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Preparation of copper nanoparticle-improved polyamide 6 composites by in-situ solution route with cupric oxide as metallic copper source and investigation of their properties

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Abstract: A novel *in-situ* solution synthesis strategy is adopted to prepare polyamide 6 (denoted as PA6) filled by copper nanoparticles (denoted as nano-Cu), with which CuO filler as the source of nano-Cu is directly reduced to metallic Cu by the amino group possessing weak reducing capability of PA6. As-prepared nano-Cu/PA6 composites are characterized by means of transmission electron microscopy and X-ray diffraction. Moreover, the ultraviolet-visible light absorption behavior, the thermal stability, and the friction and wear behavior of as-prepared nano-Cu/PA6 composites are also investigated in relation to the reinforcing effect of metallic Cu nanoparticles. Findings indicate that CuO filler can be readily reduced to metallic Cu by the reducing atmosphere in which the filled PA6 composites are prepared. Besides, the dosage (mass fraction) of CuO has significant effect on the crystalline form of PA6, and γ crystalline form of PA6 is predominant when higher dosage of CuO is introduced to fabricating nano-Cu/PA6 composites. Moreover, introducing a proper amount of CuO filler favors to generate nano-Cu/PA6 composites with improved mechanical properties and wear resistance. Particularly, nano-Cu/PA6 composite prepared at a CuO content of 0.5% possesses the best tensile strength and wear resistance, showing promising application as a functional

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polymer-matrix composite.

Keywords: Particle-reinforced composites; Mechanical properties; Nano composites

1. Introduction

Metal nanoparticles are interesting in engineering, because they have potential application in magnet, ceramic, and semiconductor [1-3]. Recently, polymer-metal nanocomposites are considered to be interesting functional materials due to their outstanding improvement on catalytic, mechanical, frictional, and electrical properties by using metal nano-materials as fillers [4-10]. The properties of polymer-metal nanocomposites depend not only on the nature of the metal but also on the distribution and valance state inside polymeric matrix. Unfortunately, metal nanoparticles usually have high surface energy and are liable to aggregation and oxidation, which greatly limits their application.

To develop simple, fast, low-cost methods for synthesis of polymer-metal nanocomposites, moreover, to get rid of the aggregation and oxidation of metal nanoparticles as improving agents of polymer, researchers usually adopt two methods in practice. One method aims at optimizing the synthesis conditions for nanoparticles nucleation, growth, and growth termination with the assistance of cryogenic technology [4], thermal oxidization and Ar^+ sputtering [5], and surface modification technique [6]. Another method focuses on the growth of inorganic particles within templates such as reversed micelle or porous membrane [7], dendrimer [8-10], and polyethylene glycol [11] while extraneously strong reductants are introduced into the reaction system.

Recently, some researchers successfully prepared metal nano-materials by solution synthesis method with monomers or solvents as reactants [12, 13], which is rarely used to fabricate nano-metal/polymer composites. As a novel synthesis strategy for preparing metal-polymer nanocomposites, the solution synthesis method involving monomers or solvents as reactants allows *in-situ* reduction of metal oxides to elemental metal in the presence of strong reductant, monomer, or solvent during the preparation process of polymer. Such an *in-situ* reduction of metal oxides is beneficial to significantly improving the dispersion of elemental metal nanoparticles in polymer matrix, and the polymer matrix as a barrier of atmosphere can help to prevent as-obtained metal nanoparticles from oxidation. Therefore, it may be feasible to drastically improve the mechanical properties of polymer by incorporating metallic nanoparticles as fillers *via* solution synthesis involving *in-situ* reduction of metal oxides generating elemental metal nanofillers.

Bearing those perspectives in mind, in the present research we pay special attention to fabricating polyamide 6-matrix composite reinforced with Cu nanoparticles which are reduced from CuO (denoted as nano-Cu/PA6). Since the amino groups of PA6 possess weak reduction capability, a reduction atmosphere is always retained by the reaction system during the preparation of nano-Cu/PA6 by solution synthesis route. Additionally, the barrier effect of polyamide 6 to atmosphere can keep the properties of as-fabricated Cu nanoparticles and the hindering effect avoids the aggregation of Copper nanoparticles. Moreover, as-prepared nano-Cu/PA6 has the improvement in antifriction and anti static, thereby broadening the application of polyamide 6.

