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## Electric-field-induced assembly of Ag nanoparticles on a CuO nanowire using ambient electro spray ionization†

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**We report a room-temperature route for synthesizing a dandelion-like CuO–Ag hybrid hierarchical nanostructure through an electric field induction of electro sprayed Ag ions or clusters. The basic preparation process involved producing charged Ag clusters by carrying out atmospheric pressure ionization and soft landing and electrostatically induced self-assembly of the generated ions on the tips of CuO nanowires.**

The controllable synthesis and preparation of new materials at the nanoscale, and even at the atomic scale, constitute a fascinating challenge in chemistry. Bottom-up and top-down approaches are two fundamental routes for constructing so-called hybrid nanostructures, *i.e.*, nanostructures with multi-functional components and hence desired chemical and physical properties.<sup>1–5</sup> Combining multi-dimensional morphologies and different components into one hybrid nanostructure and controlling the chemical composition, size, and dimensionality of these nanostructures have yielded nanostructures with remarkable properties.<sup>1</sup> Controllable assembly of noble metals and metal oxides into nanostructures is one of the most interesting frontiers in the field of heterogeneous catalysis, and has resulted in synergetic effects, in contrast to the lack of such effects in single-component materials.<sup>6,7</sup> By adjusting their compositions, hybrid materials exhibiting special optical, mechanical, and electronic properties have been produced, and have been applied to plasmon-enhanced spectroscopy,<sup>8</sup> solar cells<sup>9,10</sup> and photocatalysis.<sup>11</sup> These hybrid nanostructure materials have usually been prepared by following various traditional methods, such as co-precipitation,<sup>12</sup> impregnation,<sup>13</sup> and methods involving colloid surface chemistry.<sup>14</sup> Hybrid nanoparticles have also been

prepared using a method based on the phase separation of two different substances occurring as a result of the asymmetric structures of these substances, which allow for their controlled self-assembly.<sup>15</sup> In addition, most metal–semiconductor colloidal heterostructured materials have been obtained using seeded-growth techniques with heteroepitaxial deposition in solution media.<sup>16</sup> These methods, however, generally need to control complex synthetic conditions for constructing the various materials, and this complexity makes the preparation processes relatively expensive. To design an effective route for synthesizing metal–semiconductor hybrid nanostructure materials with high performance, a new assembly strategy should be developed.

Electrospray (ES) is an established method to produce charged and dispersive microdroplets in an atmospheric environment.<sup>17</sup> This method is not only an important method for producing ions for mass spectrometry analysis,<sup>18</sup> but has also been used to prepare nanostructures, especially granular thin films, by employing charged droplets as carriers.<sup>19,20</sup> Since the 1990s, the ES method has been used to control the morphologies, sizes and structures of microstructured and nanostructured materials.<sup>21,22</sup> It can also be used to prepare nanostructured biomaterials,<sup>23</sup> composite nanostructured solid-acid fuel-cell electrode materials,<sup>24</sup> and nanostructured metal<sup>25</sup> or oxide surfaces.<sup>26</sup> Cooks *et al.* produced nanowires made of Ag nanoparticles with these nanoparticles having controllable shapes and sizes by applying the Coulombic assembly method.<sup>27</sup> The electro spray ionization process involves several steps: (i) ejection of solvated charged droplets; (ii) de-solvation, *i.e.*, evaporation of solvent molecules from the droplets; (iii) Coulomb fission, *i.e.*, splitting of the charged droplets into smaller microdroplets as a result of electrostatic repulsion; and (iv) formation of naked ions.<sup>28,29</sup> One of the most important advantages of electro spray ionization is that it could provide charged clusters whose path of motion can be controlled by electric and magnetic fields. Recently, we found that the morphologies of Au and sizes of NaCl nanocrystals could be tailored by fine-tuning the surface electric field and carrying out de-solvation of the electro sprayed micro-droplets.<sup>30,31</sup> The crystallization and polymerization of inorganic nanoparticles could be tailored directly by the external field.

