

Cite this: *Nanoscale*, 2019, **11**, 20968

3D halos assembled from Fe₃O₄/Au NPs with enhanced catalytic and optical properties†

Ren Cai,^{‡a,d} Dan Yang,^{‡c} Keng-Te Lin,^c Thai Son Cao,^d Yifan Lv,^{a,b} Kangfu Chen,^{id e} Yu Yang,^d Jia Ge,^d Lian Xia,^d George Christou,^d Yuliang Zhao,^f Zhuo Chen,^{id a} and Weihong Tan,^{id *a,b,d}

3D structures assembled from multiple components have attracted increasing research interest based on their enriched functionalities and broadened applications. Here, we report a bottom-up strategy to fabricate 3D halos through the co-assembly of Fe₃O₄ and Au nanoparticles (NPs). Typically, Fe₃O₄ NPs assemble into a 3D core (size around 500 nm) with simultaneous growth of Au NPs on the 3D surface during the assembly process. As a general approach, a variety of 3D halos were fabricated from the co-assembly of Fe₃O₄ and Au NPs of different sizes and shapes. To demonstrate the advantages of these 3D halo structures, their catalytic activity to mimic natural enzymes was investigated. Compared with Fe₃O₄ NP building blocks, enhanced catalytic efficiency was achieved by the 3D halos. In addition, the optical behavior of the 3D halos was simulated using a three-dimensional finite-difference time-domain (3D-FDTD) method. As shown in the results, the 3D halos attached to 90 nm Au NPs could absorb more incident light owing to high electric field intensities, making these structures promising for applications in energy harvesting and detection-related fields.

Received 11th July 2019,
Accepted 17th October 2019

DOI: 10.1039/c9nr05874e

rsc.li/nanoscale

Introduction

Assembly of functional building blocks into novel 3D architectures is highly desirable for a wide range of applications in areas such as catalysis,¹ biomedical diagnosis,² sensors,³ mag-

netic resonance imaging,⁴ plasmonics,⁵ and drug delivery.⁶ Assembly of nanocrystals into well-defined ordered arrays is one of the most promising techniques to achieve novel materials with advanced functionalities. In the traditional top-down assembly technology, external instrumentation is required to remove substances from large bulk materials to create nano- or micro-sized counterparts in assembled structures. However, large-scale applications of this method are hindered by the high cost and size limitation involved in the fabrication process.⁷ In contrast, a bottom-up strategy, which brings together individual inorganic nanocrystals into a well-defined nanostructure through chemical assembly, has proven to be more flexible and efficient.^{8–10} For instance, Au nano-trucks were assembled *via* DNA hybridization and used as a photo-controllable drug delivery system for smart cancer therapy.¹¹ 3D superstructures were assembled from PbS nanocrystals with different sizes through a two-layer phase diffusion technique in vertically positioned glass test tubes.¹² Similarly, a large variety of superstructures were fabricated from the self-assembly of micro- and nanoparticles, nanowires, nanosheets, nanocubes and even cells.¹³

More importantly, the research focus in recent years has evolved into the assembly of multicomponent nanocrystals with more complex 2D or 3D architectures with the aim of integrating their optical, magnetic, electronic and catalytic properties for broadened practical applications.¹⁴ At the same time, while systematic understanding of the growth processes

^aMolecular Sciences and Biomedicine Laboratory (MBL), State Key Laboratory for Chemo/Biosensing and Chemometrics, College of Chemistry and Chemical Engineering and College of Biology, Aptamer Engineering Center of Hunan Province, Hunan University, Changsha 410082, China. E-mail: tan@chem.ufl.edu

^bInstitute of Molecular Medicine (IMM), State Key Laboratory of Oncogenes and Related Genes Renji Hospital, Shanghai Jiao Tong University School of Medicine, and College of Chemistry and Chemical Engineering, Shanghai Jiao Tong University, Shanghai 200240, China

^cCentre for Micro-Photonics, Faculty of Science, Engineering and Technology, Swinburne University of Technology, PO Box 218, Hawthorn, Australia

^dDepartment of Chemistry and Department of Physiology and Functional Genomics, Center for Research at the Bio/Nano Interface, Shands Cancer Center, UF Genetics Institute, McKnight Brain Institute, University of Florida, Gainesville, FL 32611-7200, USA. Fax: (+1)352-846-2410

^eDepartment of Mechanical and Aerospace Engineering, University of Florida, Gainesville, Florida 32611-6250, USA

^fNational Center for Nanoscience and Technology, Chinese Academy of Sciences, Beijing 100049, China

†Electronic supplementary information (ESI) available: Characterization of Fe₃O₄ NPs and Fe₃O₄ NP micelles, Au NPs, hybrid 2D nanosheets functionalized with Au NPs, and UV/Vis spectra and photographs (inset) of the catalytic properties of 3D halos with Au NRs using TMB as the substrate in the presence of H₂O₂ (pH 4.5, 25 °C). See DOI: 10.1039/c9nr05874e

‡These authors contributed equally to this work.

