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Electrically excited hot-electron dominated fluorescent emitters using individual Ga-doped ZnO microwires *via* metal quasiparticle film decoration[†]

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The generation of hot electrons from metal nanostructures through plasmon decay provided a direct interfacial charge transfer mechanism, which no longer suffers from the barrier height restrictions observed for metal/semiconductor interfaces. Metal plasmon-mediated energy conversion with higher efficiency has been proposed as a promising alternative to construct novel optoelectronic devices, such as photodetectors, photovoltaic and photocatalytic devices, etc. However, the realization of the electrically-driven generation of hot electrons, and the application in light-emitting devices remain big challenges. Here, hybrid architectures comprising individual Ga-doped ZnO (ZnO:Ga) microwires via metal quasiparticle film decoration were fabricated. The hottest spots could be formed towards the center of the wires, and the quasiparticle films were converted into physically isolated nanoparticles by applying a bias onto the wires. Thus, the hot electrons became spatially localized towards the hottest regions, leading to a release of energy in the form of emitting photons. By adjusting the sputtering times and appropriate alloys, such as Au and Ag, wavelength-tunable emissions could be achieved. To exploit the EL emission characteristics, metal plasmons could be used as active elements to mediate the generation of hot electrons from metal nanostructures, which are located in the light-emitting regions, followed by injection into ZnO:Ga microwire-channels; thus, the production of plasmon decay-induced hot-electrons could function as an efficient approach to dominate emission wavelengths. Therefore, by introducing metal nanostructure decoration, individual ZnO:Ga microwires can be used to construct wavelengthtunable fluorescent emitters. The hybrid architectures of metal-ZnO micro/nanostructures offer a fantastic candidate to broaden the potential applications of semiconducting optoelectronic devices, such as photovoltaic devices, photodetectors, optoelectronic sensors, etc.

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1 Introduction

Plasmonic metal nanostructures, used as light-harvesters with broad spectral regulatory tunability, large absorption cross sections, excellent long-standing stability, low-cost synthesis and flexible preparation technology, have been widely applied to achieve higher performances for optoelectronic devices, such as semiconducting light sources, photodetectors, photovol-

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taics, photocatalysts, etc.¹⁻⁷ Recently, the rising demand for sustainable and efficient energy conversion has become a driving force for the use of the plasmonic effect, which provides a higher conversion efficiency of plasmon energy to an electrical signal or vice versa. Specifically, by means of nonradiative decay, the excited surface plasmons can generate an energetic carrier instead of reemitting.8-15 Once the hot electrons generated from plasmonic nanostructures possess sufficient energy, this may cause the metal-semiconductor contact barrier to turn into an accessible pathway, where an interfacial potential is formed (such as a Schottky barrier).16-20 Thus, with the aid of hot electrons, metal-semiconductor hybrid optoelectronic devices as a whole may no longer suffer from semiconducting material properties such as optical bandgaps, doping levels, metal/semiconductor interfaces, etc. This great potential of hot electrons in plasmonic nanostructures possessing sufficient energies, has been extensively

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applied for plasmon-mediated photodetectors, photovoltaic and photocatalytic devices, *etc.*^{21–25} However, by means of high-energy (~30 keV) free electrons and typical low-energy routes based on inelastic electron tunneling, the fundamental physical mechanisms of hot-electron generation, injection and regeneration in plasmonic nanostructures have still not been uncovered, which greatly limits correlated academic research and practical applications for optoelectronic devices.^{26–29} Specifically, the use of metal nanostructures as active elements for generating and injecting hot electrons into semiconducting micro/nanostructures to fabricate versatile, miniaturized, and highly effective light-emitting devices is still in its infancy.^{30–32}

ZnO micro/nanostructures with easily-controlled architectures and a low cost of manufacturing, have been extensively investigated for electronic and optoelectronic applications due to their superior physical properties, such as outstanding optical and spectral characteristics, and remarkable electronic and thermal properties.^{33–37} Group III elements, such as Al and Ga, are widely used as efficient donor doping elements and are commonly employed to tune the electrical conductivities of ZnO micro/nanostructures. In particular, the presence of Ga in ZnO can not only allow tunable n-type conduction, but can also induce red-shifted near-band edge (NBE) photoluminescence (PL). The capability for tuning n-type conduction and the possibility of bandgap engineering represent an important step towards the development of ZnO micro/nanostructure-based electronic and optoelectronic devices.³⁷⁻⁴¹ In addition, metal-ZnO hybrid systems have been investigated in order to achieve higher performance optoelectronic devices, such as emission enhancement of ZnO based LEDs, lasing improvement of optical cavities from ZnO micro/nanostructures, metal plasmon-mediated energy transfer from metal to semiconductor, etc.42-44 For example, nearinfrared photodetectors comprising Au nanorod-ZnO nanowire hybrid systems have been investigated, and the generated photocurrent is ascribed to the plasmon-mediated generation of hot electrons at the metal-semiconductor Schottky barrier.^{16,17} However, metal plasmon-mediated generation, injection, and collection of energetic electrons from electrically-driven semiconductor-based hybrid devices for lightemitting applications has been described in few reports, and it is difficult to be sure of the effect.^{13,16,45–50}

In this article, hybrid architectures comprising single Gadoped ZnO microwires (ZnO:Ga MWs) *via* metal quasiparticle film decoration were fabricated to construct wavelength-tuning fluorescent emitters. By adjusting the metal sputtering times, and the well-arranged alloys (such as Au and Ag), the electrical conductivities could be modified, and the emission wavelengths were tuned from 500 nm to 650 nm. From investigating the EL emission characteristics, it was found that metal plasmons indeed dominated the emission wavelengths. Meanwhile, the enhancement of the driven currents, which were transported in ZnO:Ga MW channels, can be ascribed to the plasmon decay-induced generation of hot electrons from physically isolated metal nanoparticles. Thus, nonradiative energy transfer between metal nanostructures and ZnO:Ga MWs demonstrated that metal nanostructures can act as active elements for the generation of hot electrons and for injection into ZnO:Ga MWs. That is, metal plasmons could function as the dominant component for the EL emission characteristics. Therefore, we propose that the hybrid architectures can achieve electrically-driven generation of hot electrons from metal–semiconductor hybrid micro/nanostructures. The adaptable plasmonic energy conversion strategies that originate from the metal to ZnO electron transfer provide a promising alternative for the design of novel miniaturized wavelengthtuning light-emitting devices.

