

Orientational Ag nanoparticle alignment from a facile ‘TEG-sol’ method

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Super-aligned conductive material is a hotspot in the research of flexible and transparent conductive films. This work introduces a facile and rapid ‘TEG-sol’ method to synthesise Ag nanoparticles and their orientational alignment. Pure, well-crystallised Ag nanoparticles with polyhedron morphology are fabricated by reducing silver nitrate in TEG (triethylene glycol) solvent. Fourier transform infrared spectroscopy result reveals an organic coating layer on the surface of the Ag nanoparticles, which promotes the excellent dispersibility of these nanoparticles in TEG solvent. Orientational Ag nanoparticle alignment is obtained by spin coating the dispersion on copper foil. This proposed process provides a brand new idea for the design and fabrication of conductive microstructures.

1. Introduction: With the rapid development of wearable devices, flexible and transparent conductive nanoarrays have stimulated wide research attention in the applications of organic light-emitting diodes, touch screen, micro-coaxial cable and so on [1–3]. Having excellent conductivity and optical transparency, silver nanostructures such as ultrafine nanoparticles and nanowires are considered competitive electrodes for these emerging devices [4, 5]. Although various methods have been developed to facilitate the synthesis of silver nanostructures, it is still a difficult task to manipulate the nanostructures and fabricate well-defined superstructures to satisfy both the electrical, mechanical and optical requirements [6–10].

Self-assembly of the nanoparticle or nanowire provides a feasible way to give microstructures with controlled organisations [11, 12]. For instance, Li *et al.* [13] reported a microemulsion method to produce materials with complex organisations. Pileni [14] obtained silver nanocrystals that are able to organise in two-dimensional (2D) and 3D super lattices to form ‘supra’ crystals using reverse micelles. Hong *et al.* [15] prepared single-crystalline silver nanowire arrays by self-assembled ultrathin silver wires. Sakamoto *et al.* [16] obtained Ag nanodots by two types of sites-selective metal deposition methods. Bechelany *et al.* [17] synthesised large areas of silver grains organised in nanorings using simple metal deposition method. All these strategies are only practicable over micrometre scales, which is still a long way from manufacturable product. Recently, Wu *et al.* [18] fabricated a transparent nanofibre based on a metal nanotrough network using a polymer-nanofibre templating process. Although the randomly arranged metal fibre presented superior conductivity and flexibility, the complicated process and limited efficiency for electrospinning process remain to be a problem for the large-scale production. Therefore, simple and highly efficient methods are still desirable for the future applications. In this Letter, orientational Ag nanoparticle alignment is prepared by a facile ‘TEG-sol’ method. The experimental method was used to synthesise Ag nanoparticles alignment for the first time. Surface chemistry of the Ag nanoparticles and formation mechanism of the Ag nanoarrays are investigated. Taking advantage of the self-assembly effect of Ag nanoparticles, this method realises the large-scale feasible fabrication of silver super nanoarrays.

2. Experimental details: The silver nanoparticles are synthesised via reducing silver nitrate from a facile ‘TEG-sol’ method [19, 20].

First, silver nitrate (Sinopharm Chemical Reagent Co. Ltd, 99.9%) is dissolved in 20 ml triethylene glycol (TEG) (Sinopharm Chemical Reagent Co. Ltd, 99.9%) with a concentration of 0.05 mol/l, named solution A. Polyvinyl pyrrolidone (PVP, Sinopharm Chemical Reagent Co. Ltd, 99.9%) is dissolved in 20 ml TEG with a concentration of 0.15 mol/l, named solution B. Solution B is gradually heated to 60°C with stirring by a magnetic agitator. After that, solution A is put into solution B dropwise, and the mixture is kept at 60°C for 1 h to get a green Ag nanoparticle dispersion. It is worth noting that the dispersion is quite stable that Ag nanopowders are separated by 20 min high-speed centrifugation and drying.