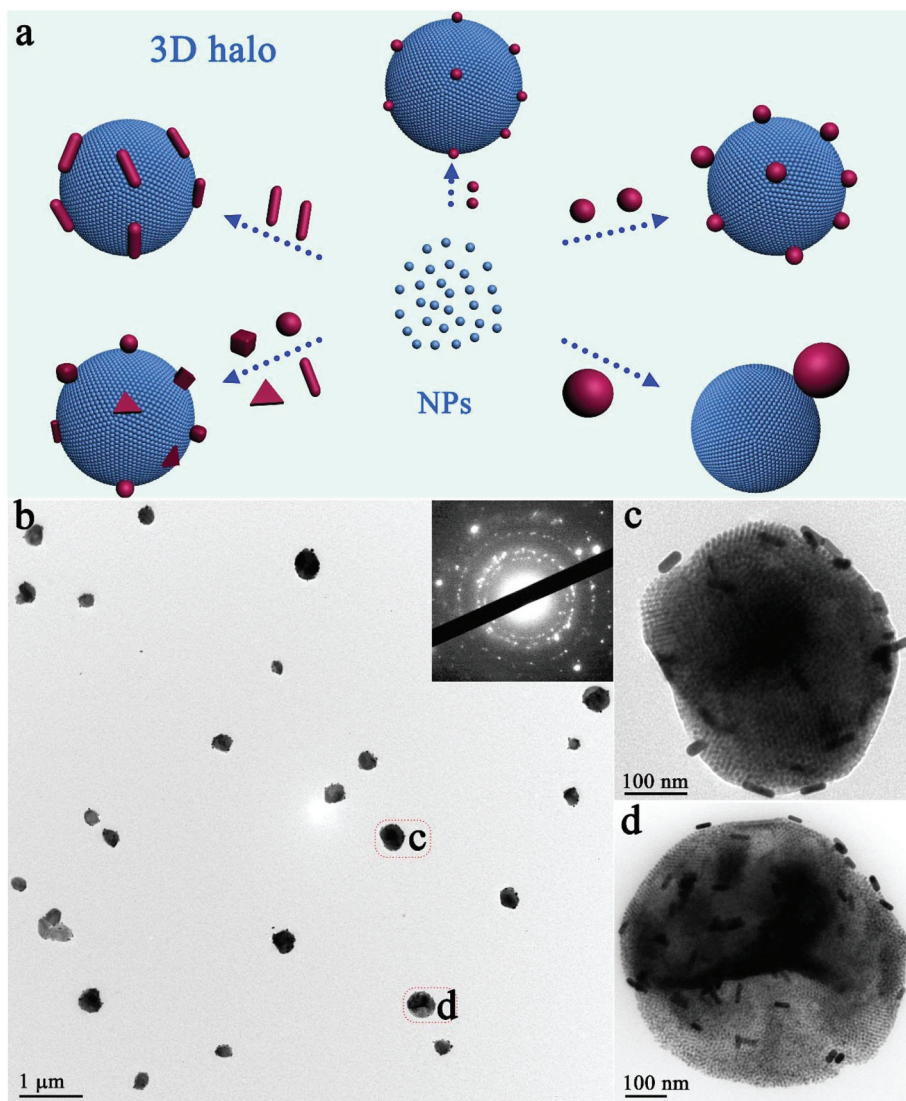


Fig. 1 (a) Scheme for the formation of 3D halos from NP self-assembly; TEM images of 3D halos with Au NRs (length of ~ 70 nm): (b) low-magnification and electron diffraction pattern (inset); (c and d) high-magnification TEM images. The volume of OA is 30 μL .

of these complex aggregates from primary NPs is consequential, the issue has remained understudied. Therefore, we herein report the controllable preparation of 3D halos through the bottom-up co-assembly of Au and Fe_3O_4 NPs without any template or substrate. Such design is expected to address the limitation(s) of single-component Fe_3O_4 -based devices by programmable integration of Au NPs. Accordingly, Fe_3O_4 NPs typically assemble into the 3D core, and Au NPs with various sizes and shapes (*e.g.*, nanocubes, nanorods, and nanotriangles) are dispersed on the surface, forming the so-called “halo” structure, as shown in Fig. 1a. The complex 3D heterostructure is generated at increased temperature and can be stably preserved in ethanol and DI water. Thus, instead of simply loading Au NPs on the Fe_3O_4 surface or mixing Au and Fe_3O_4 NPs together, which we have observed in previous studies,^{15,16} more rigid binding interaction is generated during this assembly process. The unique design of the 3D halo structure not

only brings about enhanced catalytic reactivity towards peroxidase mimicking as compared to pure Fe_3O_4 NPs, but more importantly, according to our 3D-FDTD simulation, also displays strong and remarkable broadband absorbance capability from the high electric field intensities attributed by the unique 3D architecture. Consequently, we expect that this architecture would be intriguing for applications in optoelectronics/sensors based on photo-detection or photo-thermal conversion or other related energy-harvesting devices.

Experimental section

Synthesis of 3D halos

(i) In a typical synthesis of a clear NP-micelle aqueous solution, 30 μL OA was dissolved in a hexane solution of 7 nm Fe_3O_4 NPs (1 mg, 0.4 mL) for 15 min. Then, an aqueous solu-

tion containing CTAB (100 μL , 20 mg mL^{-1}) was added to this mixture. A clear, yellow Fe_3O_4 NP-micelle solution was obtained.

(ii) At the same time, 1 mL 15 nm Au NPs, 2 mL 40 nm Au NPs, 2 mL 40 nm Au NP mixture, 1 mL 90 nm Au NPs, and 2 mL Au nanorods (length of ~ 70 nm) were centrifuged, and the supernatant was discarded, respectively. In each sample, the number of Au NPs was $\sim 4 \times 10^{10}$. Then, CTAB solution was added (50 μL , 20 mg mL^{-1}).

(iii) Under vigorous stirring, a mixed solvent (3 mL diethylene glycol (DEG) solution containing 100 mg PVP) was quickly added to this Fe_3O_4 NP-micelle solution. The mixture was vortexed for 35 s; then 150 μL of the above Au nanostructures (4×10^{10} Au NPs) were injected and further vortexed for 15 min. Next, the mixture was heated to 85 $^\circ\text{C}$ and maintained for 2 h before the solution was cooled to room temperature. Finally, the resulting products were collected by centrifugation and redispersed in ethanol.

Catalyzed oxidation

Unless otherwise stated, steady state kinetic assays were carried out at 30 $^\circ\text{C}$ in a 2 mL tube with 0.67 μg 3D halos or Fe_3O_4 NPs in 500 μL reaction buffer (0.2 M NaAc, pH 4.5) in the presence of 530 μM H_2O_2 for 3D halos and Fe_3O_4 NPs, using 800 μM 3,3',5,5'-tetramethylbenzidine (TMB) as the substrate. In a typical experiment, 30 μL H_2O_2 was added to a 430 μL reaction buffer at different pH values at 30 $^\circ\text{C}$ and vortexed for 3 min. Then, 40 μL TMB (10 mM) was added to the mixture and vortexed for another 3 min. Finally, 0.67 μL of 3D halos (1 mg mL^{-1}) was quickly added to the mixture. Immediately after the substrates were added, color changes were observed. All reactions were monitored according to the maximum intensity of absorbance in the time-scan mode at 652 nm using a Cary Bio-100 UV/Vis spectrometer (Varian). The final concentration of Fe_3O_4 NPs or NPs in the 3D halos was 2.4×10^{-11} M.