2 Experimental section

2.1 The synthesis of individual ZnO:Ga MWs

Undoped ZnO MWs and ZnO MWs with controlled Ga-incorporation were synthesized in a horizontal double high-temperature tube furnace via carbothermal reduction methods.^{40,41} To prepare the undoped ZnO MWs, ZnO and graphite (C) high-purity powders (99.99%) with a weight ratio of 1:1 served as the precursor mixture. Ga_2O_3 powder (99.999%), used as an efficient dopant, could be mixed into the precursor mixture to synthesize ZnO:Ga MWs. In this context, ZnO, Ga₂O₃, and C powders with a weight ratio of 15:1:16 served as the precursor mixture for the synthesis of ZnO MWs with shallow Gaincorporation. During the synthetic procedure, cleaned Si (100) substrates (without any catalyst coating) were placed on a ceramic boat to collect the products, and a constant flow of argon (Ar₂) (99.99%) (150 standard cubic centimeters per minute) mixed with 10% oxygen (O2) was used as the protective medium and the carrier gas was introduced into the tube furnace. After being maintained at 1100 °C for 45 minutes, the furnace was cooled down to room temperature naturally. ZnO: Ga MWs could be collected on the silicon substrate and ceramic boat. The diameters of the MWs ranged from 5-30 µm, and the length could be up to 2 cm. Meanwhile, to ensure that the as-synthesized ZnO:Ga MWs possess a high crystallization quality, the reaction temperature and the growth times should be increased and extended accordingly. Of particular note is that a cambered ceramic boat with a size of 40 mm × 35 mm × 25 mm (length, width, height) should be used due to the higher growth temperature. In addition, the temperature of the furnace body should reach its growth temperature as soon as possible to ensure that the Zn and Ga vapors are mixed adequately.

2.2 Device fabrication

Quartz substrates were cut into pieces of 3 cm \times 2 cm, and strictly ultrasonically cleaned in acetone, ethanol and deionized water separately. Subsequently, single ZnO:Ga MWs were selected and transferred onto quartz substrates. Two indium (In) particles were then applied to fix the MWs, serving as the two electrodes for the construction of metal-semiconductor-metal (MSM) structures. The metals (99.99%) (such as Ag, Al and Au) were evaporated on the surface of the MWs

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via a radio-frequency magnetron sputtering technique at room temperature with a pressure of 5×10^{-2} Pa. By adjusting the sputtering times, this can modify the thickness of the metal films. Meanwhile, for alloy quasiparticle film decoration, the metals, such as Ag and Au, could be evaporated one by one. After annealing, alloy nanoparticles could be formed. Thus, hybrid architectures comprising individual ZnO:Ga MWs *via* metal quasiparticle film decoration were fabricated, as shown in Fig. S1.† A schematic drawing was also constructed to describe the light-emitting characteristics (Fig. S2†).

2.3 Analysis instruments

Scanning electron microscope (SEM) images were produced using a Hitachi SEM S-3000N/S-4800. To analyze the hybrid architectures and their composition, elemental energy spectra, using energy-dispersive X-ray spectroscopy (EDXS), were recorded. The current–voltage (I-V) characteristics of the hybrid architectures were measured using a Keithley 2611 system. The photoluminescence (PL) measurements were performed using a 325 nm He–Cd laser, with a micro-Raman spectrometer in a backscattering geometry configuration to produce the emission spectra (model: LABRAM-UV Jobin Yvon). The electroluminescence (EL) spectra of the device were obtained using an ANDOR detector (CCD-13448) and Omni- λ 500 Spectrograph, and a Hitachi F4500 spectrometer. The EL lighting videos and images were produced using an optical microscope.

3 Results and discussion

Undoped ZnO MWs and ZnO:Ga MWs were characterized, as shown in Fig. 1(a) and (b). As shown in the insets, undoped ZnO and ZnO:Ga MWs possess a perfect hexagonal cross section. To guarantee that Ga was incorporated into ZnO, elemental mapping, using energy-dispersive X-ray spectroscopy (EDX), was performed, and the elemental mappings of Zn, O and Ga are displayed in Fig. 1(c). Within the spatial resolution of EDX mapping, the distribution of Ga dopants was uniform throughout the MWs.^{37,41} In addition, to explore the influence of Ga-incorporation on the optical properties, low temperature (100 K) photoluminescence (PL) measurements were carried out, and the PL spectra are shown in Fig. 1(d) (the corresponding weight ratios of ZnO:Ga2O3:C are marked in the inset). When compared with undoped ZnO MWs, the peaks centered at 3.363 eV and 3.378 eV can be attributed to Ga-incorporation. Therefore, Ga2O3 with a weight ratio of 15:1:16 in the precursor mixture can be used to synthesize ZnO MWs with shallow Ga-incorporation. To date, straightforward identification of the Ga-doping concentration still remains elusive at this stage, once the impurity atom concentration is estimated to be lower than ~1%. Therefore, adjusting the Ga₂O₃ weight ratio in the precursor mixture is still an adoptable approach to modify the Ga-doping concentration in ZnO MWs.^{37,38,41,48,51,52} Besides, to study the influence of metal quasiparticle films on the optical and electrical properties of ZnO:Ga MWs, room temperature PL measurements



Fig. 1 (a) An SEM image of an undoped ZnO MW, inset: the synthesized ZnO MW possesses a perfect hexagonal cross section and smooth side facets. (b) An SEM image of a ZnO:Ga MW (ZnO: $Ga_2O_3: C = 15:1:16$), inset: the synthesized ZnO:Ga MW possesses a perfect hexagonal cross section and smooth side facets. (c) The distributions of Zn, O and Ga elements detected using EDX mapping. (d) Low temperature (100 K) PL spectra for undoped ZnO MWs and ZnO:Ga MWs with weight ratios of ZnO: $Ga_2O_3: C = 15:1:16$, $ZnO: Ga_2O_3: C = 10:1:11$ and $ZnO: Ga_2O_3: C = 5:1:6.^{41.48}$ (e) The room temperature PL properties of individual ZnO:Ga MWs *via* different metal, such as Au, Ag and Al, quasiparticle film decoration (sputtering time: 60 s). (f) The *I*–*V* characteristics of single ZnO:Ga MWs *via* metal quasiparticle film decoration (sputtering time: 60 s).

