is greatly swelled by water at high pH values. In fact, nearly all of the silver ions chelated
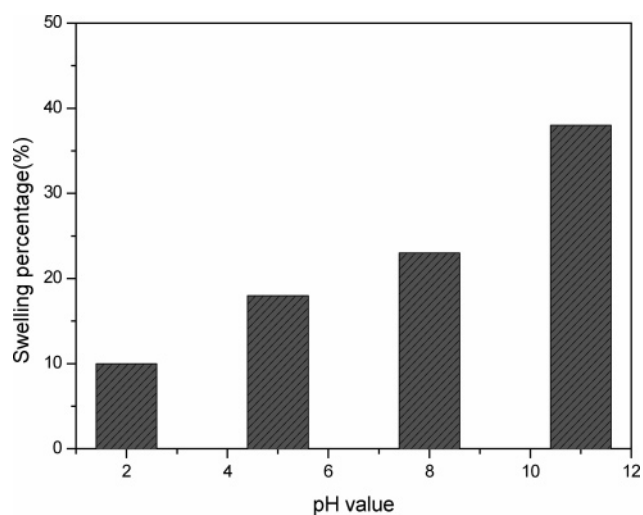

Figure 7. Swelling percentage of the GMA-IDA polymer under different pH values in aqueous solution.

by the GMA-IDA polymer distribute on the surface of the PPG-IAg$^+$ fibers. As the result of the swelling effect, the chelated silver ions within the GMA-IDA polymer can redisperse because the free volume of GMA-IDA polymer chains has become larger. In other words, the chelated silver ions, in the region near the surface of the PPG-IAg$^+$ fibers, can permeate deeply into the interior of the GMA-IDA polymer domains due to the

