

Plasmonic and quantum interactions between semiconductor quantum dots and metal nanoparticles

April 17, 2018

Weak coupling between the localised surface plasmons on metal nanoparticles, and excitons in semiconductor quantum dots, lead to the observation of either emission quenching or enhancement, which have applications in the emerging quantum dot light emitting diode technology. Further effects such as carrier multiplication and charge transfer are exclusively present in semiconductor nanocrystals, and offer new ways of improving the efficiency of solar cells. This article is summarises the effects in this hybrid structure, along with their potential application in industry.

Introduction

One of the most pressing challenges of our time is fighting climate change. Plasmonic and quantum research are extremely relevant to this area, because of their practical applications to manipulating light. As these fields develop further, better understanding of nanoscale phenomena inspire the development of advanced structures for both harvesting and the emission of light in an efficient manner.

The interactions between semiconductor quantum dots (SQDs) and metal nanoparticles (MNPs), while not an established research topic in themselves, are a recurring theme in the nanophysics literature [1, 6, 7, 9, 17, 19, 27]. Their combined properties could provide a new approach to building sustainable technology [21], improving current methods of biological sensing [22], and state of the art cancer therapy [23].

Both SQDs and MNPs are large research areas in themselves. Since the discovery of quantum dots [2] (also commonly referred to as semiconductor nanocrystals), there has been very intensive research surrounding their properties and applications. This is largely due to their unique size-tunable emission spectrum, their stability, and their compatibility with silicon technology. MNPs possess properties that are just as extraordinary. Medieval stained glass has its rich red colour due to gold nanoparticles suspended in the material [pictures if space?]. The ability of metal nanoparticles to support localised surface plasmons (LSPs) is what gives rise to these unique properties. This phenomenon has been theoretically explained in the early 20th century by solving Maxwell's equations in the appropriate geometry and it has been thoroughly documented both in textbooks and in literature [4, 8, 14]. Depending on the size of the MNP, it can be either weakly or strongly coupled to incident light. The theoretical framework behind this phenomenon is incomplete, but currently it is thought that the two regimes differ in the LSP modes

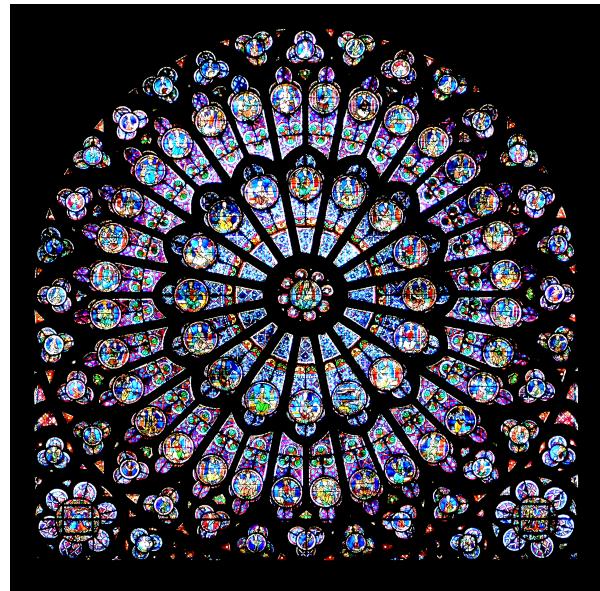


Figure 1: Gothic stained glass rose window of Notre-Dame de Paris. The colors were achieved by colloids of gold nanoparticles.

that are excited on the MNP surface. Weak coupling corresponds to dipole-like oscillations of the free electrons, while in the strong coupling regime, quadrupolar and higher order modes are excited. In this article, we will focus on effects arising due to the weak coupling between SQD emitters and MNPs. Strong coupling requires confinement of the emitter to a very small volume [5], and SQDs are usually too large to be incorporated into such structures. This renders them inappropriate for strong coupling experiments.

Historically, emission quenching due to non-radiative processes such as FRET have been widely explored due to their importance in biological sensing [33, 37], but the recent advances in this area [13, 22, 27] suggest an

increasing interest towards structures that consist of a quantum dot emitter coupled with a nanoparticle. Furthermore, there have been recent results of quantum light emitting diode (QLED) quantum yield enhancement due to such structures [6, 19, 27]. Another technology that can potentially benefit from this setup are photovoltaics (PVs). Plasmonics has opened a door towards cost, efficiency, and design improvements of solar cells [3, 10, 11, 25, 29], but progress seems to have slowed down since 2010, as few major steps have been taken, apart from using the properties of MNPs in plasmonic structures, and using new ways of sensitization (see discussion of dye-sensitized solar cells under Photovoltaics section). The incorporation of SQDs would bring additional interactions to be investigated, along with improving the photocatalytic properties of the solar cells [24, 32].

