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Graphical abstract: One-sided silver growth are transformed to two-sided growth with two silver domains oppositely achored on the semiconductor core 44x24mm (300 x 300 DPI)

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## The key role of nanoparticle seeds for site-selective growth of silver to fabricate core-shell or asymmetric dumbbell heterostructures

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Herein, a novel method is invented to induce site-specific deposition of plasmonic silver domain on controlled sites of seeded AgBr nanoparticles. Novel core-shell heterostructures and dumbbell heterostructures are fabricated by heterogeneous silver growth. A curved silver shell with thickness up to 5 nm is generated covering the AgBr core in the core-shell metal-semiconductor hybrids. However in the dumbbell hybrids, a large silver domain is exclusively grown on single side of the AgBr seed with solid contact like relationship of head and tail. Photo generated electrons are facilitated to transfer from the semiconductor head to the metal tail enhancing charge separations. The significant role of seed size during seeded silver growth has been demonstrated

#### Introduction

An important frontier in nanocrystal research is the controlled arrangement of different materials within the same architectures in order for multiple functionalities and other novel properties. Hybrid nanoparticles fabricated via siteselective growth strategy has attracted much attention, in which an additional segment is controlled grown on selective sites of preformed nanoparticles, for example, core-shell semiconductor quantum dots,<sup>1-2</sup> binary metal core-shell nanoparticles,<sup>3</sup> coreshell metal-semiconductor hybrids<sup>4-5</sup> and metal-tipped semiconductor nanorods and tetrapods.<sup>6-8</sup> Specially, hybrid metal-semiconductor particles which combines a metal domain and a semiconductor domain into the same particle have attracted great interests because of their unique optical, electrical, and catalytic properties stemming from the unusual combination of two components. In hybrid metalsemiconductor nanoparticles, the electronic or optical properties could be altered through electron communication across the heterogeneous junctions, enhancing emission efficiency<sup>9</sup> and promoting redox reactions.<sup>10-11</sup> Except for applications in electronic, magnetic, optical and catalytic properties,<sup>12</sup> the hybrid metal-semiconductor nanoparticles also

demonstrated self-assemble ability via metal tips as anchor points.<sup>13</sup>

The site-selective growth and control of metal-semiconductor heterostructures is still of central challenge to create smart materials. Herein, we firstly reported the fabrication of coreshell and dumbbell-like heterostructures by photo-induced seeded silver growth on spherical AgBr seed particles. A promising question is how to deposit metal domains on controlled sites of the semiconductor body to direct electron flows and meet smart applications, rather than with rough deposition in spacial irregularity. Mongin et al. reported on a study of the ultrafast photoinduced charge separation in single tipped CdS-Au nanorods on a timescale of sub-100 fs time scale.<sup>14</sup> Then the ultrafast transferred electron can be stored in the noble metal domain on one end of the nanorods until it reaches Fermi level equilibration, promoting charge separation efficiency. Moreover, the synthetic effect by controlled deposition of plasmonic metal domains on semiconductor body could also promote the systematic engineering of the SPR (surface plasmon resonance) effect. 15-16

To fabricate core-shells and nanodumbbells by site selective growth of silver, a novel method combined of photochemical reduction reaction and heterogeneous seeded ARTICLE

growth is used, as well with assistance of titanate nanotubes under controlled alkali pH value. To study the seed effect in highly selective seeded silver growth, size-gradient AgBr seed particles with various sizes in the range of 150 - 5 nm are preformed in which the sizes of AgBr seeds gradually varies in a gradient along a certain distribution direction. By photoinduced silver growth on different AgBr seeds of various sizes, the critical role of seed size in governing the site-selective heterogeneous growth of silver has been demonstrated.

#### **Experimental**

#### Preparation of the titanate nanotubes as mediated material

1 g P25 TiO<sub>2</sub> and 50ml 10 M NaOH are mixed and stirred for 2h. The mixture was transferred to a Teflon vessel and sealed in an autoclave at 150 °C for one day. The obtained white solid was washed with water until pH reached around 7. 4 g sample was then protonated by 750 ml 0.1 M HCl and dried at 80 °C for 30min.