SCHEME 2. Formation Mechanism of Ag Nanoparticles on the Surface of PPG-IAg$^+$ Fibers Reduced by UV Light with a Wavelength of 366 nm
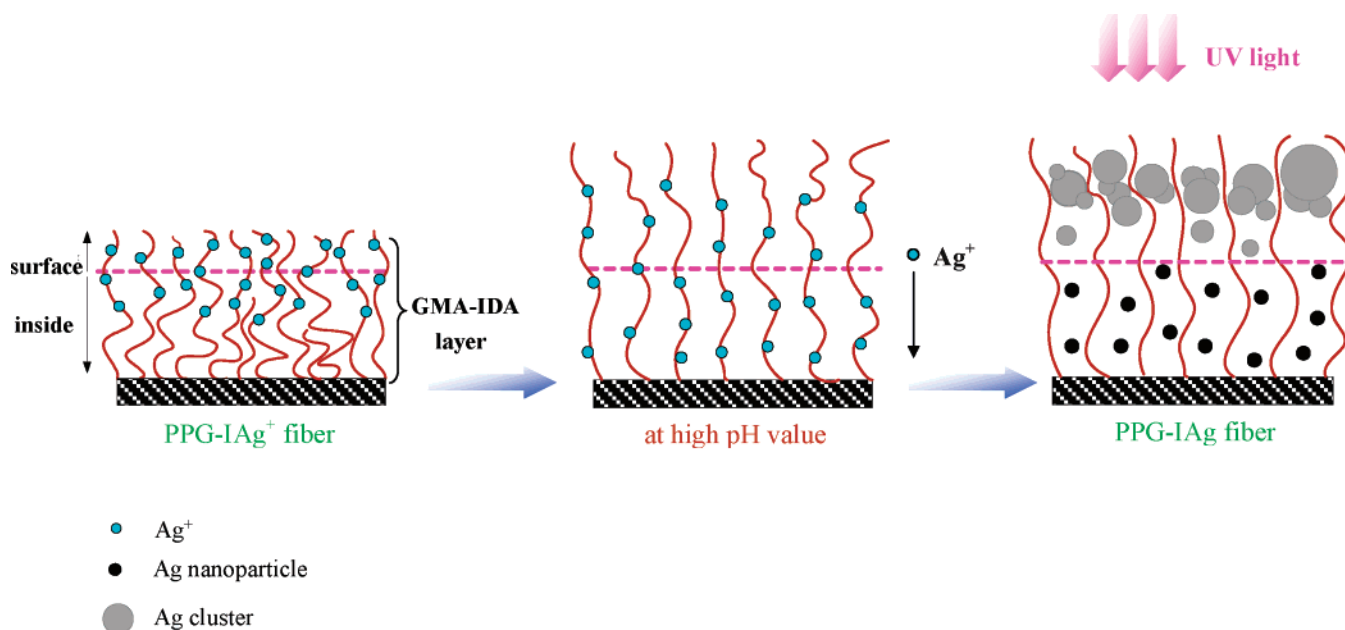
SCHEME 3: Formation Mechanism of Ag Nanoparticles on the Surface of PPG-IAg$^+$ Fibers Reduced by Formaldehyde Solutions
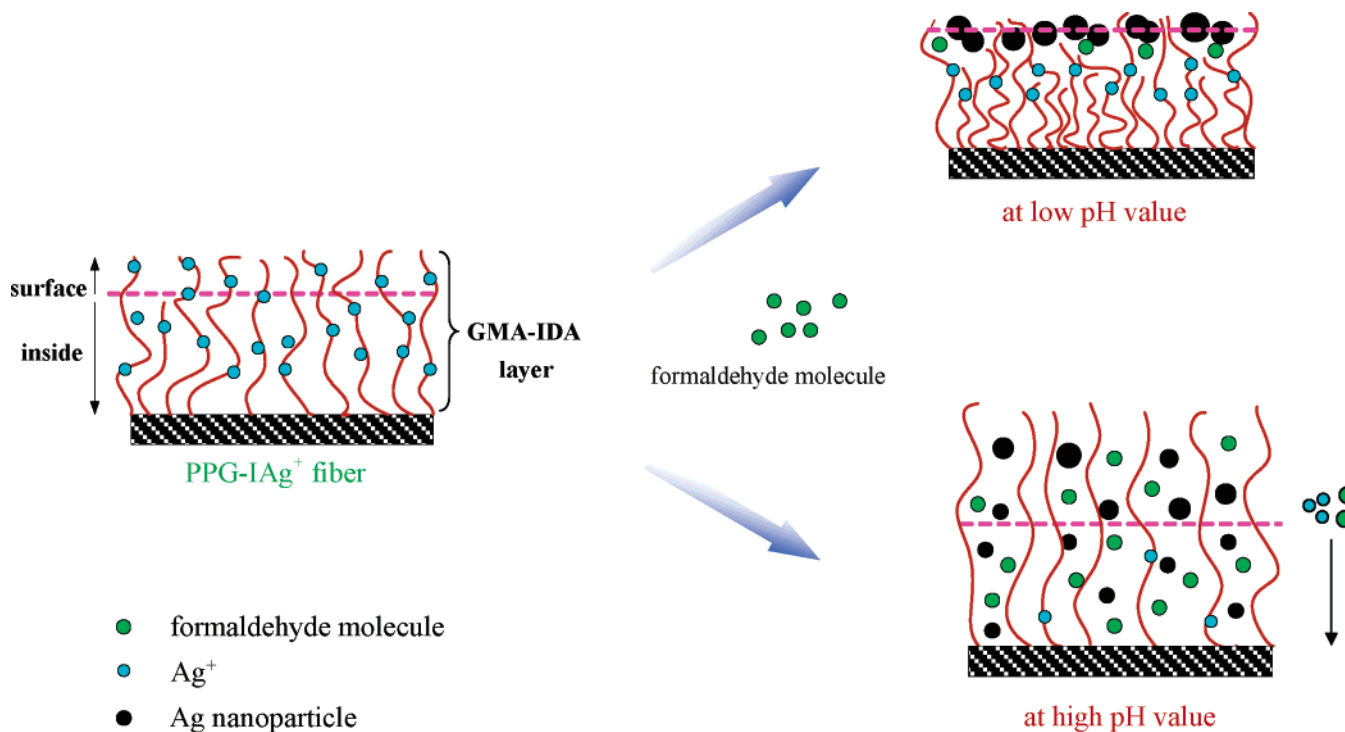
concentration equilibrium effect. Hence, the decreasing concentration of the chelated silver ions near the surface results in low particle density of Ag nanoparticles when they are reduced by UV light; thus, the nanoparticles reduced near the surface have less opportunity to collide with each other which results in a small particle size at high pH values. This hypothesis is supported by the TEM image at a pH value of 11 (Figure 6d) which shows the smallest size of Ag nanoparticles for any pH value, namely, a mean diameter of 17.5 nm around the surface and a mean diameter of 4.8 nm inside the GMA-IDA polymer domains. This result demonstrates that the silver ions in fact diffuse into the inner region of the PPG-I fibers. The formation

mechanism of Ag nanoparticles reduced by UV light is proposed in Scheme 2.