Subsequently, the reduction of CuO to elemental Cu is facilitated in the ring-opening polymerization process of ε-caprolactam, thereby affording desired nano-Cu/PA6 composite. This paper reports the fabrication of nano-Cu/PA6 composite as well as its structure characterization by transmission electron microscopy (TEM) and X-ray diffraction (XRD). Besides, the ultraviolet-visible light (UV-vis) absorption spectrum, mechanical properties and friction and wear behavior of as-prepared nano-Cu/PA6 composite are also investigated in this paper.

2. Experimental

2.1 Materials

Raw material ε-caprolactam was obtained from BASF Chemical Reagent Company China (Beijing, China). Adipic acid was supplied by Paini Chemical Reagent Factory of Zhengzhou (Zhengzhou, China). Formic acid was provided by Tianjin Kemel Chemical Reagent Company Ltd (Tianjin, China). Copper oxide was supplied by Nanjing Milan Chemical Comapny Ltd (Nanjing, China).

2.2 Sample preparation

Proper amounts of copper oxide, adipic acid, ε-caprolactam, and distilled water were sequentially added to a 250 mL three-neck flask. Resultant mixed solution was then heated with a stirring constant-temperature electrothermal cover from room temperature to 190 ºC over a period of over 3 h under magnetic stirring, followed by being heated at 230 ºC for 0.5 h to release water vapor. Upon completion of water vapor releasing, the reaction mixture was gradually elevated from 230 ºC to 260 ºC within 1.5~2 h to allow reaction. At the end of reaction, the pressure of the reaction system was gradually reduced to -0.08 MPa with a vacuum circulating water pump within about 1.5 h thereby affording target product. Thereafter, crude nano-Cu/PA6 composites were cast molded into final dumbbell-like nano-Cu/PA6 specimens.

2.3 Characterization

A TEM (Amsterdam, Netherlands) was performed at an accelerating voltage of 200 kV to observe the dispersion behavior of copper nanoparticles in PA6 matrix; and as-prepared nano-Cu/PA6 composite was ultramicrotommed into thin pieces of around 50 nm thick with a Leica EMUC6 (Wetzlar, Germany) to give the specimens for TEM analysis. size distribution

XRD pattern of as-prepared nano-Cu/PA6 composite was recorded with a D/max 2550 VX-ray diffractometer (Philips, Holland; Cu K_α radiation, $\lambda = 1.54178$ Å). UV-vis absorption spectrum of as-prepared nano-Cu/PA6 composite was measured over a wavelength range of 200~1000 nm with a Cary 100 spectrophotometer, and the specimen for UV-vis analysis was obtained by dissolving a proper amount of as-prepared nano-Cu/PA6 composite in formic acid.

The tensile strength of as-prepared nano-Cu/PA6 composite was evaluated with a WDW-10D testing machine according to Chinese national standard GB/T 1040-1992, and the impact strength was evaluated with a ZBC-1400-2 testing machine according to GB/T 1040-1993. Besides, a ubbelohde viscometer was performed to determine the molecular weight of PA6 in nano-Cu/PA6 composite, and the specimen to be tested was obtained after as-prepared nano-Cu/PA6 composite was repeatedly dissolved in formic acid and centrifuged for 3 times. Moreover, the friction and wear behavior of as-prepared nano-Cu/PA6 composite sliding against steel ring (AISI1045 steel) of 40 mm diameter and 10mm width was evaluated with an MRH-3 high speed block-on-ring test rig under a force of 150 N and a rotary rate of 150 $r\cdot min^{-1}$ over a period of 1 h.