In this review, I will provide a summary of what is known about the interactions between SQDs and MNPs, and evaluate their utility in the context of different technological applications.

Weak Coupling Interactions

Quenching

In all generality, quenching refers to the reduction in emission intensity from a fluorophore. The exact mechanism can vary, but we will concentrate on the brightness reduction of a SQD due to its coupling with a nearby MNP.

Theoretically, quenching is explained by non-radiative energy transfer mechanisms. The most commonly encountered theories in literature are Forster radiative energy transfer (FRET), surface energy transfer (SET), nanosurface energy transfer (NSET), and charge transfer (CT). FRET is a model for the coupling between two point dipoles, whose energy transfer rate decays as r^{-6} . While providing a good approximation for some situations, is often outperformed by NSET when it comes to QD-MNP interaction [22, 36, 37]. NSET and SET are fundamentally the same theory [36], but are sometimes confusingly referred to as different processes in the literature. In the surface-dipole formalism, the rate decays more slowly, as r^{-4} . CT requires contact between the donor and acceptor, and is thus useful only for specific constructs. It relies on the orbital overlap between the donor and acceptor's electrons, and the energy is transferred by the swapping between an excited and a lower energy electron [13].

Emission quenching is an established method for measuring distances in biological systems [33, 35], and it continues to be widely used and refined [31]. SQD-MNP structures provide a possibility for building a nanoruler that is comparable and in some ways superior to the previously used ones [9, 22, 37].

Experimentally, quenching by the nearby metal NPs has been investigated and characterised for the case of a

gold nanosphere layer by Zhang et al (2012) [37]. They propose the usage of NSET formalism for predicting the energy transfer efficiency, and in their argumentation provide a good illustration of the dependence of quenching on distance. Their data shows good predictions from both FRET and NSET at high donor-acceptor spectral overlap. When the spectra do not overlap however, both models give rather poor results (even though NSET is slightly better). This suggests that a better theoretical framework is called for. A study of single SQD-MNP pairs suggests the same point, while showing that NSET is a slightly better fit [30]. Both of the above results can be seen in Figure ???. An excellent account of research on the quenching of QDs from Au NPs can be found in the review by Hildebrandt, N et. al. (2017) [13], which is entirely dedicated to the topic of biosensing.

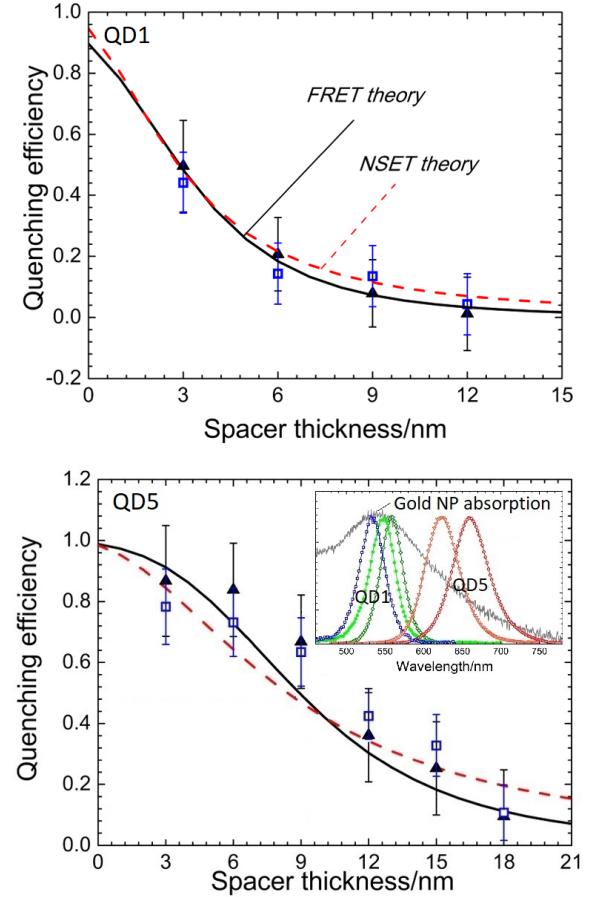


Figure 2: Quenching efficiency for the layered colloidal SQD-MNP structure produced by Zhang et al. [37]. **Above:** Theoretical fit for QD-SQD system with good spectral overlap; both models perform reasonably well. **Below:** Both models show systematic errors when the QD emits off-resonance (as seen from the inset).

