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One-step aqueous solution route toward depositing transparent carbon film onto different quartize substrate

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ABSTRACT

We report an aqueous solution route for directly depositing transparent carbon thin film on SiO_2 substrate using polyethyleneimine as carbon precursor. The conductivity of the carbon thin film is calculated to be ~1500 S/cm. Benefiting from film forming ability and permeability of PEI, homogenous and smooth carbon thin films can be deposited onto the quartz substrate with different shapes (e.g. flexible quartz fibers). Investigation finds that additional Cu ions in the precursor could prevent the decomposition and evaporation of PEI to help the graphitization of carbon thin film. Moreover, the Cu ions aggregating to Cu nanoparticles significantly enhance the absorption of carbon thin film, which may advance the application of carbon thin film in surface plasmon resonance.

1. Introduction

Transparent conducting film (TCF) is of great importance for electronic devices. Especially, TCFs on SiO_2 substrates are a requisite component in touch panels, liquid crystal displays (LCD), organic light emitting diode (OLED), and thin film solar cells [1,2]. Nowadays, indium tin oxide (ITO) is the most preferred TCFs used in industry. However, the price of ITO keeps going up due to the increasing global consumption and the limited indium ore. Therefore, exploration of economical and abundant alternative TCF materials have been drawing great attentions [3–5]. Particularly, carbon materials based TCF have been intensively studied for its outstanding electrical properties, robust chemical inertness, low toxicity and abundance on earth [6,7]. Graphene and carbon nanotubes (CNTs) have shown promise applications as TCF for solar cells, touch panels and OLED [8–10]. For instances, Li et al. grew large-area graphene films of the order of centimeters on copper substrates by chemical vapor deposition. Jia et al. fabricated nanotube–Si heterojunction solar cells by coating a thin film of double-walled carbon nanotubes on n-type silicon wafers [11,12]. Many researches have achieved excellent high-quality conducting carbon thin film as TCFs [13–15].

Herein, we report an aqueous solution route for directly depositing transparent conducting carbon thin film on SiO_2 substrate with branched polyethyleneimine (PEI) serving as carbon source. Cu ions are introduced to grow the high-quality graphitic carbon thin films. The thickness of carbon film can be tuned by controlling the concentration of PEI. As-obtained carbon thin film is dense and homogeneous at large scale with comparable conductivity (~1500 S/cm) to ITO (~2800 S/cm)/FTO (~1700 S/cm) [16,17]. The carbon film can be further deposited on the different SiO_2 substrate e.g. quartz fiber. This aqueous solution route is of great potential to further advance the application of carbon film on SiO_2 substrate.

2. Experimental section

The chemical materials, synthetic process, device fabrication, characterization and measurements are described in Electronic supplementary information, respectively. The carbon film was synthesized by employing polyethyleneimine aqueous solution as precursor. Typically, 200 mg polyethyleneimine was added into 1 mL of deionized water, and then kept stirring for 15 h. The obtained solution was spin-coated onto cleaned quartz substrates/fiber at 3000 r/min for 30 s. Finally, the film was annealed under Ar /H_2 atmosphere at 950 °C for 15 min.

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3. Results and discussion

To prepare carbon thin film, PEI precursor thin film is firstly spin-coated on SiO_2 substrate, and then is annealed at 950 °C in Ar/H_2 atmosphere for 15 min. Note that PEI is mainly composed of amine group and CH_2? CH_2 repeating unites. These single bond chains of PEI could be easily broken into small molecules while the annealing temperature goes up to 400 °C (Fig. 1(a)). However, introducing Cu ions could improve the decomposition temperature of PEI. It is found that ~20% of precursor's mass is still reserved even though annealed temperature reaches 800 °C. After that, the PEI precursor coating is transformed into carbon thin film on SiO_2 substrate. The mass ratio between PEI and Cu ions in precursor is 400:1. In fact, PEI would decompose into carbon film along with small gaseous molecules during the annealing process. The content of Cu is higher than 0.25% in the final carbon film due to the leaving small gaseous molecules. Fig. 1(b) show that the carbon thin film is uniformly decorated with 50–200 nm sized Cu nanoparticles, suggesting that the Cu ions aggregate to nanoparticles during the annealing process. The XRD patterns (Fig. S1) confirm the existence of Cu in the Cu-catalyzed carbon film. Before and after removing Cu nanoparticles (through chemical etching), the light absorption of the carbon film is decreased more than 40% from 400 nm to 800 nm (Fig. 1(c)). The absorption enhancement of carbon film should be contributed by the surface plasma enhancement from Cu nanoparticles. [18,19] After etching the Cu nanoparticles, smooth carbon film is obtained without any obvious broken holes on the carbon thin film (Fig. 1(d)) (XRD image of Cu-etched carbon film shown in Fig. S2). Hereafter, Cu-etched carbon films are used for further characterization.