3. Results and Discussion

3.1 Characterization

The UV-vis spectra of PA6 and nano-Cu/PA6 composite dissolved in formic acid are shown in Figure 1. The absorbance of nano-Cu/PA6 composite solution tends to nearly monotonically decrease with increasing wavelength, which indicates that Cu nanoparticles are well incorporated in PA6 matrix, as reported elsewhere [8]. This observation also well corresponds to the slow change of the reaction solution color from black to golden brown during the preparation of nano-Cu/PA6 composite.

Figure 2 shows the TEM image of nano-Cu/PA6 composite with 0.5% (mass fraction; the same hereafter) CuO content. It can be seen that Cu nanoparticles have an average diameter of 30-50 nm (Figure 2A), and they are well distributed in PA6 matrix and coated with PA6 molecular chains. Such a layer of PA6, as expected, is to help to establish a barrier around Cu nanoparticles thereby preventing them from oxidation upon exposure to atmosphere. Besides, Cu nanoparticles consist of some Cu nanoparticles 4-5 nm (the sample dissolve in ethanol), which can be seen from Figure 2B. Another interesting phenomenon is found in Figure 3, the size of Cu nanoparticles is the range of 4-5 nm by observing the mixture of the initial reaction, that is to say, the polymerization of the monomer of PA6 is not to happen. That is also certified by size distribution evaluated by laser diffraction particle size distribution measurements, as seen in Figure 4. Moreover, the obtained Cu nanoparticle is the polycrystalline state that is observed in the top left corner in Figure 3. Therefore, we can suppose that as-prepared nano-Cu/PA6 composite possesses improved mechanical properties and friction and wear performance as compared with PA6 matrix, due to the reinforcing action and well dispersion of nanoscale metallic Cu filler.

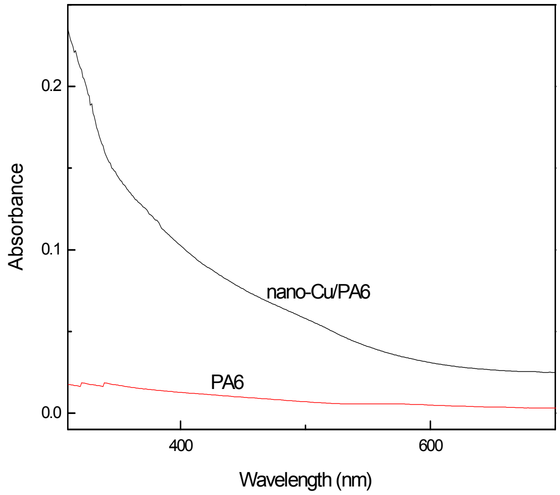

Figure 1. UV-vis spectra of PA6 and nano-Cu/PA6 composite.

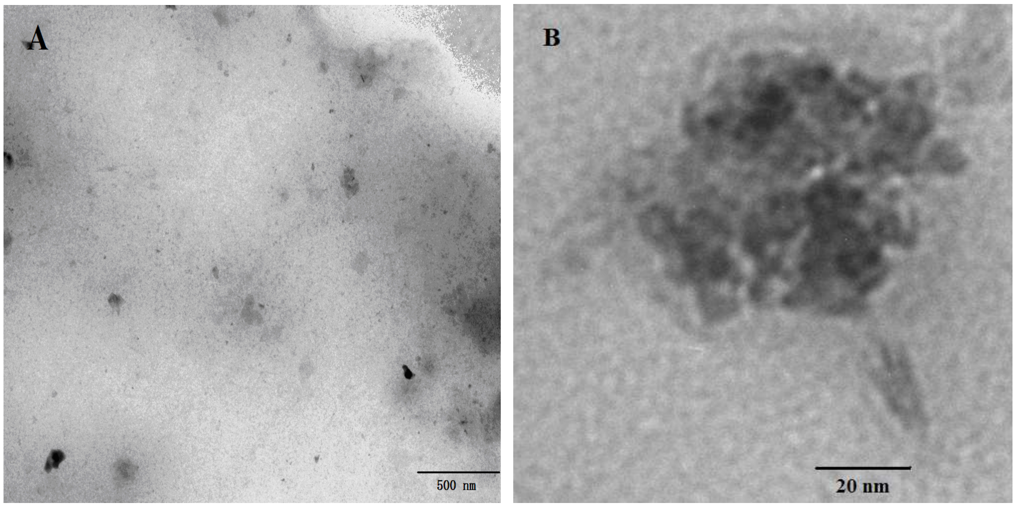

Figure 2. TEM image of nano-Cu/PA6 composite showing dispersion of Cu nanoparticles therein.