and electrical measurements, based on single ZnO:Ga MWs via metal quasiparticle film (Ag, Au and Al) decoration, were carried out. Near-band-edge (NBE) emission centered at 380 nm dominates the PL emissions, accompanied by a weak visible emission (~515 nm), as shown in Fig. 1(e).⁵³ By introducing metal quasiparticle film decoration, almost no defect emissions can be observed from metal quasiparticle filmdecorated ZnO:Ga MWs. This indicates that the introduction of metal quasiparticle film decoration provided an efficient approach for quenching the visible emission and enhancing the NBE emission. Fig. 1(f) shows the typical *I–V* characteristics of single ZnO:Ga MWs via metal quasiparticle film decoration. The introduction of metal quasiparticle film decoration can be used to enhance the electrical conductivity dramatically relative to that of bare ZnO:Ga MWs. The increased conductivities could be ascribed to the carriers produced by the metal quasiparticle films.^{54,55}

We previously reported that wavelength-tuned EL emissions have been observed for single ZnO:Ga MWs, with controlled Ga-incorporation dominated emission wavelengths.^{41,48,56} However, once the Ga₂O₃ weight ratio in the precursor mixture is lowered enough to a certain value, such as 15:1:16(ZnO:Ga₂O₃:C), EL emission cannot be observed for single ZnO:Ga MWs, even if the applied voltage is as high as 200 V. The question of whether the voltage applied is not high enough, or the Ga-doping concentration is insufficient to form productive Ga-related impurity levels, needs to be further investigated. It seems that higher resistances would result in partial voltages if the MW itself is loaded too much. Thus, the hottest spot cannot be formed towards the center of the wires under restricted bias voltages. Fortunately, by introducing metal nanostructure decoration, the electronic transport characteristics could be further enhanced, with the resistivity decreasing from $1.5 \times 10^{-1} \Omega$ cm to $3.5 \times 10^{-3} \Omega$ cm.^{54,55} With this in mind, metal materials, such as Au, Ag, and Al, were selected and evaporated on the surface of ZnO:Ga MWs, with the aim of figuring out the influence on the electronic transport properties and light-emitting properties. For comparative analysis, let us consider the Au material first (sputtering time: 30 s). The *I–V* characteristics suggest the formation of ohmic contacts between the In electrodes and ZnO:Ga MWs via Au quasiparticle film decoration, as shown in Fig. 2(a). In contrast, the assembly of the Ga-dopant and Au quasiparticle films could be responsible for the improvement in the electronic transport characteristics.^{40,41} Specifically, single ZnO:Ga MWs via Au quasiparticle film decoration began to emit bright and stable light towards the center once the drain currents exceeded a certain value. The brightness and emission regions increased with the increasing drain currents. The EL emission characteristics were investigated using a Hitachi F4500 spectrometer, and the dominant emission wavelengths were centered at 597 nm, as shown in Fig. 2(b). The visible light emissions were so bright that they could be observed by the naked eye, and the corresponding optical microscope images of the light



Fig. 2 EL emission characteristics of single ZnO:Ga MWs *via* Au quasiparticle film decoration: (a) The I-V characteristics of single ZnO:Ga MWs *via* Au quasiparticle film decoration, with a corresponding sputtering time of 30 s. (b) EL emissions were recorded for single ZnO:Ga MWs *via* Au quasiparticle film decoration, and the dominant emission wavelengths are centered at 597 nm (sputtering time: 30 s). (c) The light-emitting behavior has been investigated using an optical microscope, and the emission regions are localized towards the center of the MWs (scale bar: 300 μ m). (d) The I-V characteristics of single ZnO:Ga MWs *via* Au quasiparticle film decoration, with a corresponding sputtering time of 80 s. (e) EL emissions were recorded for single ZnO:Ga MWs *via* Au quasiparticle film decoration, with a corresponding sputtering time of 80 s. (e) EL emissions were recorded for single ZnO:Ga MWs *via* Au quasiparticle film decoration, and the dominant emission wavelengths are centered at 605 nm (sputtering time: 80 s). (f) Light-emitting phenomena have been investigated using an optical microscope, and the EL emission regions are localized towards the center of the MWs (scale bar: 250 μ m).

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emission are shown in Fig. 2(c). After increasing the sputtering time of Au to 80 s, the *I–V* characteristics suggest that the electronic transport characteristics could be further enhanced (Fig. 2(d)). Still, bright and stable light emission from Au quasiparticle film-decorated ZnO:Ga MWs can also be observed, as shown in Fig. 2(f). Intriguingly, increasing the sputtering times can result in a red-shift of the dominant emission wavelengths to 605 nm. Therefore, by introducing Au quasiparticle film decoration, tunable electronic transport characteristics and wavelength-tunable light emission for individual ZnO:Ga MWs can be realized by means of increasing the sputtering time. Therefore, individual ZnO:Ga MWs *via* Au quasiparticle film decoration, could be used to construct semiconducting fluorescent emitters.

Now, let's focus on individual ZnO:Ga MWs *via* Ag quasiparticle film decoration, with the sputtering time set to 30 s. Linear *I–V* characteristics could be obtained from single ZnO: Ga MWs and Ag quasiparticle film-decorated ZnO:Ga MWs, as displayed in Fig. 3(a). It is quite clear that Ag quasiparticle film decoration can also be used to modify the electronic transport characteristics. After continuing to increase the injection currents, the single ZnO:Ga MWs decorated with Ag quasiparticle films began to emit bright and stable light, and the dominant emission wavelengths were centered at 500 nm (Fig. 3(b). The visible light emissions were so bright that they could be observed by the naked eye, and the emission regions were located towards the center of the wires. Optical microscope images of the light emission are shown in Fig. 3(c)). By

increasing the sputtering time of Ag to 80 s, a little red-shift in the EL emissions could be observed, and the dominant emission wavelengths were centered at 522 nm. The detailed EL emission characteristics can be observed in Fig. 3(e) and (f). It is funny that by increasing the sputtering times, tunable electronic transport properties and wavelength-tunable light emission could also be achieved. Therefore, individual ZnO:Ga MWs *via* Ag quasiparticle film decoration could be used to construct semiconducting fluorescent emitters.