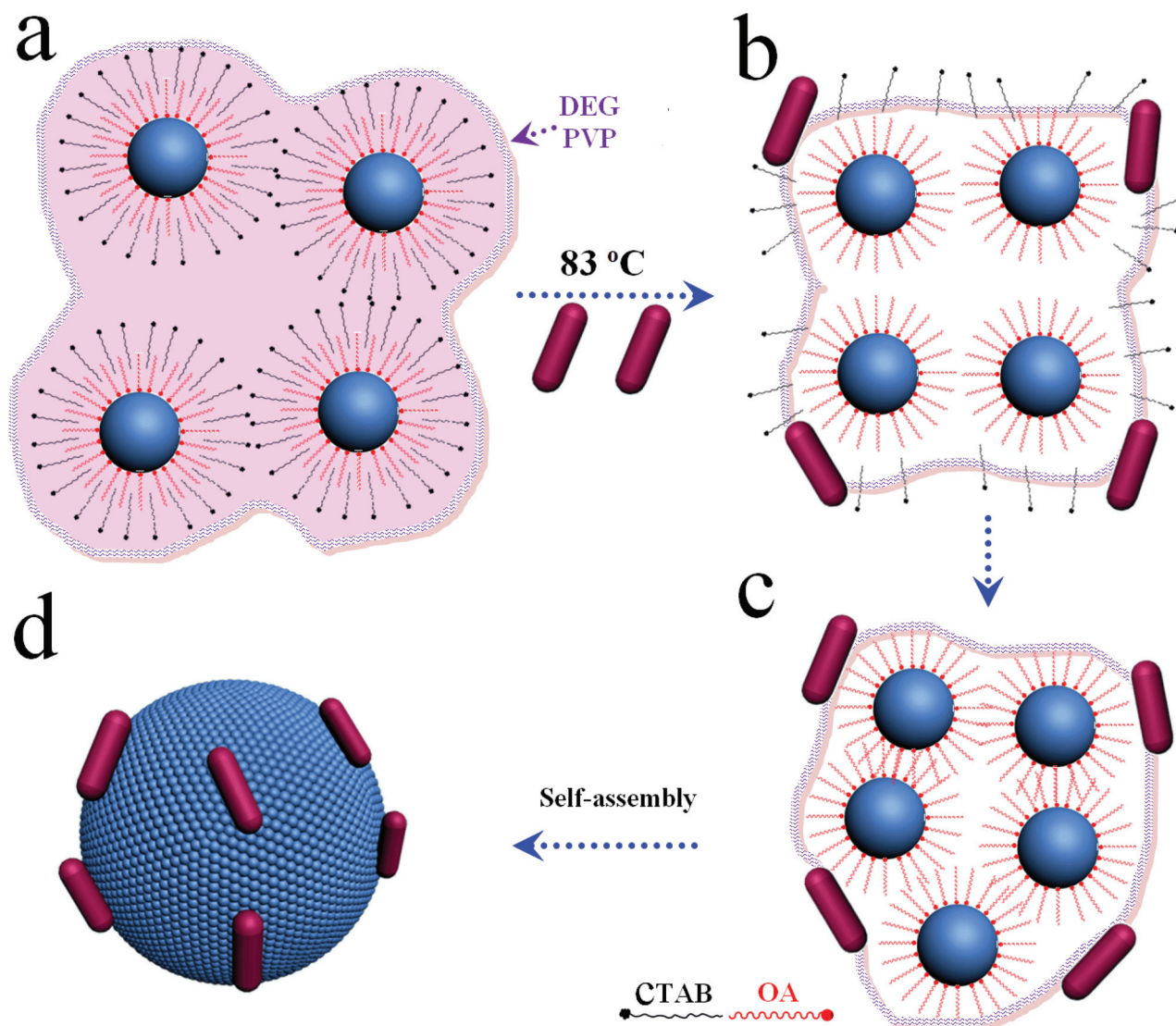
Results and discussion

Typically, Fe_3O_4 NPs (size ~ 7 nm, Fig. S1†) with oleic acid (OA) ligands were prepared according to a previously reported method.^{17a} Then, an aqueous solution of cetyltri-methylammonium bromide (CTAB) was added to a hexane solution of OA-ligated Fe_3O_4 NPs to form NP micelles by vigorous agitation. Here, CTAB works as a wrapping agent to transfer the hydrophobic NPs to the aqueous phase.¹⁸ Upon addition of CTAB, the Fe_3O_4 NPs adopted an interdigitated bilayer micelle structure with OA ligands as the inner layer and CTAB as the outer layer (Fig. S2†).^{7,8} Later, a mixed solvent (of diethylene glycol (DEG) and polyvinylpyrrolidone (PVP)) was injected into the above NP micelles (Scheme 1a). To form the halo structure, a solution of Au NRs (lengths of ~ 70 nm, Fig. S5d†) was injected. Finally, the mixture was heated to 85 $^\circ\text{C}$ (Scheme 1b) and incubated 2 h before the solution was cooled to room temperature. Transmission electron microscopy (TEM) images

showed that the as-obtained products were well-dispersed 3D particles with sizes of ~ 500 nm (Fig. 1b). The enlarged TEM images of typical 3D particles in Fig. 1c and d reveal their halo-like architecture (hereinafter termed "3D halo") in which the 3D core was close-packed with Fe_3O_4 NPs with Au NRs anchored on the core surface. As shown in Fig. 1b (inset), these halos showed a polycrystalline-like electron diffraction (ED) pattern. To investigate the magnetic properties of this 3D halo structure, the hysteresis measurements for Fe_3O_4 NPs and 3D halos were carried out and are presented in Fig. 2. The saturation magnetization of 3D halos (~ 45 emu g^{-1}) was lower than that of Fe_3O_4 NPs (~ 52 emu g^{-1}) and bulk Fe_3O_4 powder (~ 90 emu g^{-1})^{17b} due to the spin surface effects (Fig. 2). Furthermore, 3D halos exhibit smaller magnetic coercivities (~ 250 Oe) than that of Fe_3O_4 NPs (~ 390 Oe), indicating excellent superparamagnetic behavior of the 3D halos.

Different parameters, such as solvent composition, reaction temperature, and type and amount of ligands (PVP, CTAB and OA), were carefully tuned to investigate the key elements determining the formation of the 3D halos. More specifically, results show that the correct solvent and temperature are prerequisites for the assembly of the 3D cores. DEG facilitates the assembly process because of its chemical inertness, polarity, and low evaporation rate, as well as the high surface tension, which strongly influences the spreading and assembly of the nanocrystals.^{19,20} When ethanol, DI water, Tween-20 and poly(ethylene glycol) 400 were used for the assembly process instead of DEG, no assembled products were generated. Besides, addition of PVP is essential because no assembled product was collected without PVP in the DEG solvent. On the other hand, temperature also influences the self-assembly of the 3D cores. The same experimental process was carried out at 45 $^\circ\text{C}$, 65 $^\circ\text{C}$, 85 $^\circ\text{C}$ and 100 $^\circ\text{C}$, but the 3D core structure could only be collected at 85 $^\circ\text{C}$. Under lower temperatures, no assembled products (45 $^\circ\text{C}$), or few aggregated products (65 $^\circ\text{C}$), were collected (Fig. S3a†). At higher temperature (100 $^\circ\text{C}$), some irregular 3D structures were observed (Fig. S3b†). It is well known that interparticle interactions (van der Waals force) and ligand repulsive solvophobic interactions decide the assembled structure.^{8,21} During the assembly process, CTAB (outer layer) acts as a cationic surfactant to transfer the hydrophobic OA-ligated NPs into the hydrophilic solution by a ligand-wrapped reaction,²² forming Fe_3O_4 NP micelles (Scheme 1a). With increased solubility of hydrophilic CTAB in the mixed solvent (DEG and PVP) upon heating (Scheme 1b), the CTAB layer quickly detaches from the NP micelles and leaves the OA-capped NPs "wrapped" inside the mixed solvent with the assistance of the PVP surfactant (Scheme 1c).^{21,23} Thus, the successful assembly of the 3D cores (85 $^\circ\text{C}$, Fig. 1) results from a balance between the elastic repulsive force of the ligands and the van der Waals attractive forces.^{24–26} As shown in Fig. 3a, naked 3D cores (size around 500 nm) without Au NPs could be formed, just by carefully controlling the temperature and the solvent.