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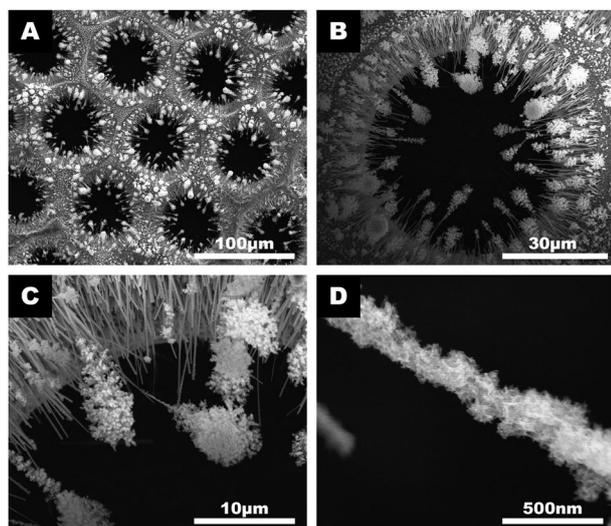
† Electronic supplementary information (ESI) available: Experimental details, the SEM images of the CuO/Ag nano-dandelion prepared with different deposition time and currents. See DOI: 10.1039/c6nj04054c

In the current work, we used an electrospray ionization process to assemble Ag nanoparticles on CuO nanowires, in which the assembly was induced by a tip electric field. The assembled CuO–Ag semiconductor–metal hybrid showed a multidimensional hierarchical nanostructure. Without using any reducing agents, the silver cluster assembly process could be controlled by adjusting the preparation parameters of the spray process. We expect this method to be a promising way to efficiently and economically construct various semiconductor–metal hybrid materials with hierarchical nanostructures.

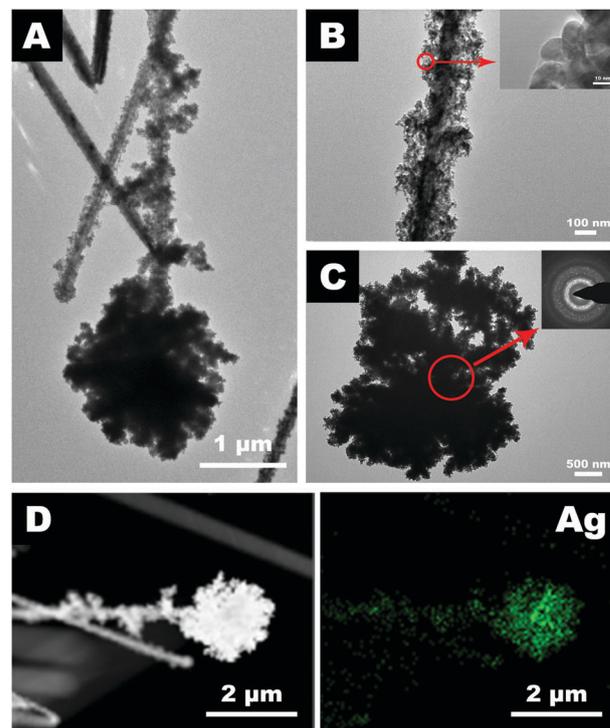
Before carrying out the nanospray process, a copper sheet, on which a Cu grid with CuO nanowires was placed, was cleaned to reveal its original yellow by softly sandpaper. This cleaning was done in order to be able to more clearly observe the subsequent deposition. Silver clusters were deposited on the sandpapered copper sheet, which was then observed with the naked eyes to be covered with a black film. SEM images of the CuO–Ag hybrid nanostructure showed it to have a dandelion-like shape (Fig. 1). The overview image of the Cu grid after deposition in Fig. 1A demonstrated that the Ag nanoparticles were uniformly deposited on every mesh of the copper grid. A dandelion-shaped hierarchical structure was clearly observed in a low-magnification image of a single mesh (Fig. 1B). The dandelion-shaped nanostructure consisted of a quasi-spherical cap and a nanowire trunk. Bigger caps tended to grow on the longer nanowires. Fig. 1C shows a high-magnification image of the dandelion-shaped nanostructure. The quasi-spherical cap was a loose structure consisted by self-assembled nanoparticles. The high-resolution SEM image shown in Fig. 1D indicated that a similarly assembled

mesostructure formed on the surface of the nanowire trunk. It is worth noting that the dandelion-shaped hybrid hierarchical nanostructures primarily appeared on the tips of CuO nanowires grown on the inner walls of the meshes. This phenomenon revealed the deposition of Ag clusters to not be a simple process of microdroplets impacting the surface of the collector. The CuO nanowires grown on the inner walls of the meshes were observed to be longer than those grown on the upper surface of the copper grid (shown in Fig. S1A, ESI†).