Unlike Au and Ag, Al is an attractive plasmonic material that enables strong plasmon resonances spanning much of the spectrum from the visible to the ultraviolet regions.57,58 Light-emitting devices have been fabricated based on individual ZnO:Ga MWs via Al quasiparticle film decoration, with a sputtering time of 30 s. Linear I-V characteristics could also be observed for single ZnO:Ga MWs and Al quasiparticle filmdecorated ZnO:Ga MWs, as shown in Fig. 4(a). Thus, Al can also be used to modify the electronic transport characteristics of individual ZnO:Ga MWs. Furthermore, by increasing the injection currents, bright and stable light could be observed, and the dominant emission wavelengths were centered at 505 nm (Fig. 4(b)). The light-emitting regions were localized towards the center of the MWs, accompanied by an increase in the brightness and emission regions with the drain currents (Fig. 4(c)). After increasing the sputtering time to 80 s, further improvement in the electronic transport as well as a little redshift in the EL emissions, could also be achieved, and the dominant emission wavelengths were centered at 525 nm



Fig. 3 EL emission characteristics of single ZnO:Ga MWs *via* Ag quasiparticle film decoration: (a) The *I*–*V* characteristics of single ZnO:Ga MWs *via* Ag quasiparticle film decoration, with a sputtering time of 30 s. (b) EL emissions were recorded for single ZnO:Ga MWs *via* Ag quasiparticle film decoration, and the dominant emission wavelengths are centered at 500 nm (sputtering time: 30 s). (c) The light-emitting behavior has been investigated using an optical microscope, and the EL emission regions are localized towards the center of the MWs (scale bar: 300 μ m). (d) The *I*–*V* characteristics of single ZnO:Ga MWs *via* Ag quasiparticle film decoration, with a sputtering time of 80 s. (e) EL emissions were recorded for single ZnO:Ga MWs *via* Ag quasiparticle film decoration, with a sputtering time of 80 s. (e) EL emissions were recorded for single ZnO:Ga MWs *via* Ag quasiparticle film decoration, with a sputtering time of 80 s. (e) EL emissions were recorded for single ZnO:Ga MWs *via* Ag quasiparticle film decoration, and the dominant emission wavelengths are centered at 522 nm (sputtering time: 80 s). (f) The light-emitting behavior has been investigated using an optical microscope, and the EL emission regions are localized towards the center of the MWs (scale bar: 250 μ m).



Fig. 4 EL emission characteristics of single ZnO:Ga MWs *via* Al quasiparticle film decoration: (a) The *I*–*V* characteristics of single ZnO:Ga MWs *via* Al quasiparticle film decoration, with a sputtering time of 30 s. (b) EL emissions were recorded for single ZnO:Ga MWs *via* Al quasiparticle film decoration, and the dominant emission wavelengths are centered at 505 nm (sputtering time: 30 s). (c) The light-emitting behavior has been investigated using an optical microscope, and the EL emission regions are localized towards the center of the MWs (scale bar: 300 μ m). (d) The *I*–*V* characteristics of single ZnO:Ga MWs *via* Al quasiparticle film decoration, with a sputtering time of 80 s. (e) EL emissions were recorded for single ZnO:Ga MWs *via* Al quasiparticle film decoration, with a sputtering time of 80 s. (e) EL emissions were recorded for single ZnO:Ga MWs *via* Al quasiparticle film decoration, with a sputtering time of 80 s. (e) EL emissions were recorded for single ZnO:Ga MWs *via* Al quasiparticle film decoration, with a sputtering time of 80 s. (e) EL emissions were recorded for single ZnO:Ga MWs *via* Al quasiparticle film decoration, with a sputtering time of 80 s. (e) EL emissions were recorded for single ZnO:Ga MWs *via* Al quasiparticle film decoration, with a sputtering time of 80 s. (e) EL emissions were recorded for single ZnO:Ga MWs *via* Al quasiparticle film decoration, and the dominant emission wavelengths are centered at 525 nm (sputtering time: 80 s). (f) The light-emitting behavior has been investigated using an optical microscope, and the EL emission regions are localized towards the center of the MWs (scale bar: 300 μ m).

(Fig. 4(e)). Bright and stable light can be observed, as shown in Fig. 4(f). Therefore, individual ZnO:Ga MWs *via* Al quasiparticle film decoration could be used to construct semiconducting fluorescent emitters.

Consequently, by introducing metal quasiparticle film decoration, the electronic transport characteristics of individual ZnO:Ga MWs could be tuned; meanwhile, wavelength-tunable EL emissions could also be achieved (Fig. S13 and S14[†]). Considering single ZnO:Ga MWs via Ag quasiparticle film decoration for instance (sputtering time: 60 s), in order to investigate the possible EL emission mechanism, temperature distributions along the MWs were probed. Since the emission regions are always localized toward the center, three regions, labelled as the non-lighting region (Fig. 5(a)), the critical zone between lighting or non-lighting (Fig. 5(b)), and the lighting regions (Fig. 5(c)), were selected.⁴¹ It is obvious that metal quasiparticle films can be converted into physically isolated nanoparticles ($D \sim 100$ nm) in the light-emitting region, which can be attributed to the resistive self-heating effect. Therefore, the current heating effect, as opposed to thermoluminescence, plays a key role in EL emissions. The brightest spot of the emission toward the center of the ZnO:Ga MWs can be derived from the maximum temperature region (Fig. S15[†]). There was little change to the surface morphologies of the metal quasiparticle films, located in the non-lighting region, and in the contact region between In electrodes and ZnO:Ga MWs as well (Fig. S16[†]). After increasing the sputtering times from 30 s to

80 s, the surface morphologies of Ag nanostructures were also investigated, as shown in Fig. 5(e) and (f). Uniform and physically isolated Ag nanoparticles could also be achieved in the lighting regions. Specifically, increasing the sputtering time can result in an increase in the size and concentration of Ag nanoparticle aggregates. In addition, the surface morphologies of Au and Al quasiparticle film-decorated ZnO:Ga MWs were also investigated and the results are shown in Fig. S3 and Fig. S4 in the ESI.[†] Metal quasiparticle films decorated in the lighting regions can also be converted into isolated nanoparticles. When compared with Au and Ag, Al forms a stable oxide (Al_2O_3) immediately after exposure to a laboratory environment during lighting, and thus it is expected to significantly influence the surface morphology of Al (relatively low melting point 660 °C and oxidized easily at room temperature).59