However, the process described above became more complicated when we tried to manipulate the assembly of both Fe_3O_4



Scheme 1 Scheme for the synthesis of 3D halos by NP self-assembly: (a) Fe₃O₄ NP-micelles in DEG; (b) self-dissociation of the CTAB layer; (c) OA guides the NP rearrangement; (d) formation of 3D halos (OA amount is 30 μ L).

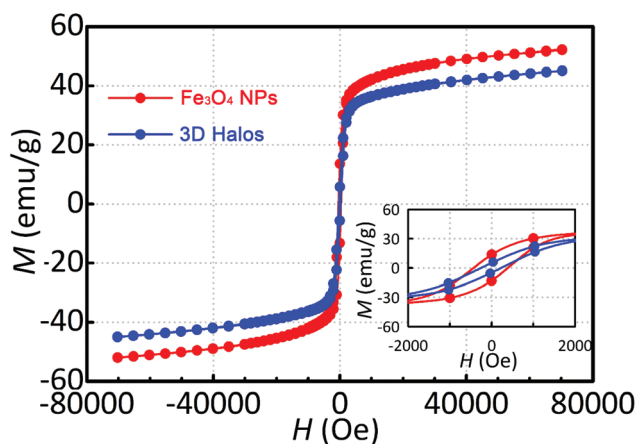


Fig. 2 Hysteresis measurements for 3D halos and Fe₃O₄ NPs at 10 K. The inset is data from -2000 to 2000 Oe.

and the Au NPs to form the halo structure. Results showed that the formation of the halo structure depends on the amount of OA ligands attached to the NP surface. For example, without OA, bulk products were formed (Fig. 3b). In contrast, upon addition of 10 μ L OA (3.159×10^3 OA per NP), Fe₃O₄ NPs aggregated to form large and irregular particles, and Au NRs were sparsely dispersed as the outer layer (Fig. 3c). Well-dispersed 3D halos composed of Fe₃O₄ and Au NRs could be formed only when the amount of OA was increased to 30 μ L (9.478×10^3 OA per NP) (Fig. 1). With further increase of OA to 40 μ L (1.264×10^4 OA per NP), the 3D core structure became semi-transparent particles/vesicles (Fig. 3d).²⁷ In sum, OA mediates the assembly of Fe₃O₄ NPs to form the 3D core, and Au NRs bind to the 3D core by van der Waals forces and hydrophobic attraction of the hydrophobic groups on the ligands.²⁸ With excess OA (40 μ L, 1.264×10^4 OA per NP), elastic repulsions of ligands are enhanced,⁸ and this promotes the dis-

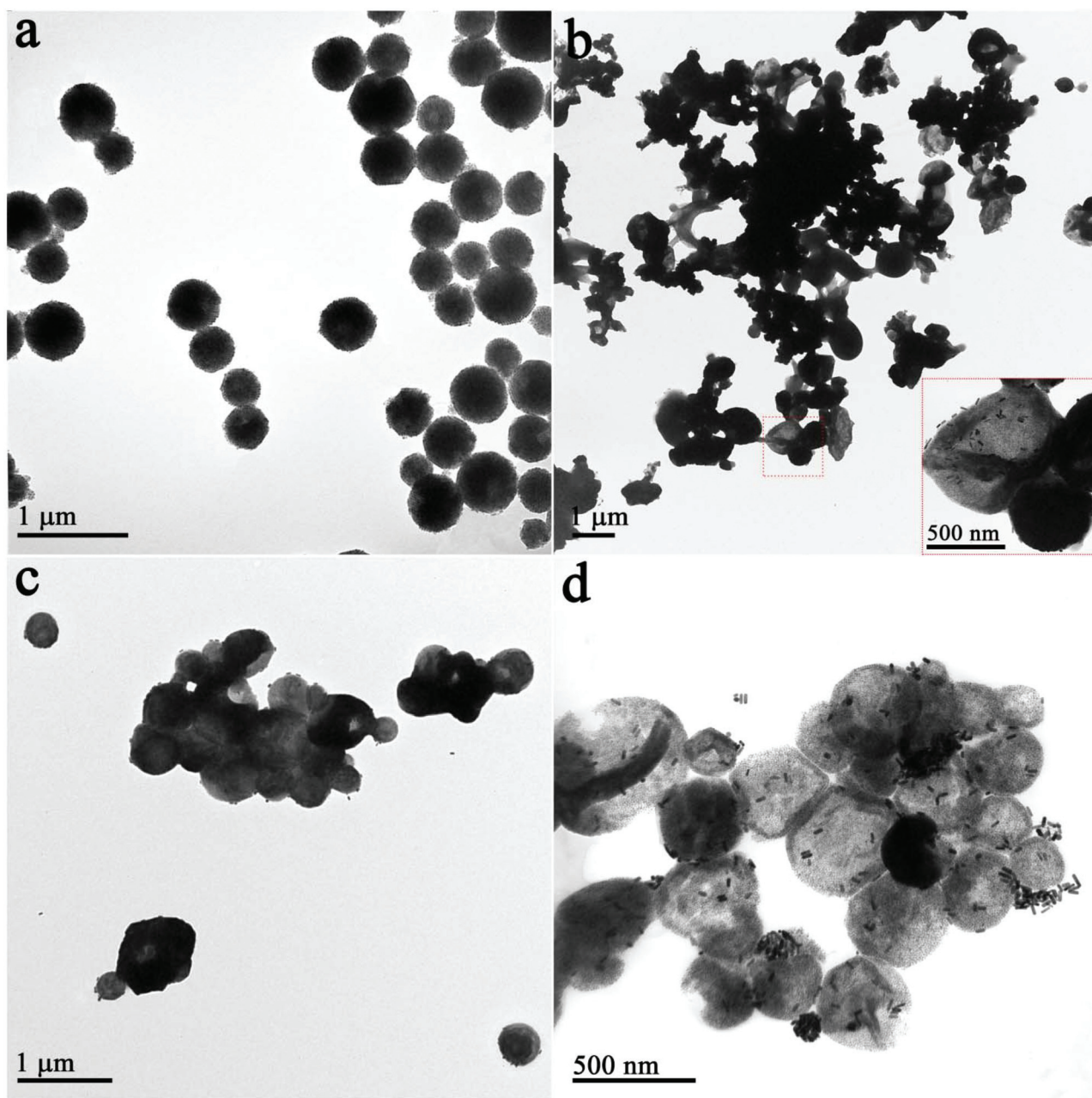


Fig. 3 TEM images of intermediate products in the assembly process. The samples prepared from NP self-assembly (Fe_3O_4 NPs and Au NRs) by adding different amounts of OA to stabilize Fe_3O_4 NPs: (a) 30 μL OA without Au NRs; (b) 0 μL OA; (c) 10 μL OA; (d) 40 μL OA.