Copper foil that is cleaned by ethanol and acetone several times is used as the substrate. There are directional processing lines on the surface of the copper foil, which can be utilised as template of the self-assembled Ag nanoparticle. The orientational Ag nanoparticle alignment is obtained by spin coating of the dispersion at 1000 rpm for 30 s on the substrate, then drying at 160°C for 30 min.

X-ray diffraction (XRD) pattern of the Ag nanopowders is obtained on a X-ray diffractometer (D/Max-2500, Rigaku Co., Tokyo, Japan) with CuK α radiation ($\lambda = 1.5418 \text{ \AA}$) operated at 40 kV and 200 mA. The morphology of the Ag nanoparticles is observed by scanning electron microscopy (SEM; JSM-7001F, JEOL Ltd, Tokyo, Japan). The surface chemical state of the nanoparticles is investigated by using a Fourier transform infrared spectroscopy (FTIR) spectrometer (Vertex 70v, Bruker Ltd, Germany).

3. Results and discussion: Fig. 1a shows the XRD pattern of the as-synthesised Ag nanopowders. It is observed that the Ag nanopowders are well crystallised without any impurity phase. The four diffraction peaks located at 38.2°, 44.3°, 64.5° and 77.5° correspond to the crystal planes of (111), (200), (220) and (311) for cubic crystal system, respectively. The crystal sizes of Ag nanoparticles were calculated using Debye Scherrer equation based on the diffraction peak of (111). The calculated results show that the crystal sizes are around 0.12 μm . Due to the small crystal size, these peaks are slightly broadened. Thus, the XRD pattern reveals a pure, crystalline and nanosize feature of the powders.

After 1 h reaction, Ag nanoparticles with polygon morphology and smooth facets are obtained, as shown in Fig. 1b. The large-scale SEM image confirms that these nanoparticles are uniform both in

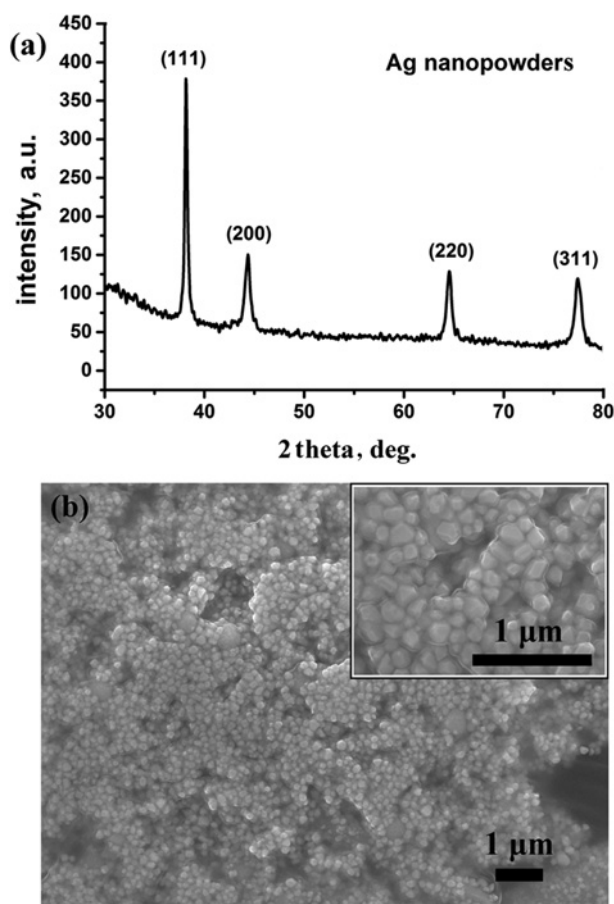


Fig. 1 XRD pattern and SEM image of the as-synthesised Ag nanopowders
a XRD pattern
b SEM image

size and morphology. The average particle size is estimated to be 130 nm over 200 particles. As obtained directly by centrifugation and drying, the Ag nanoparticles possess a transparent organic layer on the surfaces, as shown in the inset in Fig. 1*b*. This layer is formed from the solvation layer around the silver nanoparticles, which could be revealed by FTIR spectrum in Fig. 2.