The dandelion-shaped hybrid hierarchical structure was confirmed by acquiring transmission electron microscopy (TEM) images (shown in Fig. 2). Each nano-dandelion in the images was observed to have a porous quasi-sphere cap and a nanowire trunk with a coarse surface (Fig. 2A). A high-magnification image of the nanowire trunk revealed the presence of loose meso-shells (Fig. 2B). The meso-shells formed from the self-assembly of nanoparticles with dimensions of about 10 nm, as shown in the inset image of Fig. 2B. Self-assembled nanoparticles formed a loose porous quasi-spherical cap on the tip of an imaged nanowire (compare Fig. 2B and in Fig. 2C). The pattern of diffraction rings, shown in the inset to Fig. 2C, indicated disorder in the orientation of the self-assembly. In addition, the elemental mapping images of the dandelion-shaped CuO–Ag hybrid hierarchical nanostructures clearly showed that the nanoparticles included silver (Fig. 2D), and the Ag nanoparticles were mainly



**Fig. 1** SEM images of the prepared CuO–Ag hybrid nanostructure, showing its hierarchical dandelion-like shape. The precursor concentration was 10 mM and the deposition time was 15 min. The typical deposition current was 150 nA. (A) SEM image of copper grids, treated by applying the thermal oxidation method, after nanospray deposition of Ag NPs. (B) SEM image of the result of the deposition of Ag clusters on a single mesh. (C) Higher-magnification SEM image showing the loose globular structure formed by Ag NPs at the tips of CuO NWs from the same hole. (D) An even higher-magnification SEM image of this same hole showing Ag NPs with a loose morphology deposited in the middle segment of a CuO NW.



**Fig. 2** TEM images of a single dandelion-shaped CuO–Ag hybrid hierarchical nanostructure. (A) Low-magnification TEM image. (B) Image of the trunk area; inset: high-magnification TEM image. (C) Image of a dandelion-shaped nanostructure; inset: diffraction pattern. (D) Elemental mapping image of a dandelion-shaped CuO–Ag hybrid hierarchical nanostructure. Silver mapping image (right). The conditions used to prepare the samples were the same as those shown in Fig. 1.

distributed on the porous quasi-spherical cap. Assembly induced by an electric field is one of the most effective methods for preparing assembled nanostructures. For example, silicon nanowires can assemble *via* a vapor-liquid-solid (VLS) process by applying an electric field between adjacent micro-electromechanical system (MEMS) structures.<sup>32</sup> The tips of several metal oxide semiconductor nanowires, such as ZnO nanowires, exhibited field emission properties,<sup>33</sup> indicating the feasibility of controlling the assembly and growth of clusters and nanoparticles by using an electric field. The electric field is inversely proportional to curvature radius.<sup>34</sup> The strength of an electric field distributed on the tips of nanowires is much stronger than that on the side.<sup>35</sup> Thus, charged nanoparticles could be orientedly assembled in electric field.