persion of Fe_3O_4 NPs such that the distance between the NPs gradually increases, resulting in swelling of the 3D particles (Fig. 3d) (see the analysis of entropy-driven self-assembly in the ESI†). A similar process was observed by using different assembly times, as shown in Fig. S4†.

Subsequently, by simply changing to Au NPs with different sizes and shapes (Fig. S5†), we designed a series of 3D halos. As shown in Fig. 4a, Au NPs (~ 15 nm) would adhere to the surface of the 3D halos, while some Au NP clusters could also be observed. On the other hand, “large” Au NPs (~ 40 nm) grew on each halo (Fig. 4b and e).

Interestingly, only one Au NP (~ 90 nm) could be co-assembled with many Fe_3O_4 NPs to form the 3D halo (Fig. 4c), which was attributed to the limited contact area between the two curved surfaces (3D core and large Au NP (~ 90 nm)), potentially unable to support several “larger” and “heavier” Au NPs. Furthermore, Au NPs (~ 40 nm) with various morphologies, *i.e.*, nanorods, nanocubes and triangular nanoprisms, could be grafted on the surface of each 3D halo (Fig. 4d and e). As shown above, this bottom-up method is a general approach for the co-assembly of Fe_3O_4 and Au NPs to prepare 3D halos (Fig. 1a).

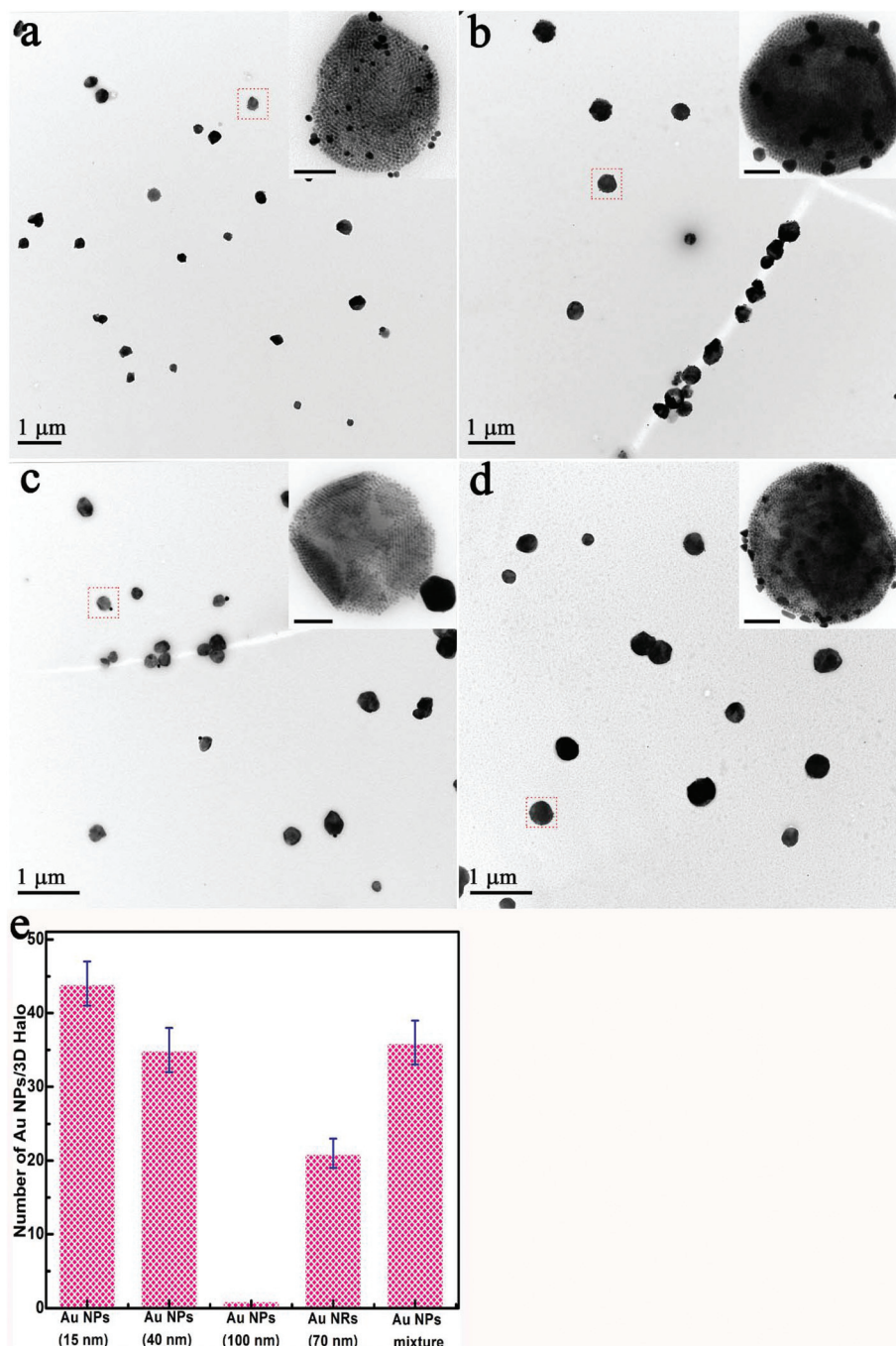


Fig. 4 TEM images of 3D halos with different Au NPs: (a) Au NPs (~15 nm); (b) Au NPs (~40 nm); (c) Au NPs (~90 nm); (d) Au NP mixture (~40 nm) (scale bars are 100 nm in the inset images). (e) Statistical analysis for an average number of Au NPs per 3D halo.