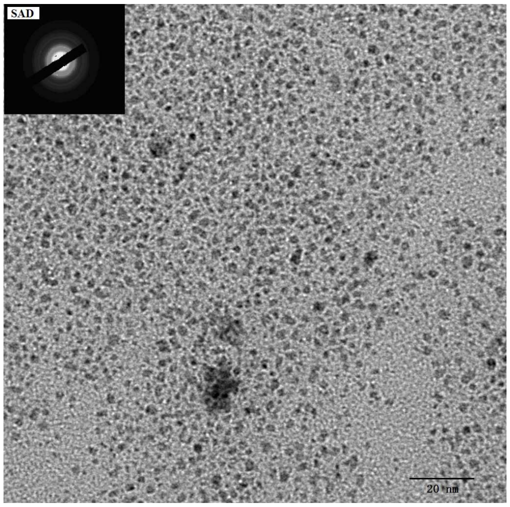

Figure 3. TEM image of Cu nanoparticles showing its size before PA6 polymerization therein.

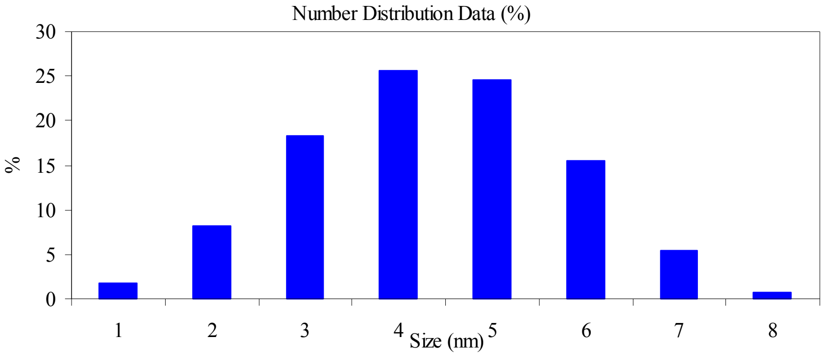

Figure 4. Size distribution of Cu nanoparticles before PA6 polymerization therein.

Figure 5 shows the XRD patterns of several nano-Cu/PA6 composites prepared with different content of CuO (i.e., different content of Cu nanoparticles). The peaks at approximately 19° and 23° correspond to PA6 in α crystalline form, and that at 21° corresponds to PA6 in γ crystalline form, as evidenced elsewhere [14-16]. Besides, PA6 in γ crystalline form is predominant in nano-Cu/PA6 composites prepared with higher content of CuO. This is possibly because the heterogeneous nucleation effect of Cu nanoparticles in PA6 matrix is concentration-dependent; as a result, the nucleation density and crystalline degree of PA6 matrix are increased at lower concentration of Cu nanoparticles, while the continual growth of PA6 crystalline is hindered at higher concentration of Cu nanoparticles thereby leading to reduced completeness of the crystalline structure of PA6 [15, 16]. Besides, the XRD peaks at 43.3°, 50.1°, and 74.1° correspond to (111), (200), (220), and (311) crystal faces of elemental Cu nanoparticles in PA6 matrix [17, 18], which indicates that Cu nanoparticles exist as metallic substance in nano-Cu/PA6 composites. The above XRD results confirm that metallic Cu nanoparticles formed through the reduction of CuO by PA6 containing amino group with reducing capability can stably exist in atmosphere, due to the presence of PA6 barrier.