As seen, the absorption band at 3427 cm^{-1} is assigned to the stretching vibration of the O–H bond from TEG molecules on the surface of the Ag nanoparticles [21]. The two bands located at 2922 and 2851 cm^{-1} are stretching vibration of the C–H bond from both PVP and TEG molecules in the surface layer [22].

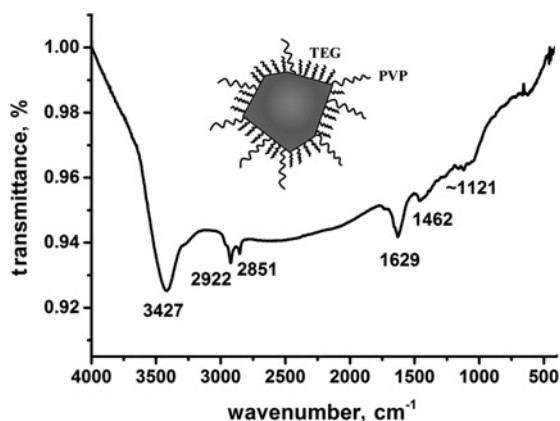


Fig. 2 FTIR spectrum and schematic structure of the Ag nanoparticles

Accordingly, the bands observed at 1629 and 1462 cm^{-1} are arose from C=O and C–N vibrations, which are characteristic bands for PVP [23]. The weak bands at $\sim 1121\text{ cm}^{-1}$ can be assigned to the stretching vibrations of C–O bonds and O–H bonds [20]. Therefore, as illustrated in Fig. 2, the surface of the Ag nanoparticles is coordinated with PVP and TEG molecules, which can form a polar organic layer and promote the uniform dispersion of the nanoparticles in TEG solvent.

Using the Ag nanoparticle dispersion, orientational Ag nanoparticle alignment is fabricated on copper foils. It is observed from Fig. 3*a* that Ag nanoparticles are directionally aligned along the processing lines of the copper foils. The formative nanoarrays are uniform in a large length scale, which is quite similar to super-aligned nanowires. In Fig. 3*b*, to verify the microstructure of these ‘nanowires’, energy dispersive spectra (EDS) were performed on the nanoarrays (named spot 1) and the empty space (named spot 2). As shown in Figs. 3*c* and *d*, the peaks for the organic matters that formed by C and O elements and the copper substrate are nearly the same for spots 1 and 2, while spot 1 contains much higher Ag element than spot 2, which quantitatively confirms the composition of the nanoarrays. In this method, the coordinated surface organic groups are key factors to the formation of the nanoarrays. Due to this organic layer, Ag nanoparticles are stabilised as colloids with a thick solvation layer in the solvent, which makes the dispersion behave like liquid medium. When spun coated to a thin layer, Ag nanoparticles align along the processing line of the copper foil under the effect of surface tension and thus form the orientational alignment with the lowest energy state.

Traditionally, Ag particles are used as conductive fillers in electronically conductive adhesives [6, 24], as shown in Fig. 4*a*, which can hardly be applied to flexible microstructures. Then Ag nanowire network was developed as transparent conducting electrodes [18]. Fig. 4*b* illustrates the conducting mechanism and SEM images of the Ag nanowire network, which still based on the connecting of randomly arranged nanowires. Based on the self-assembly of Ag nanoparticles, this method provides a brand new idea for the design and fabrication of conducting microstructures. As shown in Fig. 4*c*, the orientational Ag nanoparticle alignment can act as super-aligned nanowires and realise directional conducting property. The fabricated nanoarrays are flexible and transparent. This method is quite simple, which is promising to be applied in various wearable devices in the future. Moreover, the