A second method for reducing the PPG-IAg$^+$ fibers was also explored: reducing the fibers with 24% formaldehyde solutions with different pH values. Figure 8a−d shows the SEM images of the PPG-IAg nanocomposite fibers which were reduced by formaldehyde solutions with pH values of 2, 5, 8, and 11, respectively. The mean diameters of the nanoparticles are 12.9 nm, 129.9, 57.8, and 23.6 nm corresponding to the respective pH values 2, 5, 8, and 11. Interestingly the minimum particle size of Ag nanoparticles is shown at the lowest pH value (pH = 2) by the reduction of formaldehyde solution. This result
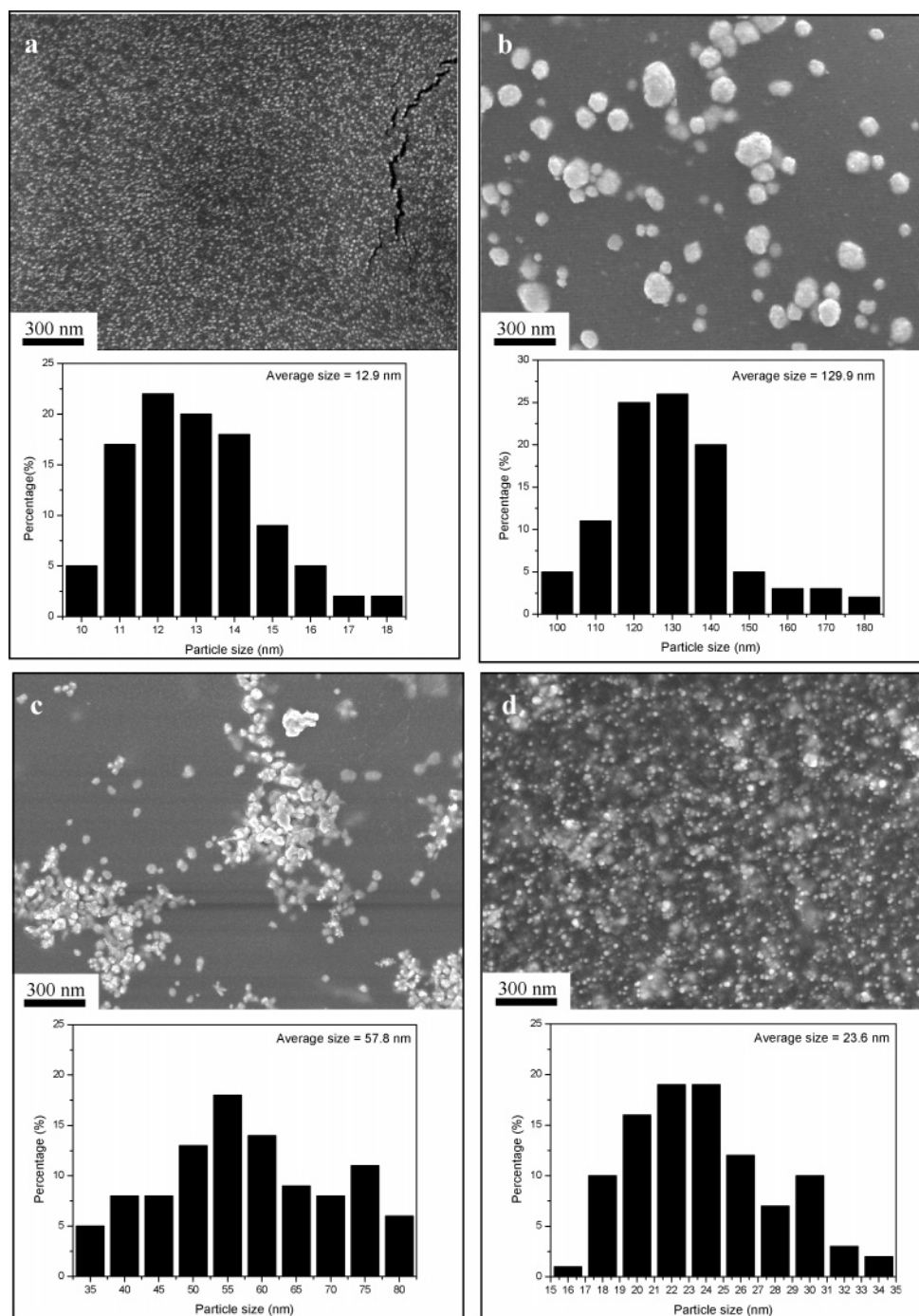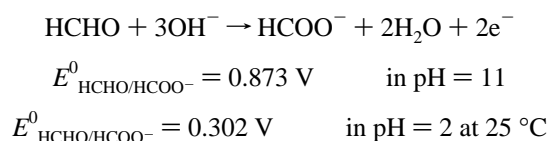
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Figure 8. SEM images of the PPG-IAg fibers reduced by 24% formaldehyde solutions under different pH conditions: (a) pH = 2, (b) pH = 5, (c) pH = 8, (d) pH = 11.