Quenching appears to become more efficient with the increase in concentration of nearby MNPs, as illustrated by Zhang's study [37]. Their data however, has been adjusted by varying the spacing between SQD and MNP

in order to achieve comparable quenching efficiencies, for different sizes of gold NPs. This approach partially obscures any additional effect of the NP size to quenching and a closer look at the trends begs the question whether a QD with an off-resonance emission peak (due to being larger) would actually be a more efficient quencher at a closer distance. A possible explanation would be that the geometry of a large NP is better approximated by an NSET formalism, which is more efficient at closer distances than FRET, due to its r^{-4} decay. If this is the case, then an investigation in the transition between FRET and NSET might be a worthwhile research topic.

The inner filter effect [28] is mentioned in a study by Li et al. (2009) [22], and they describe a method for measuring its influence in a QD-NP colloidal suspension. It is important in studying fluorescence quenching to identify when there is true emission quenching through nonradiative processes, and when the observed signal is being weakened by other channels of absorption, which has not been explicitly addressed in the study by Zhang [37]. This is an effect that should be accounted for when conducting further studies into the concentration dependence of emission quenching.

Overall, it is confirmed that quenching is a phenomenon that strongly depends on distance, acceptor concentration, and the geometry of the system. Research has been done on empirically characterising these dependencies, but the exact physical mechanisms behind them are yet to be uncovered. Quenching efficiencies of up to 98% have been reported [22], which is an indicator that applications such as light trapping could benefit from this effect.

Emission Enhancement

Emission enhancement is characterised by the faster emission of light from an emitter. This is commonly illustrated in time-resolved photoluminescence (TRPL) graphs. Systematic studies of this effect are scarce in the literature, possibly because the technological incentives were largely missing, as contrasted by the importance of quenching to biosensing.

Our current understanding is that the coupling between a quantum emitter and a metal NP is responsible both for the phenomenon of emission quenching and emission enhancement, with the latter showing its effect at distances between 5-10nm [20]. Theoretical understanding behind this phenomenon is limited to its attribution to the strong local electric field due to the MNP affecting the exciton creation and recombination processes in the SQD. The effect diminishes very quickly at distances of the order of 20nm, which results in an enhancement maximum at an intermediate distance. The results from Khachatur et. al. (2014) [26] hint at a possible mechanism for emission enhancement. There are three characteristic rates in the QD-MNP system: the QD relaxation time, the QD-MNP non-radiative chan-

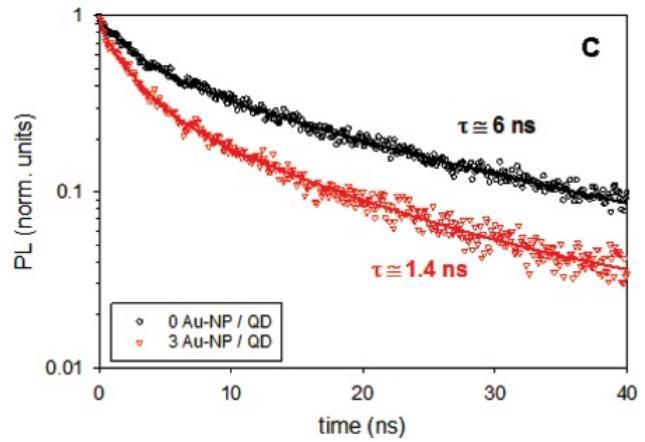


Figure 3: Time-resolved photoluminescence graph comparing the lifetime of excitons within a QD with and without neighbouring gold nanoparticles. When coupled to 3 nearby gold NPs, emission enhancement was observed (red) [30].

nel energy transfer rate, and the MNP emission rate. The QD is slow to relax and emit a photon, while the MNP does so at a much faster rate. Energy is nonradiatively transferred from the QD to the MNP at a rate that lies in between, and this process effectively speeds up the emission process in the QD-MNP system. The metal nanoparticle acts as an antenna that carries out the emission, powered by the non-radiative energy channel from the excited QD.