To demonstrate one possible application of the 3D halos, we tested their peroxidase-mimicking activities (Fig. 5), using 3,3',5,5'-tetramethylbenzidine (TMB) and H_2O_2 as the substrate ($\text{H}_2\text{O}_2 + \text{TMB} \xrightarrow{\text{3D halos}} \text{H}_2\text{O} + \text{oxidation of TMB}$). For the first set of experiments, we investigated whether the 3D halos (Au NRs) could catalyze the reaction between TMB and H_2O_2 . As shown in Fig. S6,[†] the colorless solution became light blue after about 30 s, and finally turned deep blue after

about 4.5 min, indicating excellent catalytic capability. The experimental pH and temperature for the catalysis of 3D halos were 4.5 and 30 °C, respectively, in order to match the optimal values of the natural enzyme horseradish peroxidase (HRP).²⁹ Except for the 3D halos with Au NPs (~90 nm), the data in Fig. 5a, b and Fig. S7[†] confirm the maximum initial velocity (V_{max}) of these 3D halos to be around 135% higher than that of their Fe_3O_4 NP building blocks. Catalytic efficiency to substrates, or K_{cat} , is another kinetic parameter.³⁰ With TMB or

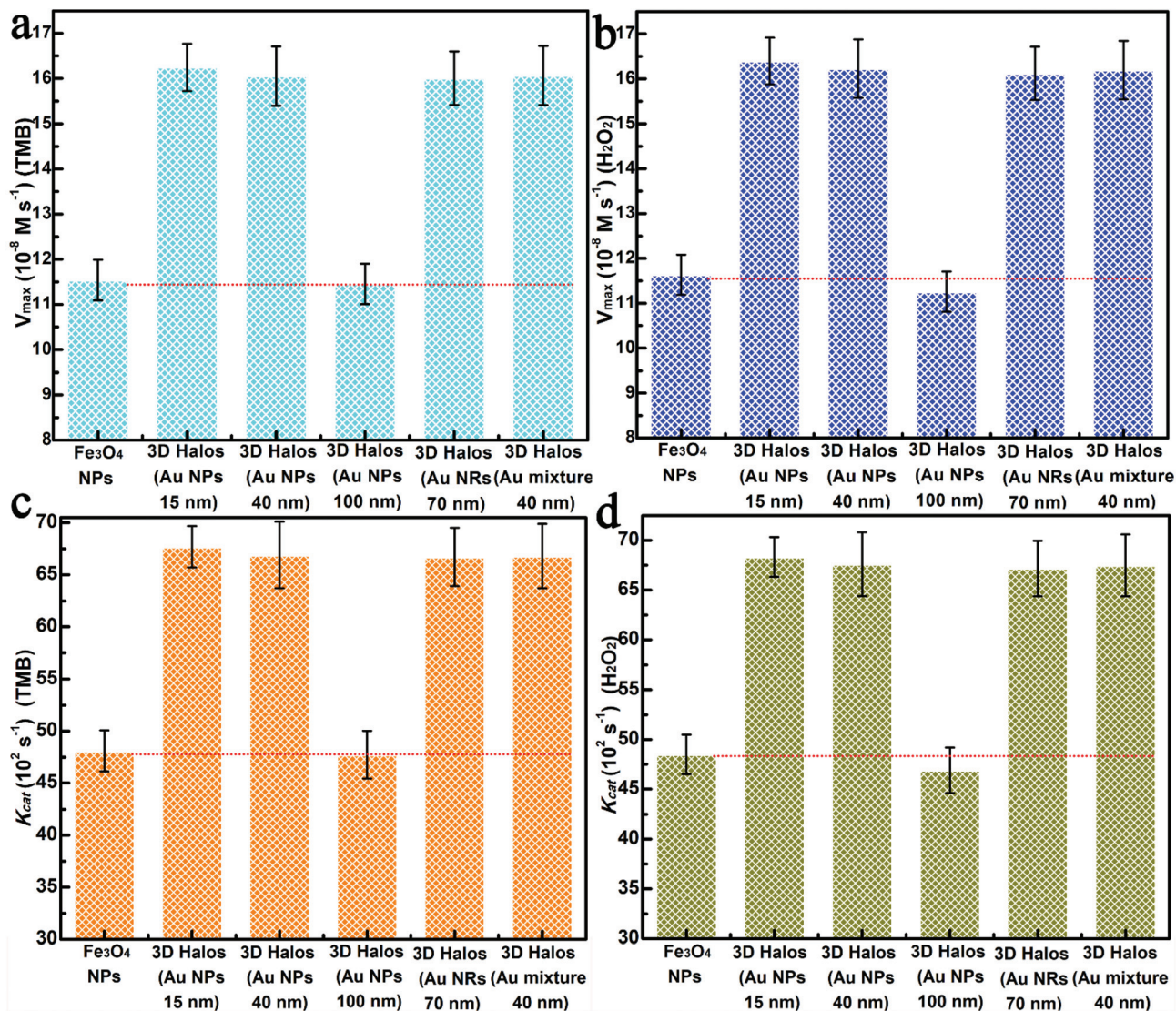


Fig. 5 Maximum initial velocity ($V_{\max}$) was measured using Fe_3O_4 NPs and 3D halos: (a) the concentration of H_2O_2 was 530 μM , and TMB concentration was varied; (b) the concentration of TMB was 800 μM , and H_2O_2 concentration was varied. The catalytic constant (K_{cat}): (c) the concentration of H_2O_2 was 530 μM , and TMB concentration was varied; (d) the concentration of TMB was 800 μM , and H_2O_2 concentration was varied. $K_{\text{cat}} = V_{\max}/[E]$, where $[E]$ is the enzyme (or NP) concentration (2.4×10^{-11} M), and K_{cat} is the maximum number of substrate molecules converted into the product per enzyme molecule per second.

H_2O_2 as the substrate, the apparent K_{cat} value is about 35% higher than that of their Fe_3O_4 NP building blocks (Fig. 5c and d), which have a K_{cat} value about 60% higher than that of HRP,³⁰ indicating more favorable catalytic properties and enhanced catalytic reactivity, characteristics which would be useful in mimicking HRP. This apparent successful mimicry can be attributed to the collective properties of the building blocks (Fe_3O_4 NPs) and the good distribution of Au NPs on 3D halos, leading to higher catalytic activity and efficiency for TMB and H_2O_2 interaction.³¹ Here, 3D halos with Au NPs (~ 90 nm) was noted above because they displayed lower catalytic activity resulting from fewer Au NPs and fewer active sites interacting with the substrates. Regardless, these results demonstrate that the 3D halos could serve as a better enzyme

system for TMB oxidation than Fe_3O_4 NPs or the natural enzyme (HRP).