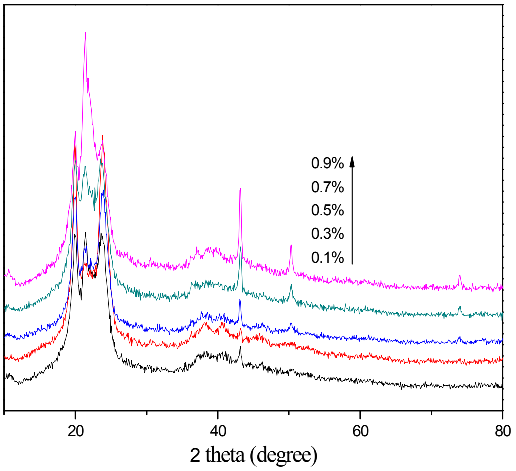

Figure 5. XRD patterns of nano-Cu/PA6 composites with different content (mass fraction, the same hereafter) of CuO (Cu nanoparticles).

3.2 Mechanical Properties as well as Friction and Wear Behavior

Figure 6 shows the relationship between tensile strength of dumbbell-shaped standard specimens of nano-Cu/PA6 composites and CuO content. When CuO is added in PA6 matrix at a content of 0.1% and 0.3%, resultant nano-Cu/PA6 composites have significantly increased tensile strength. Particularly, the composite made from PA6 containing 0.3% CuO has the maximum tensile strength of 45.7 MPa, and it is higher than that of PA6 by 47.5%. When the content of CuO rises from 0.3% to 0.5% and 0.7%, the tensile strength of resultant nano-Cu/PA6 composites tends to slightly decline but is syill higher than that of PA6 matrix. However, the tensile strength of nano-Cu/PA6 composite prepared at a CuO content of 0.9% declines significantly and is even much lower than that of PA6 matrix. This is mainly because, when ubbelohde viscometer is performed to determine the viscosity average molecular weight ($\overline{M\eta}$) of nano-Cu/PA6 composites dissolved in formic acid, as-measured $\overline{M\eta}$ tends to decrease gradually with increasing CuO content, as certified in Figure 7. During the preparation process of nano-Cu/PA6 composites in the absence of any extraneous reductant, CuO is reduced only by the end amino group of PA6, 6-aminocaproic acid, or the prepolymer of PA6, while amino group is oxidized to oxime (=NOH) that is difficult to continually react with other functional groups of the reaction system [19]. As a result, both the molecular weight and tensile strength of nano-Cu/PA6 composites tend to decrease at a too high content of CuO, due to excessive reduction of CuO generating excessive oxime.

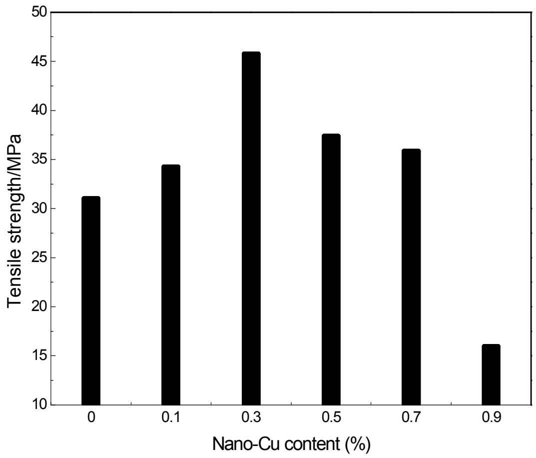

Figure 6. Tensile strength of PA6 and nano-Cu/PA6 composites with different content of nano-Cu (Cu nanoparticles).

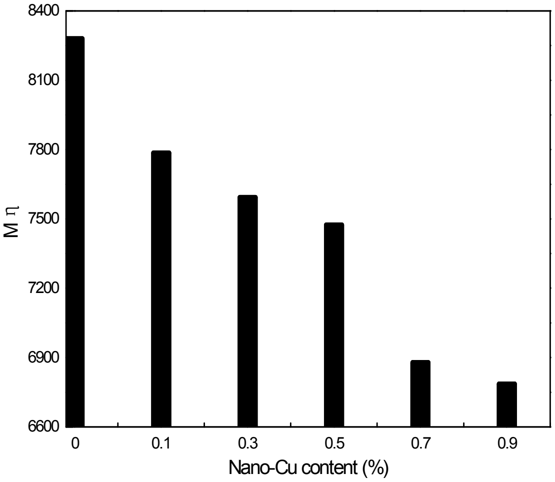

Figure 7. Viscosity average molecular weight ($\overline{M\eta}$) of PA6 and nano-Cu/PA6 composites.