Multiple studies have found that there is an optimal distance for emission enhancement [18, 20], usually quoted as $\sim 11\text{ nm}$. Kim et. al. (2013) [18] conducted an investigation of the balance between emission enhancement and emission quenching, illustrating the existence of the optimal distance for enhancement (Figure 6). They claimed that enhancement could also remain completely unobserved for large enough concentrations of Au NPs, but it remains unclear whether this is caused by true quenching as opposed to inner filtering, which has been shown to become significant as metal NP concentrations become higher [22].

Photovoltaics

Photovoltaic (PV) technology suffers from low cost-effectiveness and this prevents it from entering the market as a serious competitor to fossil fuels. Sunlight is the most abundant energy source on our planet and there is huge incentive for making solar cells more efficient.

There are many proposed nanoscale solutions to this problem [21]. A purely plasmonic approach has been proposed that employs metal nanoparticles as scatterers, and LSP modes as a potential mechanism for trapping light [3, 11, 25, 29]. While having great potential, there is still a way to go with optimising design, and dealing with unwanted phenomena such as backscattering.

Quantum dot solar cells have also been in the spotlight lately [16], but they have their own design problems. They are a subset of a new family of solar cells called dye-sensitised solar cells (DSC) [12], whose operating principle relies on using a liquid redox electrolyte in contact with the light absorbing layer of dye molecules. QDs can be tuned more easily than dye, thus are a promising alternative, but suffer from corrosion due to the electrolyte. Combining the QDs with plasmonic nanoparticles in such a structure could speed up the electron transfer due to weak coupling between the dipole LSP modes and the excitons [21], but it should be noted that metal nanoparticles also suffer from corrosion [15]. Such structures seem to be missing from the literature, so their full behaviour is an open topic.

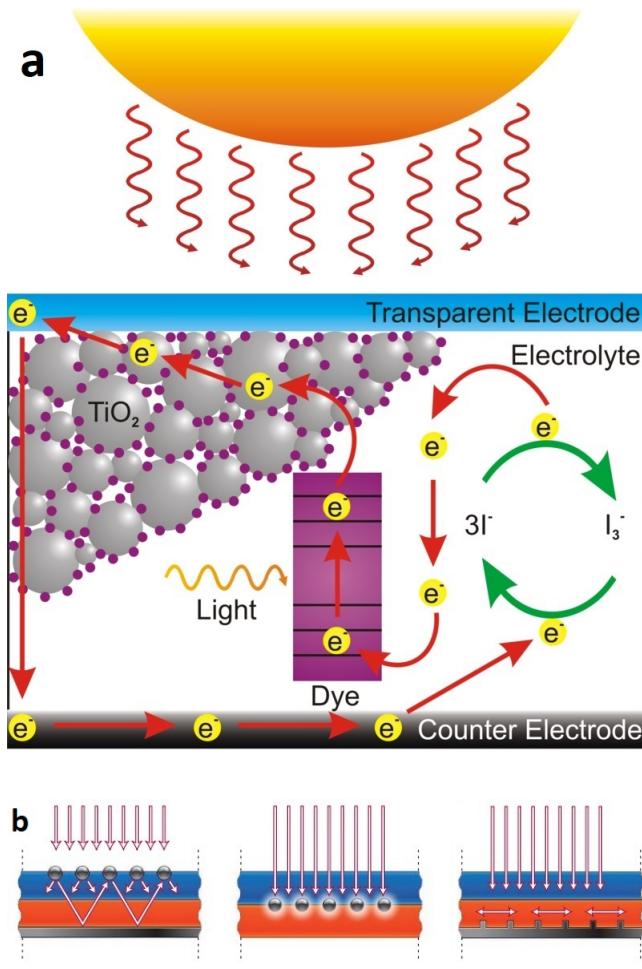


Figure 4: Different approaches to designing enhanced solar cells. a) Dye-sensitised solar cell; the dye molecules can be replaced with QDs, and TiO_2 with Au NPs as an alternative. b) Plasmonics-enhanced solar cells. From left to right: incorporating MNPs to increase the effective light path within the semiconductor (this approach might suffer from backscattering); better generation of excitons through strong local field enhancement; converting solar energy into surface plasmon polaritons (SPPs) through a striated metallic substrate [3]