To investigate the optical properties of the 3D halos, we used a 3D-FDTD method to simulate the electric field distributions of the $\text{Fe}_3\text{O}_4/\text{Au}$ (~ 90 nm) structure at different wavelengths. In the simulation, we set the 3D core (packed with Fe_3O_4 NPs) and a single Au NP to have diameters of 500 nm and 90 nm (Fig. 4c), respectively, and plane waves with transverse-electric (TE) polarization propagating from 1 μm above the composite structure in water. All of the optical constants of the materials (Fe_3O_4 , Au, and water) were obtained from the literature.³² Fig. 6a–e display the electric field distributions of incident light at wavelengths of 580 nm, 650 nm, 770 nm, 840 nm, and 940 nm, respectively, passing through the 3D halo structure

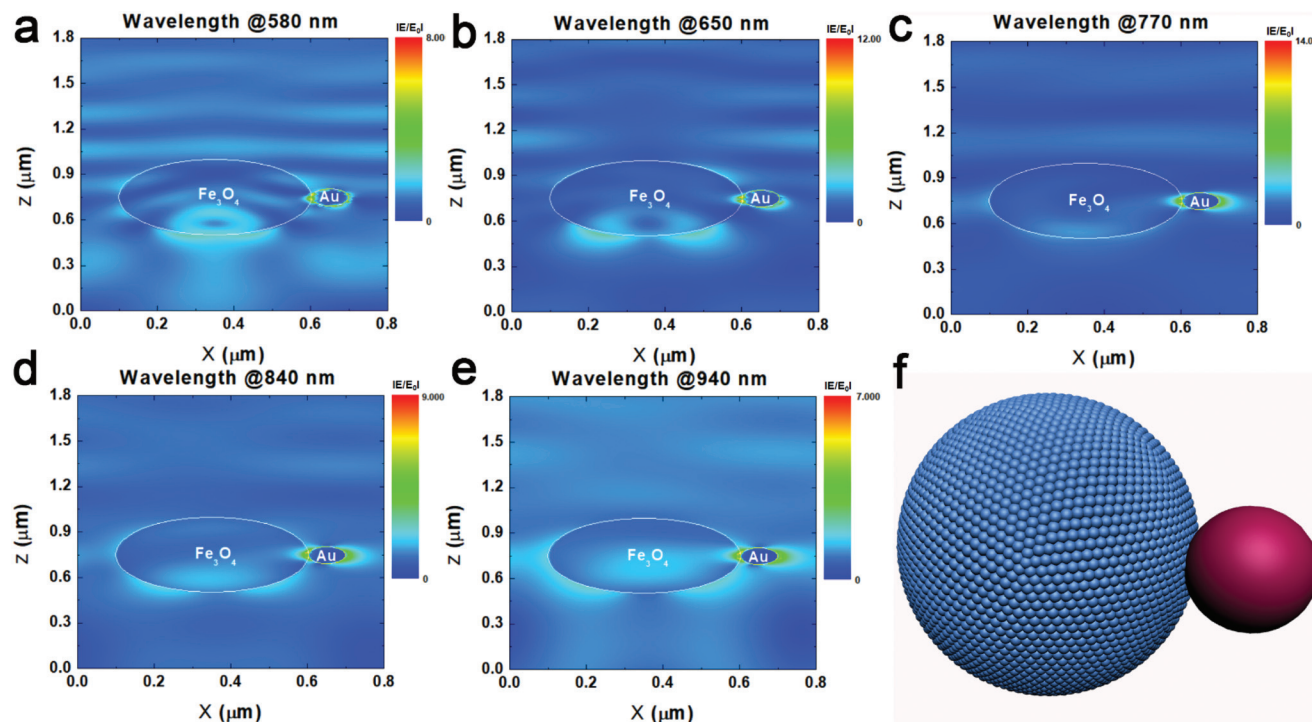


Fig. 6 Near-field electric field distributions of incident light at wavelengths of (a) 580 nm; (b) 650 nm; (c) 770 nm; (d) 840 nm; and (e) 940 nm passing through the Fe_3O_4 -Au NP halo structure (f) in water.

(Fe_3O_4 -Au NP composite). We found that the 3D halo structure provided strong electric fields within the near field around the Fe_3O_4 -Au interface at these wavelengths. Furthermore, the 3D halo structures provided high electric field intensities (IE/E_0I) from the visible (Fig. 6a-c) to the near-infrared (NIR, Fig. 6d and e) regions. We attribute these phenomena to the excited surface plasmon polaritons (SPPs) confined in the high refractive index material such as treated glass or polymer. The high electric field intensities cause more incident light to be absorbed by the 3D halo structures. In addition, we investigated the optical properties of the 3D halo structures with distinct dimensions at different wavelengths (for details, see Fig. S8-S10†). We therefore suggest that the 3D halos can provide good electric field confinement over the visible and NIR range and good energy conversion capability for use in energy harvesting, detection, and biosensing-related applications.

Conclusions

In conclusion, we have developed a bottom-up route to fabricate 3D halos through the co-assembly of Au and Fe_3O_4 NPs. As a general approach, Fe_3O_4 and Au NPs of different sizes and shapes can co-assemble into a variety of 3D halos, creating new opportunities to explore assembled materials with enriched functionalities. When used as a catalyst for TMB oxidation, the 3D halos exhibited higher catalytic efficiency compared with Fe_3O_4 NP building blocks, and they demonstrated functional mimicry of the natural enzyme. Moreover, as

demonstrated by our simulation process, these 3D halos could absorb more incident light owing to the intensified electrical field from the assembled structure, making them suitable for applications in energy harvesting and detection-related areas. Therefore, the as-developed assembly method can be regarded as a general approach to hybridize noble metal NPs with 3D particles to form functional materials. We believe that this novel method will stimulate the design of multidimensional materials based on a structural design that is similar to that of our 3D halos, thereby expanding the potential applications of such materials in catalysis or optoelectronics/sensors based on photo-detection and photo-thermal conversion.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

The authors are grateful to Dr Kathryn Williams for her critical comments during the preparation of this manuscript. This work is supported by the NSFC grants (NSFC 21521063), and by the NIH GM R35 127130 and the NSF 1645215.