To estimate the robustness of the EL emissions from single ZnO:Ga MWs *via* metal quasiparticle film decoration (using Ag for example), instantaneous electrical breakdown measurements were performed, as shown in Fig. S5.† The brightest lighting regions, which correspond to the hottest spots, would become the broken spots. Magnified high-resolution images showed that after the recrystallization procedure, a change from single crystalline into polycrystalline pearl-like structures could happen towards the broken regions, accompanied by plenty of pearled nanostructures. Magnified SEM images indicate that the Ag nanoparticles decorated on the ZnO:Ga MWs



Fig. 5 SEM images of the surface morphologies of single ZnO:Ga MWs *via* Ag quasiparticle film decoration: (a) An SEM image of Ag-decorated ZnO:Ga MWs in the non-lighting region, with a sputtering time of 60 s. (b) An SEM image of Ag quasiparticle films towards the critical region between lighting or non-lighting (sputtering time: 60 s). (c) An SEM image of Ag quasiparticle films in the middle lighting region (sputtering time: 60 s). (d) A magnified SEM image of Ag quasiparticle films in the center of the lighting region, the average diameter of the isolated Ag nanoparticles is $d \sim 100$ nm (sputtering time: 60 s). (e) An SEM image of Ag nanoparticles towards the center of the lighting region (sputtering time: 30 s). (f) An SEM image of Ag nanoparticles towards the center of the lighting region (sputtering time: 30 s). (f) An SEM image of Ag nanoparticles towards the center of the lighting region (sputtering time: 30 s).

undergo a process of continuous melting and recrystallization during the electrical breakdown moment. In the critical region, the Ag nanoparticles become disorganized, together with the disappearance of the quasiparticle films. However, there was little influence in the non-lighting regions. Thus, Joule heating can be considered as the major factor for the electrical breakdown behavior.^{41,60–63} In addition, if the injected currents remain unchanged, and are below the broken currents, for a period, the applied voltage holds constant. Stable and reproducible bright visible light emission from Ag quasiparticle film-decorated ZnO:Ga MW devices can be acquired. Therefore, individual ZnO:Ga MWs *via* metal quasiparticle film decoration has been proven to be a potential fluorescent emitter.⁴¹

As mentioned above, the sputtering time played a significant role in the electronic transport properties and EL emission characteristics. For example, when the sputtering time was shorter than 30 s, the modification of the electronic transport properties was relatively limited, thus, physically isolated metal nanoparticles could not be formed towards the center even if the applied voltage was as high as 200 V. If the sputtering time was longer than 200 s, the injected electrons would be transported by means of the superficial metal films, rather than the ZnO:Ga MWs. Considering Ag quasiparticle film decoration further in order to figure out the influence on the EL emissions, Ag (99.99%) was deposited on the c-face sapphire, and subsequently annealed under a N2 atmosphere at 400 °C to form isolated Ag nanoparticles. The morphologies of the samples were investigated, and the results are shown in Fig. S6.[†] Increasing the sputtering time from 30 s to 80 s can also lead to an increase in the size and concentration of Ag nanoparticle aggregates. The absorption spectra of the Ag nanoparticles were recorded using a Shimadzu UV-3101PC scanning spectrophotometer (Fig. S6(b)[†]). It was found that by increasing the sputtering times, a red-shift in the absorption peaks could be achieved, and the dominant resonant wavelengths ranged from 441 nm to 485 nm. The peaks could be attributed to dipole surface plasmon resonances.⁶⁴ This is in accordance with the red-shift in the EL emissions for the single ZnO:Ga MWs via Ag quasiparticle film decoration. To further verify the tuning of the dipole surface plasmon resonances, theoretical calculations and simulations for the isolated Ag nanoparticles were carried out (Fig. S7†). For comparison, localized surface plasmon resonances for Au (Fig. S8[†]) and Al (Fig. S9, S10 and S11[†]) were also investigated, and detailed information can be found in the ESI.† It was confirmed that metal plasmons play a pivotal role in modulating the EL emission characteristics.

By adjusting the sputtering times, as well as the wellarranged Au–Ag alloys, the tunable dipole plasmonic resonances could be significantly modulated in the visible regions. For example, by means of optimizing the sputtering time ratio of the alloys, such as Ag:Au = 1:0, 2:1, 1:1, 1:2, 1:3 and 0:1 (total sputtering time: 100 s), dipole surface plasmon resonances, ranging from 483 nm to 606 nm, could be realized, as shown in Fig. 6(a). On account of the manoeuvrability of metal plasmons, hybrid architectures comprising single ZnO:Ga MWs *via* alloy quasiparticle film decoration were constructed. The *I–V* characteristics demonstrate that the electronic transport characteristics of individual ZnO:Ga MWs can be modified gradually (Fig. 6(b)). In particular, to characterize the EL emission characteristics from single ZnO:Ga MWs *via* alloy



Fig. 6 (a) Localized surface plasmon resonances of alloy nanoparticles comprising Ag and Au, the absorption peaks were tuned in the visible region, the corresponding alloy weight ratios were 1: 0, 2: 1, 1: 1, 1: 2, 1: 3 and 0: 1 (total sputtering times:100 s). (b) The *I*–*V* characteristics of the metal quasiparticle film-decorated ZnO:Ga MWs. (c) Normalized EL spectra for individual ZnO:Ga MWs *via* different metal quasiparticle film decoration, with the dominant emission wavelengths centered at 500 nm, 527 nm, 560 nm, 602 nm and 622 nm. (d) EL emissions with visible light-emitting behavior have been investigated using an optical microscope on the basis of different metal quasiparticle film-decorated ZnO:Ga MWs, with the light-emitting regions localized towards the center of the MWs (scale bar: 250 μ m). (e) A schematic diagram of the hot-electron generation and injection processes at the metal–ZnO:Ga interface, the light-emitting process consists of nonradiative energy transfer between the ZnO:Ga MWs and metal nanostructures, the inelastic collision between energetic electrons and the host lattices of ZnO:Ga MWs, and finally the radiation recombination between the electrons located in the Ga-related impurity levels and the holes distributed in the valence band (the yellow solid line encircling the electrons is defined as the Ga-related impurity band).

quasiparticle film decoration, it was noted that when the alloy was composed of Ag, the EL emission characteristics revealed that the emission wavelengths were centered at 515 nm, and the lighting behaviors are displayed in Fig. 6(d). By increasing the Au sputtering times in the alloy with a ratio of Ag: Au = 1:1, this showed that the dominant emission wavelengths were red-shifted, and centered at 527 nm. Accordingly, EL emissions with wavelengths centered at 560 nm could be observed by continuously increasing the Au sputtering time ratio in the alloys, such as Ag:Au = 1:2 (Fig. 6(c)). Considering the alloy composed of Au, Fig. 6(c) shows that the dominant emission wavelength was centered at 615 nm. Consequently, bright, stable, and localized EL emission toward the center of the MWs could be achieved for the five samples. Fig. 6(d) shows the optical microscope images of the light emission. It was confirmed that tunable metal plasmons can be used to dominate the emission characteristics.