seems to contradict the formation mechanism that the particle size shrinks with the increase of pH value as the PPG-IAg$^+$ fibers were reduced by the UV light method, which we proposed in the last paragraph. However, we suppose that in addition to the swelling effect, some other factor is a key influence on the formation of Ag nanoparticles on the PPG-IAg$^+$ fibers as reduced by a formaldehyde solution. According to reports in the literature,[27] the reduction potential of formaldehyde will change by pH value, as follows:

$$HCHO + 3OH^- \rightarrow HCOO^- + 2H_2O + 2e^-$$

$$E^0_{HCHO/HCOO^-} = 0.873 \text{ V} \qquad \text{in pH} = 11$$

$$E^0_{HCHO/HCOO^-} = 0.302 \text{ V} \qquad \text{in pH} = 2 \text{ at } 25 \text{ °C}$$

This process is governed by the fact that at a high pH value (pH = 11) the formaldehyde solution has a much higher reduction potential than that of a low pH value (pH = 2). Therefore, the low reduction potential of the formaldehyde solution contributes to a weak reduction ability which can only reduce part of the silver ions on the PPG-IAg$^+$ fibers. The smaller mean diameter of Ag nanoparticles on the surface of the PPG-I fibers is attributed to a small number of Ag nanoclusters formed together even though the GMA-IDA polymer chains are densely spaced at a low pH condition. This result can be confirmed by the observation using a TEM (Figure 9a) which displays only a thin filmlike distribution of small particles of mean diameter of 10.6 nm near the surface region under a low pH condition. The number of Ag nanoparticles on
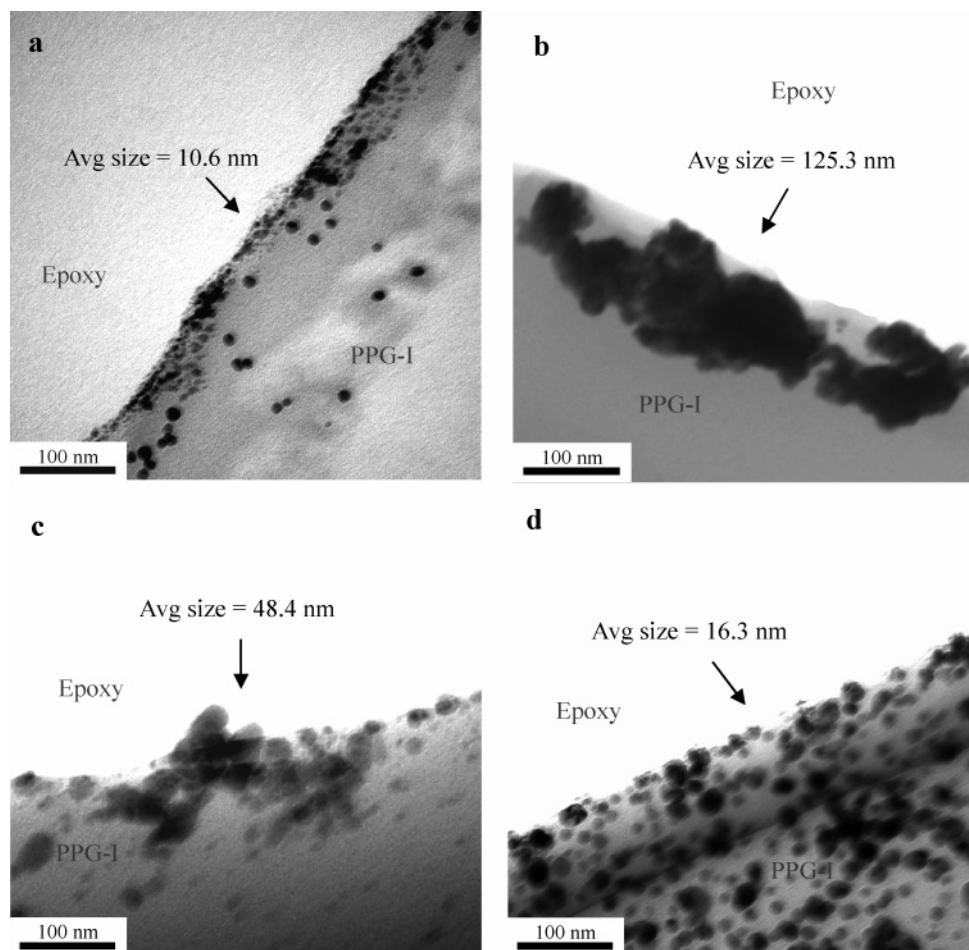
Figure 9. TEM images of the PPG-IAg fibers reduced by 24% formaldehyde solutions under different pH conditions: (a) pH = 2, (b) pH = 5, (c) pH = 8, (d) pH = 11.