## Synthesis of gradient AgBr seed particles with various sizes in a gradient distribution

0.1g AgNO<sub>3</sub> is dissolved in 10ml distilled water and then added with drops of ammonia until transformed to clear silver ammonia solution. 0.1g protonated titanate nanotubes are dispersed in this newly made solution. The mixture is then treated carefully at 60 °C for about 40min in dark light environment until yellow colour powders are obtained. This step is to complex silver cations by surface hydroxyl groups of protonated titanate nanotubes. The powders are subsequently transferred to 50 ml distilled water with addition of 5 ml of hydrobromic acid (40%). Then they are sealed in the autoclave to protect from light and treated at 100°C for 1h. The silver cations are ionexchanged in acid solution and slowly released from the surface of protonated titanate nanotubes, and then diffused gradually into the HBr solution leading to formation of AgBr nanoparticles with gradient size distribution. The produced precipitates are washed by distilled water to reach to neutral pH value. Thus size-gradient AgBr seed particles (about 150 - 5 nm) are obtained.

#### Heterogeneous seeded silver growth on AgBr seeds

The as obtained mixture of various sized AgBr seeds and titanate nanotubes in the previous synthetic process is noted as AgBr-HTNTs system in which the various AgBr NPs are surrounding the stacked titanate nanotubes. 0.2 g AgBr-HTNTs powder is herein used as precursor, and exposed under room light for 20 min to accumulate photogenerated electrons on AgBr surface. AgBr has a direct band gap of 4.29 eV and an indirect band gap of 2.6 eV (absorption edge at 477 nm), with extensively application as a photosensitive material in photographic films. In the indirect case, electrons are injected to the conduction band of AgBr under visible light excitation below 477 nm. Then this AgBr-HTNTs powder is dispersed in 10 ml 0.06 M silver ammonia solution to photo-chemically induce seeded silver growth. The reaction is then shifted to the

dark light condition to keep off excessive irradiation in consideration of reaction control. And finally it is carefully heated under  $60\Box$  for about 60 min in the dark. During the growth stage of silver metal on AgBr seeds, the photo-induced electrons on the indirect conduction band of AgBr seed nanoparticles played a role of reducing agent to reduce Ag ion to Ag particle. The site-selective seeded growth behaviour of silver on various sized AgBr seeds is investigated.

#### Characterization

Transmission electron microscopy (TEM), high resolution TEM (HRTEM) images, selective area electron diffraction (SAED) and energy diffraction spectrum (EDS) were obtained by a JEM-2100 electron microscope. The absorbance spectra were obtained on a Shimadzu 2550 UV-vis spectrophotometer.

#### Photocatalytic activities test

The photocatalytic activities were tested by using methylene orange (MO) as the probe molecule under visible light irradiation. 0.1g photocatalysts were dispersed into a 100 mL cylinder containing 60 mL methyl orange (MO) solution (10 mg L<sup>-1</sup>). The dispersion was kept in the dark for 20min for dark adsorption experiment. This is a typical time for MO to reach adsorption equilibrium, after which the photocatalytic degradation was carried out. The light source was a 500 W Xenon lamp (>400 nm).

#### **Results and discussion**

Semiconductor-metal hybrid nanostructures with two components of different functionality have been given rise recent years due to their promising applications. Heterogeneous seeded growth is a novel strategy to fabricate hybrid architectures by growth of a second inorganic domain directly from the surface of pre-existed nanoparticle seeds. In this experiment, the site-selective seeded growth of silver has been performed on various AgBr seed particles leading to formation of different morphologies. To better understand the seeded growth mechanism of silver, the critical effects of AgBr seed size to silver growth has been demonstrated. A unique kind of size-gradient AgBr seeds (as shown in Electronic Supplementary Information Fig S1) which with gradient size variation along a distribution direction are pre-formed to induce heterogeneous silver growth and illustrate the influence of seed sizes on seeded silver growth. Despite reaction conditions that promote heterogeneous nucleation such as lattice mismatching, solvent polarity and surfactant concentration have been evaluated recent years,<sup>17</sup> however, there still lack of direct observation on the influence of seed-size to the final hybrid morphology. Surprisingly, core-shell heterostructures and anisotropic nanodumbbells by highly selective silver growth are fabricated relating to different sizes of AgBr seeds under the same other conditions.