It has been reported that EL emissions from biased single semiconductor components, such as microwires, nanowires,

nanotubes, etc., can contribute to a bipolar EL mechanism, a unipolar impact excitation process assisted by hot carriers, and thermal light emission due to the Joule heating effect.^{30,33,65} However, EL emissions from single ZnO:Ga MWs via metal quasiparticle decoration cannot be compatible with the above three emission mechanisms. The Ohmic contact characteristics between the In electrodes and ZnO:Ga MWs indicate that there were no junctional depletion layers. The emission regions were always localized towards the center, even if they were driven by an alternating current. To rule out thermal light emission, an electrical breakdown measurement of the ZnO micro/nanostructures was carried out and the breakdown temperature was estimated to be 1050 K, which is far below the critical temperature for thermal radiation (~2800 K). It is noteworthy that a lower temperature environment can lead to an enhancement of the EL emission.^{30,48,62} The possible EL emission mechanism can be summed up as follows:^{41,48,56} (1) the improvement in the electrical conductivities for single ZnO:Ga MWs via metal quasiparticle film

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decoration is high enough for them to be treated as quasimetallic wires (Fig. S17[†]); (2) by applying a bias onto individual ZnO:Ga MWs, the hottest spots were formed towards the center of the wires due to the Joule heating effect, thus the voltage applied between both electrodes could produce a sufficiently strong electric field located towards the hottest spot to accelerate the transported carriers; (3) the transported electrons could be accelerated and could become energetic electrons, with the aid of an inelastic collision with ZnO:Ga crystalline host lattices, the electrons could be excited and transported into the conduction band, after relaxation and radiative recombination with holes located in the valence band. Therefore, emitted photons could be collected towards the hottest spots. Particularly, by introducing metal quasiparticle film decoration, physically isolated metal nanoparticles can be formed towards the hottest spots after a self-annealing process. The electric field intensity $\sim 10^6$ V m⁻¹ could be calculated when the applied voltage exceeded a threshold value $V_{\rm th}$ (for example, light emission could be observed towards the center). The electric potential difference was so high that it was in close proximity to the threshold electric field for the impact excitation. Thus, the transported electrons in the MW-channel could be accelerated and could become energetic electrons, which are spatially localized at the center of the MWs.^{26,28,30} Then, an inelastic collision was employed to stimulate plasmons between the transported energetic electrons and the free electrons from the metal nanoparticles assisted by nonradiative energy transfer. By the action of the external electric potential, hot electrons could be generated by plasmon decay, and they could experience a transition from the initial state located below the Fermi level to the final state, which is above the Fermi level, thus creating a distribution of "hot electrons" well above the Fermi energy of the metal.^{13,58,66} To quantify the energy of the hot electrons, a model has been developed, and the calculated energy was 3.65 eV, which is higher than the bandgap of ZnO.²⁰ Simultaneously, with the aid of theoretical analysis and calculations (Fig. S6-S11[†]), the generated hot electrons would be injected into the conduction band of ZnO:Ga at the metal-ZnO:Ga MWs interface. The hot-electron generation and injection processes are estimated to take place on the order of subpicoseconds, thus contributing to the enhancement of the component of electronic transport, which is in agreement with the experimental observations. It should be noted that although the conventional Ag-ZnO Schottky junction barrier cannot be formed towards the contact regions, the plasmon-mediated hot-electron injection process that was previously described is still allowed to occur, in what is by all means an interface chemically bonded assembly.²⁰ The excited hot electrons in the Ag nanoparticles have a probability to be excited either above whatever barrier is formed or to tunnel through the contact region. This EL emission behavior supports the hypothesis that radiative recombination originates from surface defect states localized within the segregation region created by the impurity

band, which consists of intrinsic defects, such as Zn interstitial and oxygen vacancies, as well as Ga_{Zn} -induced impurity levels (Fig. 6(e)).

Consequently, the hybrid architectures comprising single ZnO:Ga MWs via metal quasiparticle film decoration enable electrically-driven generation of hot electrons. These energetic hot electrons can migrate across the contact barrier between metal/ZnO:Ga interfaces, thus diffusing into the ZnO:Ga MWs. This process would supply more electrons into the MWchannel, leading to an enhancement in the conductivities of ZnO:Ga MWs. The larger the applied voltage on the hybrid architectures, the higher the number of migrated hot electrons produced, which is in accordance with the expected driving current response as a function of EL intensities. Meanwhile, the plasmonic energy transfer procedures were dominated by metal plasmons, which originated from the metal nanostructures confined in the hottest spots. Therefore, localized plasmonic energies could be converted to electrical charges and their flow.²⁶ Combined with the versatility of plasmonic nanostructures for wavelength-tunability, the hybrid architectures offer an ultra-wide spectral range that can be used in light-emitting devices.

4 Conclusion

To summarize, wavelength-tunable fluorescent emitters have been fabricated using single ZnO:Ga MWs via metal quasiparticle film decoration. Meanwhile, the optimization of metal sputtering times and the well-arranged alloy weight ratios could be used to tune the metal plasmons, which could control the EL emission characteristics. By investigating the possible EL emission mechanism, it was found that the hybrid architectures could allow tunable n-type conduction, with the resistivity further decreasing from $1.5 \times 10^{-1} \Omega$ cm to $3.5 \times 10^{-3} \Omega$ cm by introducing metal quasiparticle film decoration. The enhancement of the electrical conduction, associated with the presence of Ga in ZnO, could contribute to the formation of the hottest spots towards the center, together with the evaporated quasiparticle films being converted into isolated nanoparticles. These properties facilitate the spatially localized accumulation of hot electrons, making the hybrid architectures potential candidates for the construction of fluorescent emitters. Therefore, we have introduced a new paradigm for electrically-driven metal plasmonmediated generation of hot electron dynamics by developing single ZnO:Ga MWs via metal quasiparticle film decorationbased resistive heaters for the fabrication of physically isolated nanoparticles, which function as a predominant component in the construction of wavelength-tunable emitters. This measurable modulation could break through the constraints of semiconducting material properties, such as bandgap engineering, doping, metal-semiconductor interfacial characterization, etc., to achieve the reengineering of the bandgap configuration, which can be used to construct novel optoelectronic devices.