The friction and wear behavior of PA6 and nano-Cu/PA6 composites is shown in Figure 8 and Figure 9. It can be seen that nano-Cu/PA6 composites have much lower friction coefficient and wear scar diameter than PA6 matrix. The friction coefficient of the composites tends to decrease with increasing CuO content of up to 0.7%, and then it rises to some extent when the content of CuO reaches 0.9%. Besides, the introduction of 0.1% CuO drastically reduces the wear scar diameter of nano-Cu/PA6 composite from 8.54 mm (that of PA6 matrix) to 5.41 mm; and the smallest wear scar diameter of the composite is obtained at a CuO content of 0.5%. Moreover, when the content of CuO rises from 0.5% to 0.7% and 0.9%, the wear scar diameter of the composites tends to slightly increase therewith. The reason may lie in that copper nanoparticles in nano-Cu/PA6 composites have good antiwear and friction reducing performance and play an important role in reducing the friction and wear of PA6-matrix composites. However, when the content of CuO is too high, resultant nano-Cu/PA6 composites possess decreased mechanical strength and molecular weight. As a result, the wear resistance of the composite prepared at a too high CuO content is also reduced. Moreover, we also examined the crystallization behavior, thermal stability, and electric resistance of nano-Cu/PA6 composites. Interestingly, PA6 matrix and nano-Cu/PA6 composites have almost the same crystallization behavior and thermal stability, but the composites possess obviously lower resistance than PA6 matrix (the resistance value of PA6 is above 10^{14} Ω, and that of nano-Cu/PA6 composites is drastically reduced to 10^{8} Ω). This, naturally, is attributed to the incorporation of metallic Cu nanoparticles in PA6 matrix.

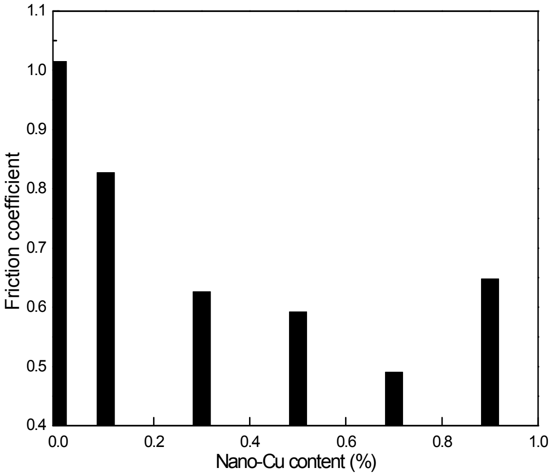

Figure 8. Friction coefficient of PA6 and nano-Cu/PA6 composites with different nano-Cu content.

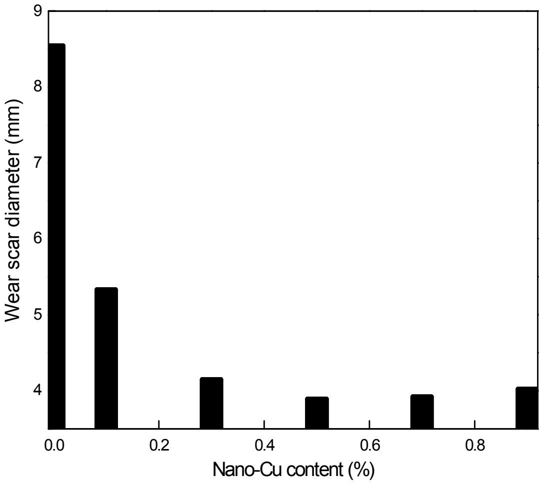

Figure 9. Wear scar diameter of PA6 and nano-Cu/PA6 composites with different nano-Cu content.