Another approach is to boost efficiency through car-

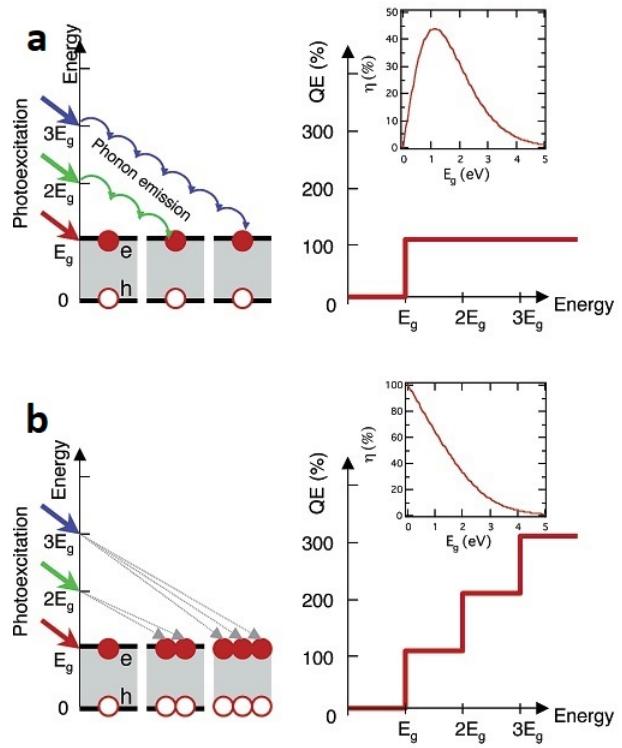


Figure 5: a) Traditional operation of solar cell (idealised). Every photon with energy above the band gap E_g produces exactly one exciton. The additional energy is dissipated as heat and the quantum efficiency can be 100% at maximum. The inset shows that the power conversion efficiency η can be at most 44% (Shockley-Queisser limit). b) With the CM effect, higher energy photons can produce multiple excitons. This breaks the theoretical limit imposed above, and the maximum solar cell efficiency depends only on the employed material's band gap.

rier multiplication (CM) [32], which is not feasible for bulk semiconductor, but can only be exploited in nanocrystals. It is potentially a very efficient way to harvest energy that would otherwise be dissipated as heat. Research into this approach has not investigated how a complementary MNP affects the performance of the overall device.

So far, a limited number of colloidal SQD-MNP structures have been explored for their light harvesting capabilities. Research is focused on the usage of single effects (electron lifetime increase, charge multiplication, plasmonic MNP enhancement) in the light harvesting enhancement process. However, more complex structures that attempt to combine these plasmonic and quantum effects have not been explored. As we are nearing the practical limitations of silicon for light capturing, research might progress more rapidly if it focuses on tandem solar cells that are designed with multiple band gaps [34]. Perhaps the key to getting the most out of solar cells is combining a number of effects into a structure that exploits scattering, energy transfer, along with the plasmonic properties of MNPs and the tunability of

QDs. However, a more quantitative understanding of the relevant physical effects might be necessary before such advanced solar cell designs can be achieved.

A structure that I would like to propose for investigation is a solar cell that employs a distribution of SQDs of different sizes and thus different band gaps. This has not been investigated and could offer an improvement in solar cell efficiency through providing a more suitable structure for capturing a wider spectrum of photons. In conventional single-junction cells, this additional energy is stored in the excited electron, but soon lost as heat through the creation of lattice vibrations. As discussed above, this can be avoided through the CM effect, but trying to create a continuum of band gaps could potentially replicate the effect. A similar device could be investigated that includes a distribution of gold NPs that act as antennas for capturing light instead of QDs, employing energy transfer from metal to semiconductor.

QLED Technology

As discussed in the previous section, the modification of an emitter's properties near a MNP can result both in quenching of the emission, and in enhancement. In the context of QLED technology, quenching is undesired, as it reduces the efficiency of a device. Emission enhancement on the other hand, can increase the brightness of a LED with an intensity enhancement of 176% having been reported in literature [6]. In designing the SQD-MNP construct, these two effects compete at small distances [18, 27] (see Figure 6). Constructing a device with appropriate separation of emitter and MNP is the first step towards building an efficient QLED device.

Another factor to consider is the size of the MNP. It has been shown [14, 37] that the LSP resonance peak of a MNP is redshifted on increasing its size. In the study by Pan et al. (2016) [27] they demonstrate that PL intensity of the system exhibits a maximum for the gold nanosphere radius of 27nm, decreasing both for particles of higher and lower dimension. This is attributed to maximising the overlap between emission spectrum of the QD and the LSP resonance peak of the complementary gold NPs.