X-ray photoelectron spectroscopy (Fig. 2(a)) analysis reveals that the carbon thin film is composed of 95% of C, 2.2% of N and 2.8% of O. Fig. 2(b) shows N 1s spectrum mainly centered at 401.2 eV corresponding to the graphitic form [20]. The strongest peak of C 1s spectrum (Fig. 2(c)) centered at 284.8 eV is attributed to sp^2 hybridization of C–C bonds. It is well known that the sp^2 hybridization of the hexagon structure in the carbon film ensures the excellent conductivity of carbon thin film. The Raman spectrum (Fig. 2(d)) displays a higher ratio of G band (1600 cm^{-1}) to D band (1350 cm^{-1}) and a rather wide band from 2585 cm^{-1} to 3030 cm^{-1}, suggesting that the carbon film was partially graphitized [21]. In addition, the low contrast and clear edge in Fig. 2(e) reveal that the carbon film is ultra-thin. As shown in Fig. 2(f), both straight and curved graphite atom layers could be clearly observed in the carbon thin film.

To prove the controllability and reliability of the aqueous solution approach, a group of carbon films with different thickness were synthesized by tuning the precursor concentration. The film thickness and sheet resistance were measured by AFM and four-point probe. As shown in Fig. 3(a), the sheet resistance is 3.6 kΩ sq^{-1}, 1.9 kΩ sq^{-1} and 0.9 kΩ sq^{-1}corresponding to the film thickness of 2.1 nm, 4.2 nm and 6.3 nm, respectively. The conductivity was roughly calculated to be ~1500 S/cm for all the films. The optical transparence of the carbon film was measured using UV–vis spectroscopy (Fig. 3(b)). The transparence of the carbon films decreases from 86%, 80%, to 70% at a wavelength of 550 nm while film thickness increasing from 2.1 nm, 4.2 nm to 6.3 nm. The inset of Fig. 3(b) shows that the carbon thin film with 2.1 nm has a great transparency. Taking advantages of the PEI's excellent film forming ability and permeability, the carbon film

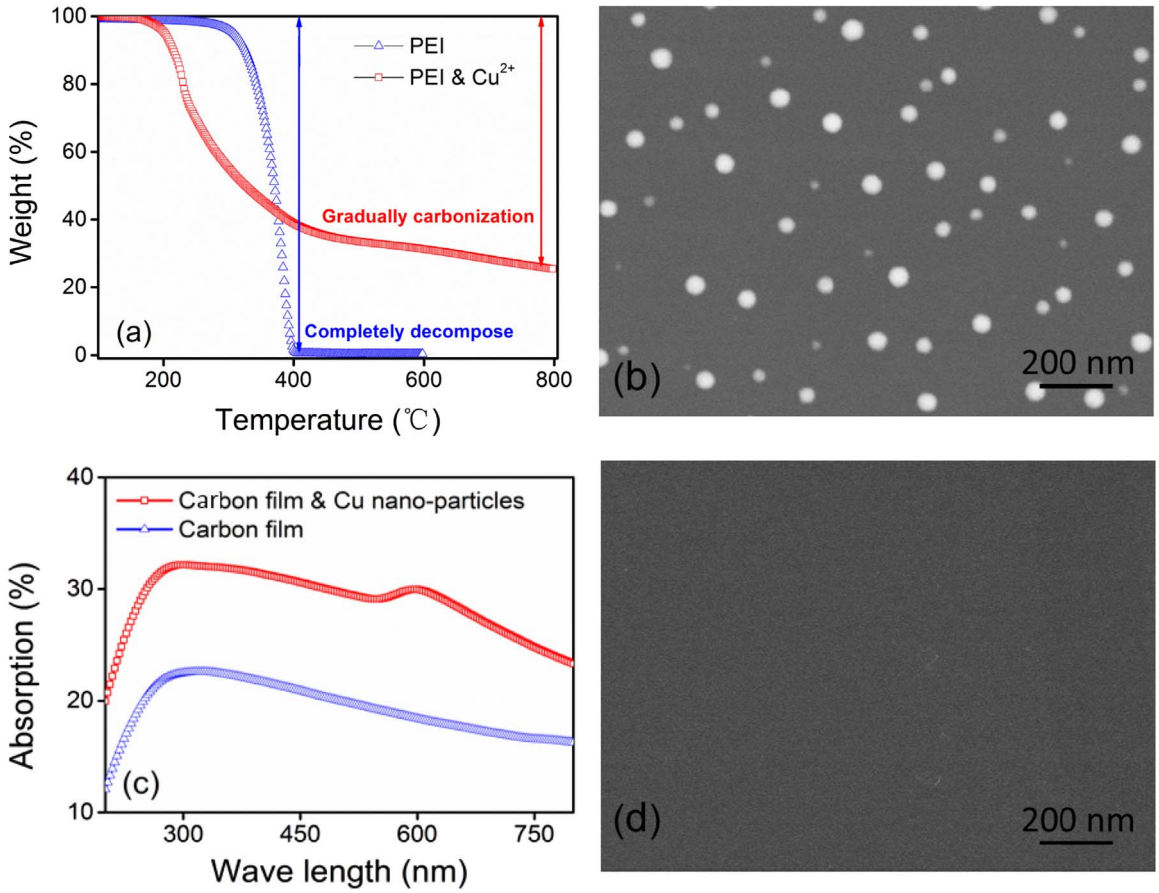

Fig. 1. (a) TGA spectrum of pure PEI and Cu^{2+}coordinated PEI. (b) SEM image of as deposited carbon thin film with Cu nanoparticles on surface. (c) Absorption spectrum of carbon thin film with/without Cu nanoparticles. (d) SEM image of carbon thin film after removing Cu nanoparticles.