Deposition time has an important influence on the morphology of the deposition product. SEM images of the dandelion-shaped CuO–Ag hybrid nanostructures prepared with various deposition times are shown in Fig. S2 (ESI<sup>†</sup>). Different deposition times yielded significantly different morphologies for these samples. When the deposition time was 5 min, assemblies of Ag nanoparticles were not observed on the nanowire and no dandelion-shaped hybrid nanostructure formed (Fig. S2A, ESI<sup>†</sup>). A higher-magnification SEM image of the same sample (inset of Fig. S2A, ESI<sup>†</sup>) showed that few Ag nanoparticles were deposited on the CuO nanowires. When the deposition time was increased to 15 min, dandelion-shaped hybrid nanostructures appeared on the tips of the CuO nanowires (Fig. S2B, ESI<sup>†</sup>), and Ag nanoparticles were also deposited on the CuO nanowire trunks (inset of Fig. S2B, ESI<sup>†</sup>). Larger dandelion-shaped hybrid nanostructures were observed when the deposition time was increased to 30 min and 60 min (Fig. S2C and D, ESI<sup>†</sup>). By comparing the insets in Fig. S2A–D (ESI<sup>†</sup>), we also found that the size of meso-shells on the nanowire trunks improved as the deposition time was increased. We further adjusted the deposition current to obtain a better understanding of the formation process. SEM images of the dandelion-shaped CuO–Ag hybrid nanostructures prepared with different deposition currents are shown in Fig. S3 (ESI<sup>†</sup>). As the deposition current was increased from 10 nA to 150 nA, the caps formed by Ag nanoparticles increased in size. The deposition current may have affected the discharge behavior of the charged Ag clusters and hence how often they softly landed onto the collector. The increase of the deposition current was achieved by increasing the applied voltage, which resulted in an increase in the electric field intensity and in the number of charged Ag clusters landing softly on the collector per unit time. Then, more charged Ag clusters assembled to form the bigger caps.

In order to further explore the forming process of CuO–Ag hybrid nanostructure, its nanospray plume and nanoparticles were characterized. The plume ejected from the nanospray emitter was checked using mass spectrometry. The mass spectrum revealed the presence of solvated silver ions ( $\text{Ag}^+$  and  $\text{Ag}(\text{H}_2\text{O})^+$ ) in the microdroplets as shown in Fig. 3A. A schematic diagram of the Coulomb fission of the charged microdroplets containing solvated Ag ions is shown in the inset of Fig. 3A. High-resolution transmission electron microscopy (HRTEM) and X-ray photoelectron spectroscopy (XPS) analyses of our structures were also

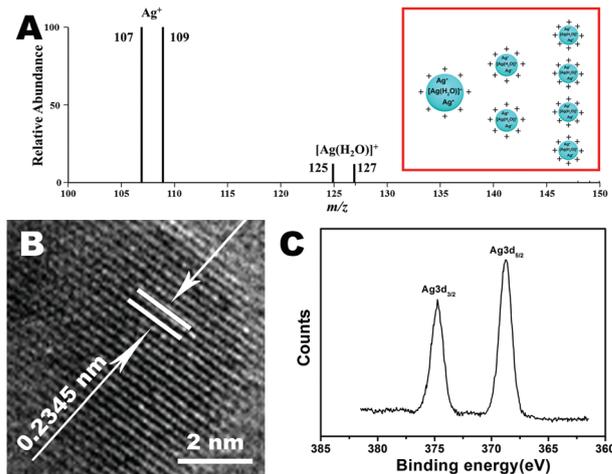


Fig. 3 (A) Mass spectrum of the spray we produced, showing the presence of Ag and solvated Ag ions. The inset shows the proposed process by which charged microdroplets underwent Coulomb fission. (B) HRTEM image of a single Ag NP, showing an Ag lattice plane. (C) X-ray photoelectron spectrum of a CuO–Ag nano-dandelion. The conditions used to prepare the samples for the HRTEM and XPS analyses were the same as those shown in Fig. 1.

carried out (Fig. 3B and C). The lattice fringe spacing was marked in the HRTEM image (Fig. 3B). The lattice fringe spacing was measured to be 0.2345 nm, which matched that of the (111) crystal face of Ag. The X-ray photoelectron spectrum (XPS) analysis showed that the  $3d_{5/2}$  peak of Ag from the CuO–Ag hybrid nanostructure occurred at 368.7 eV, supporting the existence of the Ag(0) state in this structure (Fig. 3C).