Figure 1. The site-selective growth of silver domains on size-gradient AgBr seed particles. (a) Silver heterogeneous growth on spherical seeds of various size, (b)(f) Representative core-shell heterostructures grown where the seeds are about 50 - 40 nm, (c) Adjacent core-shell and nanodumbbell particles grown where the seeds are about 40 - 30 nm, and (d)(e)(g) Representative nanodumbells (NDBS) with silver grown exclusively on one side on the seed particles where the seeds are 30 - 5 nm

Fig 1 shows the TEM image of the solution after silver seeded-growth on the gradient AgBr seeds of various sizes (max size ~150 nm, min size ~5 nm). The gradient size distribution of the pre-formed seeds is analysed and shown in Fig 2. Generally, the as-prepared AgBr nanoparticle seeds are distributed in a wide range from about 5 - 150 nm with population density reversely correlated to seed sizes (as shown in Fig2). Since the pre-formed gradient AgBr seeds gradually vary the nanoparticle size in a wide range along a distribution direction, thus the influence of different seed size to the heterogeneous silver growth could be directly demonstrated and observed. When the silver ion precursor is added to the solution, Ag<sup>+</sup> ions are reduced to Ag<sup>0</sup> by the photoexcited electrons from those AgBr nanoparticle seeds. The question is whether the foreign silver growth could directly occurred from the surface of these semiconductor seeds in order for formation of multicomponent nanostructures. In general, for large AgBr seeds in the gradient distribution of Fig 1a where with seed size larger than 50 nm, no silver overlayers are heterogeneously attached on the surface of these seeds (50 -150 nm) to generate multi-domain nanostructures. Those seeds larger than 50 nm could not promote heterogeneous seededgrowth of silver; instead, the silver nanoparticles are crystallized in a homogenous way with separation to the preformed AgBr seeds. However, for smaller seeds below 50 nm in the gradient distribution of Fig 1a (representative distribution area b, c, d and e in Fig 1a with corresponding to TEM morphologies in Fig 1b, Fig 1c, Fig 1d and Fig 1e), the highly selective Ag metal growth on different locations of AgBr seeds is achieved including formation of core-shell structures and nanodumbbells (NDBs). Fig 1b, Fig 1c, Fig 1d and Fig 1e

show TEM examination on four representative areas from Fig 1a (as marked in Fig 1a with b, c, d, and e) with representation of silver growth on four different levels of seed size. The nanoparticle seed sizes in the marked area b, c, d and e in the gradient distribution of Fig 1a are b > c > d > e. The nanoparticle seeds in the distribution area of b and c in Fig 1a are between 50 - 40 nm and 40 - 30 nm, while the seeds in the marked area of d and e are between 30 - 20 nm and 20 - 5 nm respectively. Surprisingly, whether to preferentially form core-shell or dumbbell heterostructures during seeded-growth of silver is significantly dependent on the seed sizes.



Figure 2. Size distribution of the pre-formed AgBr seeds with gradient variation from about 5 nm to 150 nm

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Figure 3. Heterogeneously seeded silver growth respectively on preformed seeds with uniform size about 20 nm (a), 10 nm (b) and 5 nm (c).

The core-shell heterostructures are as demonstrated in Fig 1b, Fig 1c and Fig 1f, the cores of the two-domain hybrids are pre-existed AgBr nanoparticle seeds. The core and shell could be significantly distinguished by the contrast as illustrated in Fig 1f. The silver shell shows a light contrast compared to the core with shell thickness up to 4 - 5 nm. As suggested from Fig 1b, Fig 1c and Fig 1f, the cores of the heterostructures are with core-size larger than 30 nm and below 50 nm. However, for seeded silver growth on smaller seeds which with seed size below 30 nm as shown in Fig 1d, Fig 1e and Fig 1g, no coreshell nanostructures are grown. It can be concluded that, the formation of silver shells by seeded silver growth on AgBr seeds only occurred on the seeds with an appropriate size ranging from 50 nm to 30 nm.

For the smaller seeds below the critical size about 30 nm, nanodumbbells (Fig 1d, Fig 1e and Fig 1g) are preferentially generated by highly selective silver growth on single one side of the spherical seed particles. In this novel dumbbell-like structure as shown in Fig 1g, the Ag metal domain grew with longest length up to 20 nm like a tail locating with opposition to the semiconductor seed counterpart on the other end of the hybrid nanosystem. In this case of Ag metal deposition, the silver domain is selectively grown on one side of the nanoparticle seeds like the relationship of 'head' and 'tail' (Fig 1g). As shown by Fig 1d and Fig 1e, the dumbbell structure becomes the dominated heterostructure for silver growth on smaller seeds between 30 - 5 nm.