the surface of the PPG-I fibers is clearly lower than that of the other samples. In other words, the effect of the reduction ability of formaldehyde solution in the formation of the Ag nanoparticles is a more important factor than that of the GMA-IDA polymer chains at low pH condition. Apart from a pH value of 2, the results of pH = 5, 8, and 11 (Figure 9b−d) corresponding to the respective mean diameter of 125.3, 48.4, and 16.3 nm, produced a similar result to the UV light reduction method, in which the mean diameter of Ag nanoclusters consistently decrease with the increase of pH value. Notably, the Ag nanoparticles distribute more deeply in the surface layer of PPG-I fibers at pH = 11 than that at pH = 5. This is because at higher pH values of the formaldehyde solutions not only do the silver ions diffuse into the interior of the PPG-I fibers, the reduction agent, formaldehyde molecules, diffuse inward as well. Hence, the distribution region of Ag nanoparticles in the surface layer of the PPG-I fibers becomes deeper with the increase of pH value. The formation mechanism of Ag nanoparticles reduced by a formaldehyde solution is proposed in Scheme 3.

In summary, the hybrid PPG-IAg nanocomposite fibers are successfully fabricated by both the reduction of UV light with a wavelength of 366 nm as well as the formaldehyde solution according to this investigation. The formation mechanism of nanoparticles is that metal ions are first chelated by a chelating group, then reduced in situ by a reduction agent. This approach can be further utilized for preparing various other nanomaterials such as copper (Cu) and nickel (Ni) metal nanocomposites, as well as cadmium sulfide (CdS) and zinc sulfide (ZnS) semiconductor nanocomposites.

Conclusion

The GMA-IDA chelating groups are successfully grafted onto PP fibers via a plasma-induced method from which the resulting PPG-I fibers are used as the template to grow Ag nanoparticles. SEM and TEM images demonstrate that the particle sizes of Ag nanoparticles decrease with the increase of pH value in the UV light reduction method. However, when a formaldehyde solution is used as the reduction agent, the particle size reaches a minimum at the lowest pH value due to the weak reduction ability of the formaldehyde solution. The method of using functional chelating groups as a template in preparation of Ag nanoparticles is highly efficient and feasible. Through this method, the particle size can be controlled on a nanoscale at specific pH conditions.

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