Conflicts of interest

There are no conflicts to declare.

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References

- 1 Z. Fan and H. Zhang, Chem. Soc. Rev., 2016, 47, 63.
- 2 J. Dana, P. Maity and H. N. Ghosh, Nanoscale, 2017, 9, 9723-9731.
- 3 U. Aslam, S. Chavez and S. Linic, *Nat. Nanotechnol.*, 2017, **12**, 1000.
- 4 Y. Shiraishi, N. Yasumoto, J. Imai, H. Sakamoto, S. Tanaka, S. Ichikawa, B. Ohtani and T. Hirai, *Nanoscale*, 2017, **9**, 8349–8361.
- 5 O. Lupan, V. Postica, F. Labat, I. Ciofini, T. Pauportlé and R. Adelung, *Sens. Actuators, B*, 2017, **254**, 1259–1270.
- 6 A. Zubair, A. Nourbakhsh, J. Y. Hong, Q. Meng, S. Yi,
 D. Jena, K. Jing, M. Dresselhaus and T. Palacios, *Nano Lett.*, 2017, 17, 3089–3096.
- 7 P. Zilio, M. Dipalo, F. Tantussi, G. C. Messina and F. D. Angelis, *Light: Sci. Appl.*, 2017, **6**, e17002.
- 8 S. Peng, G. Xing and Z. Tang, *Nanoscale*, 2017, 9, 15612– 15621.
- 9 M. L. Brongersma, N. J. Halas and P. Nordlander, *Nat. Nanotechnol.*, 2015, **10**, 25.
- 10 C. V. Hoang, K. Hayashi, Y. Ito, N. Gorai, G. Allison, X. Shi, Q. Sun, Z. Cheng, K. Ueno and K. Goda, *Nat. Commun.*, 2017, 8, 771.
- 11 G. Hergert, J. Vogelsang, F. Schwarz, D. Wang, H. Kollmann, G. Petra, C. Lienau, E. Runge and P. Schaaf, *Light: Sci. Appl.*, 2017, 6, e17075.
- 12 M. Moskovits, Nat. Nanotechnol., 2015, 10, 6-8.
- 13 K. Wu, J. Chen, J. R. Mcbride and T. Lian, *Science*, 2015, 349, 632–635.
- 14 H. Jia, X. M. Zhu, R. Jiang and J. Wang, ACS Appl. Mater. Interfaces, 2017, 9, 2560–2571.
- 15 S. Tan, L. Liu, Y. Dai, J. Ren, J. Zhao and H. Petek, *J. Am. Chem. Soc.*, 2017, **139**, 6160–6168.
- 16 A. Pescaglini, A. Martĺłn, D. Cammi, G. Juska, C. Ronning,
 E. Pelucchi and D. Iacopino, *Nano Lett.*, 2014, 14, 6202–6209.
- 17 K. H. Shokri, J. H. Yun, Y. Paik, J. Kim, W. A. Anderson and S. J. Kim, *Nano Lett.*, 2016, **16**, 250–254.
- 18 P. Christopher and M. Moskovits, Annu. Rev. Phys. Chem., 2017, 68, 379.

- 19 S. Ganti, P. J. King, E. Arac, K. Dawson, M. J. Heikkilä, J. H. Quilter, B. Murdoch, P. Cumpson and A. O'Neill, ACS Appl. Mater. Interfaces, 2017, 9, 27357.
- 20 J. Liu, A. Manjavacas, V. Kulkarni and P. Nordlander, ACS Nano, 2014, 8, 7630–7638.
- 21 C. Clavero, Nat. Photonics, 2014, 8, 95-103.
- 22 A. Sheikh, A. Yengantiwar, M. Deo, S. Kelkar and S. Ogale, *Small*, 2013, **9**, 2091.
- 23 O. Lupan, V. Postica, R. Adelung, F. Labat, I. Ciofini, U. Schlźrmann, L. Kienle, L. Chow, B. Viana and T. Pauportlę, *Phys. Status Solidi RRL*, 2017, 12, 1700321.
- 24 Z. Chen, X. Li, J. Wang, L. Tao, M. Long, S. J. Liang, L. K. Ang, C. Shu, H. K. Tsang and J. B. Xu, ACS Nano, 2016, 11, 430–437.
- 25 X. Meng, L. Liu, S. Ouyang, H. Xu, D. Wang, N. Zhao and J. Ye, *Adv. Mater.*, 2016, 28, 6781.
- 26 P. Rai, N. Hartmann, J. Berthelot, J. Arocas, d. F. G. Colas, A. Hartschuh and A. Bouhelier, *Phys. Rev. Lett.*, 2013, **111**, 026804.
- 27 P. Bharadwaj, A. Bouhelier and L. Novotny, *Phys. Rev. Lett.*, 2011, **106**, 226802.
- 28 Y. Vardi, E. Cohenhoshen, G. Shalem and I. Barjoseph, *Nano Lett.*, 2015, **16**, 748–752.
- 29 M. Buret, A. V. Uskov, J. Dellinger, N. Cazier, M. M. Mennemanteuil, J. Berthelot, I. V. Smetanin, I. E. Protsenko, G. Colasdesfrancs and A. Bouhelier, *Nano Lett.*, 2015, **15**, 5811–5818.
- 30 Y. D. Kim, H. Kim, Y. Cho, J. H. Ryoo, C.-H. Park, P. Kim, Y. S. Kim, S. Lee, Y. Li, S.-N. Park, *et al.*, *Nat. Nanotechnol.*, 2015, **10**, 676–682.
- 31 T. C. Jr, Y. W. Lan, C. Zeng, J. H. Chen, X. Kou, A. Navabi, J. Tang, M. Montazeri, J. R. Adleman and M. B. Lerner, *Nano Lett.*, 2015, 15, 7905–7912.
- 32 C. Zeng, E. B. Song, M. Wang, S. Lee, C. M. T. Jr, J. Tang, B. H. Weiller and K. L. Wang, *Nano Lett.*, 2013, 13, 2370– 2375.
- 33 J. Dai, C. X. Xu and X. W. Sun, Adv. Mater., 2011, 23, 4115.
- 34 Y. Q. Bie, Z. M. Liao, P. W. Wang, Y. B. Zhou, X. B. Han, Y. Ye, Q. Zhao, X. S. Wu, L. Dai and J. Xu, *Adv. Mater.*, 2010, 22, 4284–4287.
- 35 B. Zhao, F. Wang, H. Chen, Y. Wang, M. Jiang, X. Fang and D. Zhao, *Nano Lett.*, 2015, **15**, 3988–3993.
- 36 Y.-Y. Lai, Y.-P. Lan and T.-C. Lu, Light: Sci. Appl., 2013, 2, e76.
- 37 G. D. Yuan, W. J. Zhang, J. S. Jie, X. Fan, J. X. Tang, I. Shafiq, Z. Z. Ye, C. S. Lee and S. T. Lee, *Adv. Mater.*, 2008, 20, 168–173.
- 38 X. Zhang, L. Li, J. Su, Y. Wang, Y. Shi, X. Ren, N. Liu, A. Zhang, J. Zhou and Y. Gao, *Laser Photonics Rev.*, 2014, 8, 429–435.
- 39 O. Lupan, T. Pauporte, T. L. Bahers, B. Viana and I. Ciofini, *Adv. Funct. Mater.*, 2011, 21, 3564–3572.
- 40 Y. Liu, M. Jiang, G. He, S. Li, Z. Zhang, B. Li, H. Zhao, C. Shan and D. Shen, *ACS Appl. Mater. Interfaces*, 2017, 9, 40743-40751.
- 41 M. Jiang, G. He, H. Chen, Z. Zhang, L. Zheng, C. Shan, D. Shen and X. Fang, *Small*, 2017, 13, 1604034.