For the normal reported photocatalytic Ag@Ag(Cl, Br, I) hybrid system,<sup>18-20</sup> the tiny Ag metal clusters are always deposited randomly on the semiconductor surface without spatial control on the plasmonic metal domain addition. However, this newly fabricated two-domain nanodumbbell structure (max diameter below 50 nm) is quite different, in which a single Ag domain (max length about 20 nm) is exclusively connecting onto one side of the photocatalytic

semiconductor nanoparticle seed (30 - 5 nm) by site-selective addition.

The high-yield generation of nanodumbbells by one-sided silver growth was further presented in Fig 3.(More illustration in Fig S2-S4) Heterogeneous seeded silver growth was performed on uniform AgBr nanoparticle seeds respectively with average seed sizes about 20 nm, 10 nm and 5 nm. No coreshell structures are observed on these smaller seeds below 30 nm. In this case, nanodumbbells with a silver tail attached on the seed particles are grown in much high yield.



Figure 4. The seeded growth of silver domains on different sized seeds to fabricate core-shell and dumbbell-like heterostructures

As demonstrated by TEM analysis in Fig 1 and Fig 3, the location of seeded silver growth onto AgBr nanoparticle seeds could be highly selectively correlating to the size of seeds. The site-selective deposition leads to fabrication of silver shells covering the seed or silver tails connecting to one side of the seed. Significantly, the generation of two-domain nanodumbbells by one-sided silver growth needs the seed particles to below the critical size (30 nm). No silver shells could be grown on the smaller seeds below this critical size value as shown in Fig3. The schematic illustration of seeded silver growth behaviours on various AgBr seeds are illustrated in Fig 4.

Possible mechanisms are discussed to explain the sizedependence phenomenon in fabricating core-shells and dumbbells by silver growth. During the heterogeneous crystal growth process on sphere-like seeds, lower free-energy barriers are existed for crystal nucleation on larger seeds as computed by S. Auer.<sup>21</sup> According to the numerical simulation,<sup>21</sup> smooth spherical seed particles with larger diameter are easy to be covered by the crystallites that they spawn. This tendency is similar to the phenomenon observed in silver growth that silver crystals during seeded growth could form silver shells covering larger seeds, but could not well cover the smaller seeds below 30 nm. In the latter occasion, silver crystals adopt to grow on single one-side of the seed to lower the cover area. In addition, from the view of strain energy, the silver overlayers grown on a curved substrate need to maintain a strained structure unless break away from the substrate. In the formation of core-shell heterostructure by coating silver shells on spherical seeds of various sizes, the tension during the shells  $\Box P$  is as a function of the radii of seeds Rs which can be interpreted as

#### $\Delta P = \gamma / R_s$

, where  $\gamma$  is the compress tension of silver shell and Rs is the radii of the curved shell. When the silver shell heterogeneously grown on the curved surface of spherical AgBr seeds, the smaller radii *Rs* of the seeds makes the silver shell highly curved and more difficult to maintain the strained structure. This also increased the thermodynamic instability. Instead, during silver growth on smaller seeds nearly flat structure like a tail is observed with attachment on single one side the seeds forming nanodumbbells.

However, the particles of core-shell and dumbbell structures grown on various sized seeds are not separated in the current experiment. If purification of core-shells or nanodumbbells from the mixed particles is needed, density gradient centrifugation would be effective for separating particles of different sizes, shapes, materials, and polymorphs.<sup>22-24</sup> But actually the yield of core-shell structure can be neglected if compared to the large yield of nanodumbbells (Fig 3). This is because the formation of dumbbell structure is preferable on smaller AgBr seeds under 30 nm as shown in Fig 3. So the high yield of nanodumbbells makes this dumbbell structure rather than the core-shell structure to be the dominant product.

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Figure 5. (a) High resolution TEM image and selected-area electron diffraction (b) on the metal-semiconductor hybrids fabricated by seeded silver growth



Figure 6. EDS analysis on the AgBr seed particles before silver growth (a) and Ag-AgBr hybrid dumbbells after silver growth (b)