Based on the above results, we derived a possible mechanism explaining how the CuO–Ag hybrid nanostructure formed. First, a high-voltage power supply formed a powerful electrostatic field between the nanospray emitter and collector. Then, according to the proposed mechanism, the microdroplets containing the precursor ( $\text{AgOAc}$ ) became charged, and were then ejected from the nanospray emitter by the strong electric field force, during which time solvent (ultrapure water) evaporated from the charged microdroplets in flight. According to the Coulomb fission theory, a sufficiently high surface charge density would cause microdroplets to break up, resulting in the appearance of smaller droplets.<sup>36</sup> The newly formed droplets would further increase the evaporation rate of solvent, thus rapidly raising the surface charge density. In such a dynamic process, the aggregation of charged Ag clusters was accomplished (schematic representation shown in Fig. S4A, ESI<sup>†</sup>). Secondly, according to the proposed mechanism, the microdroplets softly landed onto the CuO nanowires as driven by the electric field force (schematic representation shown in Fig. S4B, ESI<sup>†</sup>), and the charged Ag clusters obtained electrons and became elemental Ag. This discharge could be monitored by measuring the deposition current during this soft-landing process. After nucleation and growth, the Ag nanoparticles finally formed, according to the mechanism. Thirdly, field emission theory predicts that the electric field strength near the CuO nanowires was strongly enhanced with field lines radiating out from these nanowires, and that the electric field strength was especially

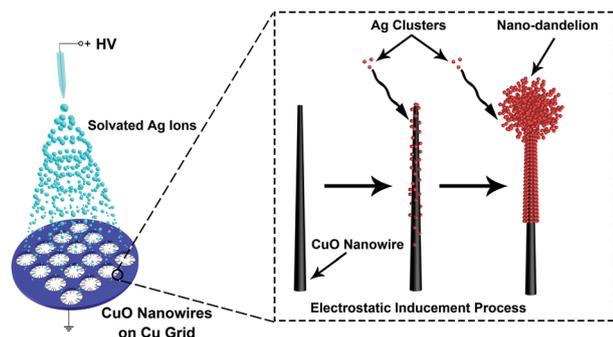


Fig. 4 A schematic representation of the electrostatically induced preparation of the dandelion-shaped CuO–Ag hybrid hierarchical nanostructure using the nanospray method.

strengthened at the tips of the nanowires.<sup>35</sup> This would have resulted in the charged microdroplets tending to land on the tips of the nanowires. After a few Ag nanoparticles formed on the CuO nanowires, the field emission effect would be further enhanced, leading to more nanoparticles self-assembling and resulting in the electrostatically induced formation of dandelion-shaped structures. A schematic representation of the electrostatically induced preparation of dandelion-shaped CuO–Ag hybrid hierarchical nanostructures using the nanospray method is illustrated in Fig. 4.

In conclusion, we have proposed an effective method to assemble semiconductor–metal hybrid nanostructures. Dandelion-shaped CuO–Ag hybrid hierarchical nanostructures were formed as a result of electric field induction of electro sprayed Ag ions or clusters at room temperature in an atmospheric environment. The preparation process included three steps: (i) producing charged Ag clusters by carrying out atmospheric pressure ionization, (ii) soft landing of charged microdroplets onto CuO nanowires as driven by an electric field force, and (iii) self-assembly of Ag nanoparticles on the tips of CuO nanowires as a result of electric field induction. The hierarchical nanostructure combined nanowires and assembled Ag nanoparticles. In particular, a loose globular structure of Ag nanoparticles formed at the tips of the CuO nanowires. Thus, we were able to carry out the preparation and assembly of the silver nanoparticles using the electro spray ionization method without a reducing agent and end-capping reagent. By adjusting the deposition time and deposition current, we realized a controllable assembly of Ag nanoparticles on the CuO nanowires. This method is a promising way to construct hybrid hierarchical nanostructures under atmospheric pressure.

## Experimental

For all assembly experiments, nanospray emitters were used to spray charged microdroplets, containing aqueous solution of silver acetate, onto a collector placed on the top of copper sheet. The inner diameter of emitter tip was 20–30  $\mu\text{m}$ . The copper sheet was grounded through an electrometer. The aqueous solution of silver acetate (10 mM) was filled into the nanospray emitter. The collector was prepared from a copper grid

(that usually used for transmission electron microscopy (TEM)) by applying thermal oxidation.<sup>37</sup> Detailed SEM and XRD characterizations of the CuO nanowires are shown in Fig. S1 (ESI<sup>†</sup>). A static positive voltage (1.5–2.0 kV) was applied to the solution through a Pt wire electrode (whose diameter was 0.2 mm). The typical deposition current was 150 nA. The distance between the nanospray emitter and collector was set to 5 mm using a three-dimensional control platform prior to carrying out the deposition. Experimental details are described in ESI.<sup>†</sup>

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