- 42 M. M. Jiang, B. Zhao, H. Y. Chen, D. X. Zhao, C. X. Shan and D. Z. Shen, *Nanoscale*, 2014, **6**, 1354–1361.
- 43 C. Xu, J. Dai, G. Zhu, G. Zhu, Y. Lin, J. Li and Z. Shi, *Laser Photonics Rev.*, 2014, **8**, 469–494.
- 44 E. Matioli, S. Brinkley, K. M. Kelchner, Y. L. Hu, S. Nakamura, S. Denbaars, J. Speck and C. Weisbuch, *Light: Sci. Appl.*, 2012, **1**, e22.
- 45 M. Achermann, J. Phys. Chem. Lett., 2010, 1, 2837–2843.
- 46 Y. Chen, T. Yang, H. Pan, Y. Yuan, L. Chen, M. Liu, K. Zhang, S. Zhang, P. Wu and J. Xu, *J. Am. Chem. Soc.*, 2014, **136**, 1686–1689.
- 47 I. Gryczynski, J. Malicka, Z. Gryczynski, K. Nowaczyk and J. R. Lakowicz, *Anal. Chem.*, 2004, 76, 4076–4081.
- 48 G. H. He, M. M. Jiang, L. Dong, Z. Z. Zhang, B. H. Li, C. X. Shan and D. Z. Shen, *J. Mater. Chem. C*, 2017, 5, 2542– 2551.
- 49 A. Jamshidi, P. J. Pauzauskie, P. J. Schuck, A. T. Ohta, P. Y. Chiou, J. Chou, P. Yang and M. C. Wu, *Nat. Photonics*, 2008, 2, 86.
- 50 G. Lozano, S. R. Rodriguez, M. A. Verschuuren and J. G. Rivas, *Light: Sci. Appl.*, 2016, 5, e16080.
- 51 W. Liu, F. Xiu, K. Sun, Y.-H. Xie, K. L. Wang, Y. Wang, J. Zou, Z. Yang and J. Liu, *J. Am. Chem. Soc.*, 2010, 132, 2498–2499.
- 52 D. O. Demchenko, B. Earles, H. Y. Liu, V. Avrutin, N. Izyumskaya, U. Özgür and H. Morkoç, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2011, 84, 075201.
- 53 W. Ruane, K. Johansen, K. Leedy, D. C. Look, H. von Wenckstern, M. Grundmann, G. C. Farlow and L. J. Brillson, *Nanoscale*, 2016, 8, 7631–7637.

- 54 W. K. Hong, J. I. Sohn, D. K. Hwang, S. S. Kwon, G. Jo, S. Song, S. M. Kim, H. J. Ko, S. J. Park and M. E. Welland, *Nano Lett.*, 2008, 8, 950–956.
- 55 Y. K. Lee, C. H. Jung, J. Park, H. Seo, G. A. Somorjai and J. Y. Park, *Nano Lett.*, 2011, **11**, 4251–4255.
- 56 M. M. Jiang, G. H. He, Z. Zhang, B. H. Li, H. Zhao, C. X. Shan and D. Shen, *J. Mater. Chem. C*, 2017, 5, 10938– 10946.
- 57 M. W. Knight, N. S. King, L. Liu, H. O. Everitt, P. Nordlander and N. J. Halas, *ACS Nano*, 2014, 8, 834–840.
- 58 T. Gong and J. N. Munday, Appl. Phys. Lett., 2017, 110, 021117.
- 59 C. Langhammer, M. Schwind, B. Kasemo and I. Zoric, *Nano Lett.*, 2008, 8, 1461–1471.
- 60 T. Westover, R. Jones, J. Huang, G. Wang, E. Lai and A. A. Talin, *Nano Lett.*, 2008, 9, 257–263.
- 61 Y. Wei, P. Liu, K. Jiang, L. Liu and S. Fan, *Appl. Phys. Lett.*, 2008, **93**, 023118.
- 62 J. Zhao, H. Sun, S. Dai, Y. Wang and J. Zhu, *Nano Lett.*, 2011, 11, 4647–4651.
- 63 J. Chen, V. Perebeinos, M. Freitag, J. Tsang, Q. Fu, J. Liu and P. Avouris, *Science*, 2005, **310**, 1171– 1174.
- 64 M. M. Jiang, H. Y. Chen, B. H. Li, K. W. Liu, C. X. Shan and D. Z. Shen, *J. Mater. Chem. C*, 2013, 2, 56–63.
- 65 Y.-J. Doh, K. N. Maher, L. Ouyang, C. L. Yu, H. Park and J. Park, *Nano Lett.*, 2008, 8, 4552–4556.
- 66 K. G. Stamplecoskie and P. V. Kamat, *J. Phys. Chem. Lett.*, 2015, 6, 1870–1875.