Further characterization on the hybrids by high resolution TEM analysis (HRTEM, Fig 5a), selected-area electron diffraction (SAED, Fig 5b) and energy-dispersive X-ray spectroscopy (EDS, Fig 5) confirmed that the two domains of different contrast in the hybrids are two separated phases. The lattice fringes in Fig 5a resolved by HRTEM on the two domains of different contrast confirmed they are Ag metal domain and AgBr semiconductor domain respectively. In the EDX analysis as shown in Fig 6, the element content in AgBr seed particles are determined to be Br of 50 mol% and Ag of 50 mol%. However, the element content in the nanodumbbells after seeded silver growth is determined to be Ag of 70 mol % and Br of 30 %. The significant change of silver content further confirmed that the tail-like domain anchored on the AgBr seed particles with light contrast in TEM analysis are grown by silver. And the head and tail of the nanodumbbells are respectively AgBr seed particle and silver domain selectively grown on one side of the seed. Specially, the length of silver tail in the dumbbell could grow longer up to 20 nm (Fig 1g). This is different from the metal-tipped heterostructures<sup>6-8</sup> where the metal domain as a small tip of several nanometers deposited on the tip of semiconductor nanorods or dots.

Besides the highly selective one-sided silver growth, twosided growth of silver domain is also obtained by repeating one-sided silver growth for two runs (As shown in Fig 7). The



Figure 7. (a) Ag-AgBr nanodumbbells by one-sided silver growth on AgBr seeds (b) Ag1-AgBr-Ag2 nanodumbbells by two-sided silver growth transformed by repeating one-sided growth for two runs. (c) Mechanisms of electron transfer and enhanced charge separation within the dumbbell-like particles fabricated by one-sided and two sided silver growth

second Ag metal domain (max length about 20 nm) is anchored on the Ag-AgBr dumbbell selectively on the other side, thus with two Ag metal domains opposite to each other. Fig 7(b) represents the TEM image of the two-sided silver growth on AgBr seed particles. Their fabrication follows the strategy for fabricating nanodumbbells with a single silver domain on one side but repeats the seeded silver growth procedure for a second run. The transforming of one-sided silver growth to two-sided silver growth leads to the formation of symmetric Ag<sub>1</sub>-AgBr-Ag<sub>2</sub> heterostructures, which with two silver domains (Ag<sub>1</sub> and Ag<sub>2</sub>) anchored on the AgBr seed particle like wings (As shown in Fig 7(b)).

Hybrid nanoparticles combine two or more disparate materials in the same particle represent a powerful way for fabricating smart materials with multi-functionalities stemming from the novel combination of unusual material. The possible electron transfer and charge separation processes in these nanodumbbells are schematically illustrated in Fig6(c), including nanodumbbells by one-sided and two-sided silver growth. The Femi level alignment in the semiconductor-metal interface promotes rapid transfer of the excited electrons in the semiconductor conduction band into the metal energy levels.<sup>14,25-27</sup> The charge transferred through solid state interface to the metal domain can be stored in the case of Au and Ag domain which act as good electron acceptor, leading to a shift in the Fermi level due to the single electron charging energy.<sup>28-</sup> <sup>29</sup> Thereby, as illustrated in Fig 7(c), the photoexcited electrons can be transferred to the silver domains (max length 20 nm) located on one side or two side of the hybrid particle(max

diameter about 50 nm), leaving holes localized on the opposite direction in the semiconductor domain. The charging of the metal domain under illumination will continue until it reaches Fermi level-conduction band equilibration, thus promoting charge separations across the nanodumbbell system.



Figure 8. Absorbance spectrums for Ag-AgBr nanodumbbells during one-sided seeded silver growth monitored with increased growth time.

Plasmonic structured metals (Au, Ag, Pt etc) have enhanced effects on the optical absorption of plasmonic metalsemiconductor hybrid materials. The optical absorption of Ag-AgBr nanodumbbells during highly selective seeded silver growth is as shown in Fig 8. The visible light absorption of the dumbbell hybrids between 800 - 400 nm significantly rises with increasing seeded silver growth time. However, the typical absorption range of AgBr is below 478 nm. The enhanced visible-light absorption ability may be due to the SPR effect of silver domain on one side. The surface plasmon reflectance (SPR) effect of noble metal is tunable according to the size, shape and local dielectric environment. By silver growth on various sized AgBr seed particles, silver domains of different size (max length up to 20 nm, min length around 10 nm, as shown in Fig 1d and Fig 1e) are regularly anchored on one side of the semiconductor seeds, leading to broadening of the SPR absorption. Besides, the nanosized plasmonic metal domains located on the surface of the semiconductor substrate also result scattering and anti-reflection effects to reduce the reflection of incident light.30-31 These combined factors enhanced the visiblelight absorption of the as-prepared hybrid nanodumbbells from 400 - 800 nm.