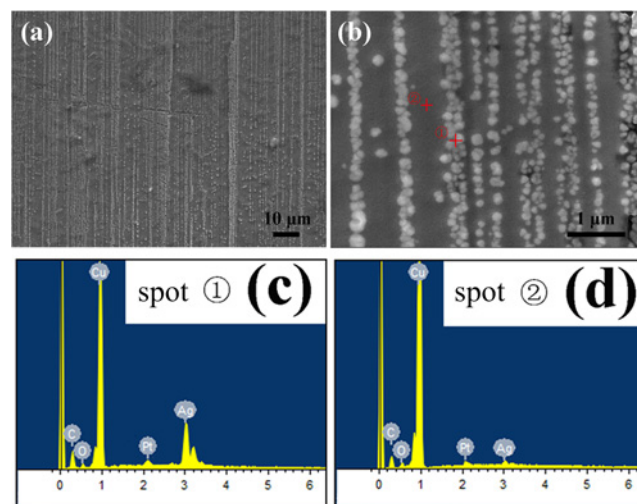


Fig. 3 SEM images and EDS results
a, *b* SEM images of the orientational Ag nanoparticle alignment
c EDS results for spot 1
d EDS results for spot 2

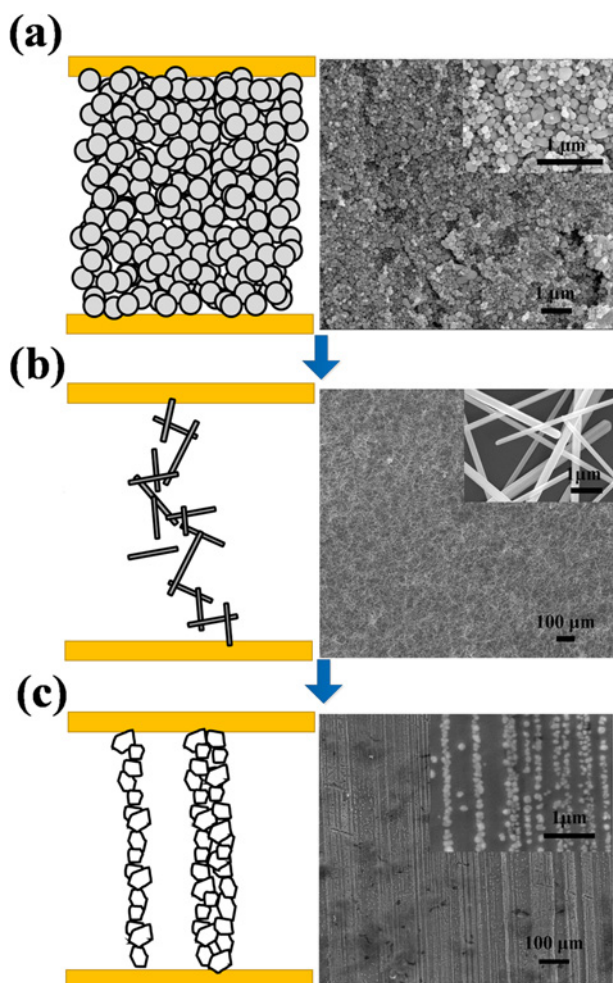


Fig. 4 Conducting mechanism illustration and SEM images for
a Conducting adhesive
b Nanowire network
c Orientational Ag nanoparticle alignment

macroscopical manipulation of Ag nanoparticles might also be helpful to realise directive effect of Ag nanoparticles in catalyst, medicine and other field.

4. Conclusions: Ag nanoparticles and their orientational alignment are fabricated by a facile ‘TEG-sol’ method. Coordinated with a TEG and PVP surface layer, these nanoparticles can form a stable dispersion in TEG solvent. When spun coated to a thin liquid layer, the nanoparticles can self-assemble to orientational alignment under surface tension. Moreover, the as-obtained Ag nanoarrays are uniform both microscopically and macroscopically, which is promising to be used as directional conducting materials in the future wearable devices. This method also provides a new idea for the macroscopic structure design with nanoparticles, and shows potential in directive control of Ag nanoparticles in catalyst, medicine and other field. A further study on the characters of the nanoparticles alignment would be taken in the follow time. We would attempt to reveal more properties of the Ag nanoparticles alignment, such as electrical conductivity and dielectric characteristics, which would greatly broaden the applications of Ag nanoparticles alignment.

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6 References

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