3.3 Analysis of Mechanism for CuO to be Reduced by PA6

It is reported that amino groups is regard as reducing agent to prepare metallic nanoparticles. Kinyanjui, Newman, Zhang, Blinova, et al have justified that amines can serve as reducing agents to form gold nanoparticles [19-22]. Bearing these reported results, in order to understand the reduction mechanism of CuO in the preparation process of nano-Cu/PA6 composites, we designed two experimental solutions to confirm the proposed reaction mechanisms. On the one hand, CuO is not reduced when it is mixed with ε-caprolactam in the reaction system and heated at 200 ^{o}C for 5 h. On the other hand, when CuO is mixed with ε-caprolactam and heated also at 200 ^{o}C for 5 h while H_2O is introduced into the reaction system, the reaction solution turns gold brown owing to the formation of metallic Cu. To sum up, H_2O as a ring-opening agent induces the ring-opening reaction of ε-caprolactam generating 6-aminocaproic acid containing amino group which is able to reduce CuO thereby affording Cu elemental substance (see Figure 10) [19-23].

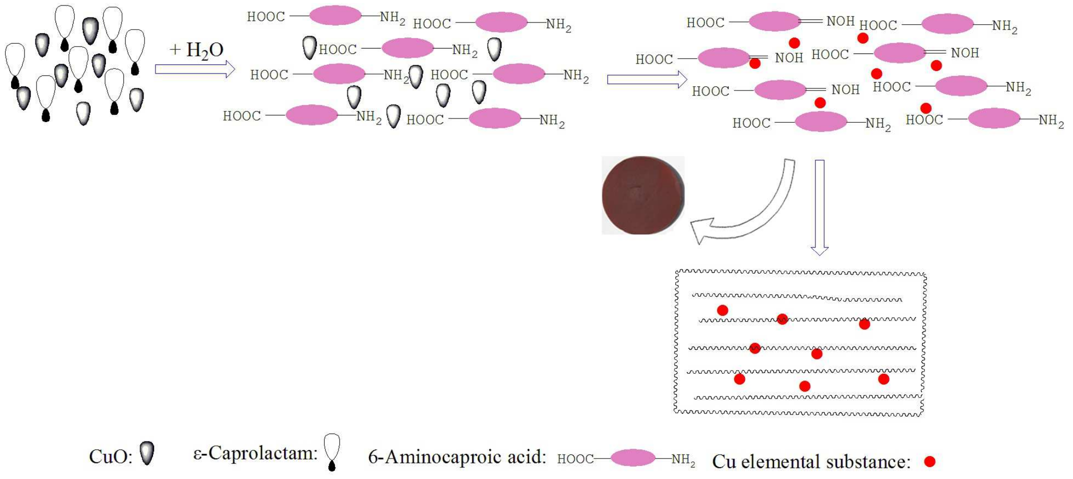

Figure 10. Mechanism for CuO to be reduced by PA6 during preparation of nano-Cu/PA6 composites.

4. Conclusions

In-situ solution polymerization method can be well adopted to prepare nano-Cu/PA6 composites. The reducing atmosphere of PA6 for preparing the composites is able to directly reduce CuO to metallic Cu thereby affording nano-Cu/PA6 composites in the absence of any external reducing agents. Besides, the dosage of CuO filler has significant effect on the crystallization behavior of PA6 matrix, and γ crystalline form of PA6 is predominant in nano-Cu/PA6 composites prepared with higher content of CuO. Moreover, metallic Cu nanoparticles are well encapsulated by a layer of PA6, and hence their dispersibility in polymer matrix and antioxidation ability are highly improved. As a result, as-prepared nano-Cu/PA6 composites possess greatly improved mechanical properties and wear resistance than PA6 matrix. Hopefully, the present approach may be extended to preparing other similar polymer-matrix composites reinforced by inorganic nanoparticles.

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