The high efficient visible-induced photocatalytic activity was explored by using methylene orange (MO) as a probe molecule under visible light irradiation (>400 nm). For comparison, the photocatalytic performances of N-doped TiO2, irregular Ag@AgBr plasmonic hybrid and dumbbelllike Ag-AgBr plasmonic hybrid have been investigated as shown in Fig 9. For normal reported irregular Ag@AgBr heterostructures, the tiny plasmonic silver clusters are scattered randomly on the surface of AgBr semiconductor surface, harvesting visible light and promoting charge



Figure 9. Comparison of photocatalytic degradation on probe molecules MO(10 mg  $L^{-1}$ ) under visible light irradiation using different catalysts.

transfers on the semiconductor surface. However in the novel Ag-AgBr nanodumbbells, the silver domain is anchored onto each of the AgBr seed particles by selectively on one side. Both irregular Ag@AgBr and dumbbell-like Ag-AgBr exhibit significant photocatalytic activity for degradation of probe molecules. However, for nanodumbbell heterostructures by site-specific growth of silver domains on AgBr seed particles, much higher MO degradation rate is demonstrated comparing to the normal Ag@AgBr structure.

As reported, conjoining of semiconductor and metal domains into the same nanosystem promotes rapid charge separations. However, the type and size of each domain of the heterostructures can affect the nature of charge transfer dynamics and the charge accumulation along the nanosystem. Herein, compared to the normal Ag@AgBr hybrids with irregular deposition of tiny silver domains on the semiconductor body, the Ag-AgBr nanodumbbells are anchored with silver domains on one side like a long tail( longest as 20 nm) opposite to the semiconductor core. In the case of nanodumbbells, the Ag metal domain which acts as electron acceptor is regularly localized on one end of the dumbbell system unlike the reported randomly deposition of metal nanoparticles on semiconductor surface. Thereby, the photoinduced electron flows in the nanodumbbells are expected to transfer along the axis of this hybrid particles (max diameter 50 nm) by across the metal-semiconductor conjunction in the middle of the particle to localize in the metal domain. The transfer of electron flows to the Ag metal tail (max length 20 nm) on one end of the dumbbell particle lead to photogenerated holes localized on the opposite end of the dumbbell which is the photocatalytic AgBr domain, promoting sufficient electronhole separations. The localization of the electrons and holes on the two opposite ends of dumbbell particle also inhibited charge combinations. The better photocatalytic activity of novel Ag-AgBr dumbbells than Ag@AgBr structure might be attributed to the synthetic effect of nanodumbbells and the unique transfer of electron flows along the nanodumbbell system. Besides, the SPR effect of the large silver domains (max length 20 nm)

anchored on the hybrid nanodumbbells could also ensure enough visible light to be utilized by the nanosystem, enhancing visible light photocatalytic efficiencies.

Besides photocatalytic application, nanodumbbells by growing a silver domain onto a semiconductor nanoparticle would show more potential applications in self-assembly and building complex nano-devices. <sup>32</sup> The single metal tip in the nanodumbbell can serve as preferential anchoring points for molecule linkers assembling nancrystals. <sup>32, 33</sup> By bearing two different domains in the metal/semiconductor nanodumbells, it yields these nanocrystals equivalent to bi-functional molecules in self-assemly with two-sided chemical connectivity.<sup>34</sup> Besides, the integrity of two different functional materials into the same nanoparticle provides multi-functionality to nanodumbells, leading to more smart applications.

#### Conclusions

To summarize, a facial and novel method is demonstrated to anchor Ag metal domains selectively on specific sites of photocatalytic AgBr nanoparticle seeds. The preferential formation of core-shell or dumbbell heterostructures by seeded silver growth is significantly dependent on the seed size. The key role of different AgBr seed size in governing heterogeneous growth of silver is discussed. The highly selective one-sided silver growth on single one side of AgBr seed is revealed to occur when the seeds below a critical size about 30 nm, leading to formation of novel structured metalsemiconductor nanodumbbells. Much higher photocatalytic activity is obtained due to the significant charge separation in the nanodumbbells. The asymmetric dumbbell-like hybrid nanoparticle exhibit complex structure with a metal domain on one end of the particle and a semiconductor counterpart connected on the opposite end. The combination of two domains of materials with different functionality into the same nanoparticle would open up more promising applications in catalysis, bio-chemical functionality, and other physical properties.

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#### Notes and references

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