Notes and references

- 1 Y. J. Kang, X. C. Ye, J. Chen, L. Qi, R. E. Diaz, V. Doan-Nguyen, G. Z. Xing, C. R. Kagan, J. Li, R. J. Gorte,

- E. A. Stach and C. B. Murray, *J. Am. Chem. Soc.*, 2013, **135**, 1499–1505.
- 2 G. Zhu, R. Hu, Z. Zhao, Z. Chen, X. Zhang and W. Tan, *J. Am. Chem. Soc.*, 2013, **135**, 16438–16445.
- 3 (a) J. B. Liu, S. H. Fu, B. Yuan, Y. L. Li and Z. X. Deng, *J. Am. Chem. Soc.*, 2010, **132**, 7279–7281; (b) W. Ma, P. Fu, M. Sun, L. Xu, H. Kuang and C. Xu, *J. Am. Chem. Soc.*, 2017, **139**, 11752–11759; (c) A. Qu, M. Sun, L. Xu, C. Hao, X. Wu, C. Xu, N. A. Kotov and H. Kuang, *Proc. Natl. Acad. Sci. U. S. A.*, 2019, **116**, 3391–3400.
- 4 O. Chen, L. Riedemann, F. Etoc, H. Herrmann, M. Coppey, M. Barch, C. T. Farrar, J. Zhao, O. T. Bruns, H. Wei, P. Guo, J. Cui, R. Jensen, Y. Chen, D. K. Harris, J. M. Cordero, Z. Wang, A. Jasanoff, D. Fukumura, R. Reimer, M. Dahan, R. K. Jain and M. G. Bawendi, *Nat. Commun.*, 2014, **5**, 5093.
- 5 H. Chen, L. Shao, Q. Li and J. Wang, *Chem. Soc. Rev.*, 2013, **42**, 2679–2724.
- 6 L. Y. T. Chou, K. Zagorovsky and W. C. W. Chan, *Nat. Nanotechnol.*, 2014, **9**, 148–155.
- 7 N. Vogel, M. Retsch, C. A. Fustin, A. del Campo and U. Jonas, *Chem. Rev.*, 2015, **115**, 6265–6311.
- 8 M. A. Boles, M. Engel and D. V. Talapin, *Chem. Rev.*, 2016, **116**, 11220–11289.
- 9 E. Auyeung, T. Li, A. J. Senesi, A. L. Schmucker, B. C. Pals, M. O. de la Cruz and C. A. Mirkin, *Nature*, 2014, **505**, 73–77.
- 10 R. J. Macfarlane, B. Lee, M. R. Jones, N. Harris, G. C. Schatz and C. A. Mirkin, *Science*, 2011, **334**, 204–208.
- 11 L. Qiu, T. Chen, I. Öçsoy, E. Yasun, C. Wu, G. Zhu, M. You, D. Han, J. Jiang, R. Yu and W. Tan, *Nano Lett.*, 2015, **15**, 457–446.
- 12 S. M. Rupich, E. V. Shevchenko, M. I. Bodnarchuk, B. Lee and D. V. Talapin, *J. Am. Chem. Soc.*, 2010, **132**, 289–296.
- 13 J. Guo, B. L. Tardy, A. J. Christofferson, Y. Dai, J. J. Richardson, W. Zhu, M. Hu, Y. Ju, J. Cui, R. R. Dagastine, I. Yarovsky and F. Caruso, *Nat. Nanotechnol.*, 2016, **11**, 1105–1111.
- 14 K. Miszta, J. de Graaf, G. Bertoni, D. Dorfs, R. Brescia, S. Marras, L. Ceseracciu, R. Cingolani, R. van Roij, M. Dijkstra and L. Manna, *Nat. Mater.*, 2011, **10**, 872–876.
- 15 Y. Xiang, H. Yang, X. Guo, Y. Wu, Y. Ying, Y. Wen and H. Yang, *Microchim. Acta*, 2018, **185**, 195.
- 16 S. Villa, P. Riani, F. Locardi and F. Canepa, *Materials*, 2016, **9**, 826.
- 17 (a) Y. Li, F. Ma, X. Su, C. Sun, J. Liu, Z. Sun and Y. Hou, *Catal. Commun.*, 2012, **26**, 231–234; (b) H. Iida, K. Takayanagi, T. Nakanishi and T. Osaka, *J. Colloid Interface Sci.*, 2007, **314**, 274–280.
- 18 D. V. Talapin, *ACS Nano*, 2008, **2**, 1097–1100.
- 19 V. Aleksandrovic, D. Greshnykh, I. Randjelovic, A. Frömsdorf, A. Kornowski, S. V. Roth, C. Klinke and H. Weller, *ACS Nano*, 2008, **2**, 1123–1130.
- 20 Z. Yang, T. Altantzis, D. Zanaga, S. Bals, G. V. Tendeloo and M.-P. Pileni, *J. Am. Chem. Soc.*, 2016, **138**, 3493–3500.
- 21 R. Cai, D. Yang, L. Yan, F. Tian, J. Zhang, Y. Lyu, K. Chen, C. Hong, X. Chen, Y. Zhao, Z. Chen and W. Tan, *ACS Appl. Nano Mater.*, 2018, **1**, 5389–5395.
- 22 R. Cai, Y. Du, D. Yang, G. Jia, B. Zhu, B. Chen, Y. Lv, K. Chen, D. Chen, W. Chen, L. Yang, Z. Chen and W. Tan, *Nanoscale*, 2019, **11**, 12169–12176.
- 23 M. Grzelczak, J. Vermant, E. M. Furst and L. M. Liz-Marzán, *ACS Nano*, 2010, **4**, 3591–3605.
- 24 P. Jenkins and M. Snowden, *Adv. Colloid Interface Sci.*, 1996, **68**, 57–96.
- 25 K. L. Young, M. R. Jones, J. Zhang, R. J. Macfarlane, R. Esquivel-Sirvent, R. J. Nap, J. Wu, G. C. Schatz, B. Lee and C. A. Mirkin, *Proc. Natl. Acad. Sci. U. S. A.*, 2012, **109**, 2240–2245.
- 26 L. Gao, J. Zhuang, L. Nie, J. Zhang, Y. Zhang, N. Gu, T. Wang, J. Feng, D. Yang, S. Perrett and X. Yan, *Nat. Nanotechnol.*, 2007, **2**, 577–583.
- 27 R. Cai, D. Yang, K.-T. Lin, Y. Lyu, B. Zhu, Z. He, L. Zhang, Y. Kitamura, L. Qiu, X. Chen, Y. Zhao, Z. Chen and W. Tan, *J. Am. Chem. Soc.*, 2019, **141**, 1725–1734.
- 28 Y. Guo, L. Deng, J. Li, S. Guo, E. Wang and S. Dong, *ACS Nano*, 2011, **5**, 1282–1290.
- 29 R. Cai, D. Yang, S. Peng, X. Chen, Y. Huang, Y. Liu, W. Hou, S. Yang, Z. Liu and W. Tan, *J. Am. Chem. Soc.*, 2015, **137**, 13957–13963.
- 30 E. D. Palik, *Handbook of Optical Constants of Solids*, Academic Press, San Diego, 1998.
- 31 P. B. Johnson and R. W. Christy, *Phys. Rev. B: Solid State*, 1972, **6**, 4370–4379.
- 32 L. Luo, C. Ge, Y. Tao, L. Zhu, K. Zheng, W. Wang, Y. Sun, F. Shen and Z. Guo, *Nanophotonics*, 2016, **5**, 139–146.