Conclusions and Outlook

I have outlined multiple effects that have been investigated through, or closely relate to, plasmonic and quantum interactions between SQDs and MNPs. I have also presented some practical applications of these constructs, along with the challenges that their implementation faces.

The SQD-MNP structure has not been explored in depth for in its own right, but could potentially become a fundamental building block in the next generation of devices for light manipulation.

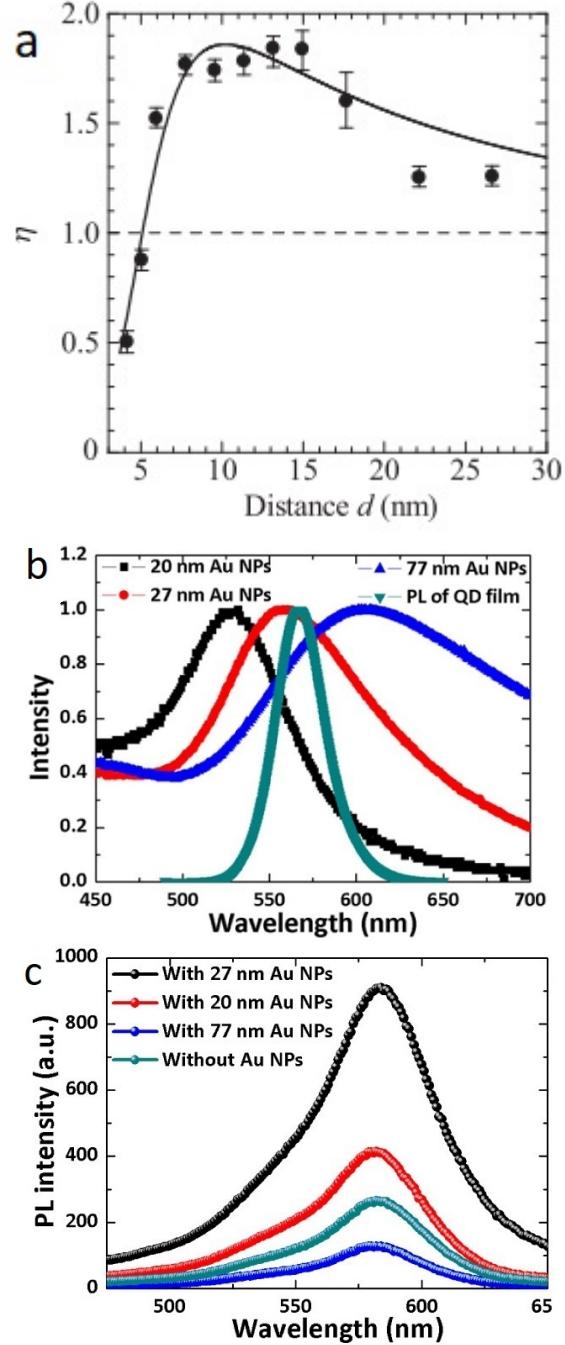


Figure 6: a) Illustration of the competing effects of quenching at low distances and enhancement around 11nm. The ratio of PL intensity relative to the normal emission of the device is shown on the y axis [18]. b) LSP resonance curves along with QD emission spectrum. The resulting enhancement of the QD-MNP LED can be seen in c). Complete overlap maximises PL intensity. [27]

References

References

- [1] S. Akhavan, M. Zafer Akgul, P. L. Hernandez-Martinez, and H. V. Demir. Plasmon-Enhanced Energy Transfer in Photosensitive Nanocrystal Device. *ACS NANO*, 11(6):5430–5439, JUN 2017.
- [2] A. Alivisatos. Semiconductor clusters, nanocrystals, and quantum dots. *SCIENCE*, 271(5251):933–937, FEB 16 1996.
- [3] H. A. Atwater and A. Polman. Plasmonics for improved photovoltaic devices. *NATURE MATERIALS*, 9(3):205–213, MAR 2010.
- [4] W. Barnes, A. Dereux, and T. Ebbesen. Surface plasmon subwavelength optics. *NATURE*, 424(6950):824–830, AUG 14 2003.
- [5] R. Chikkaraddy, B. de Nijs, F. Benz, S. J. Barrow, O. A. Scherman, E. Rosta, A. Demetriadou, P. Fox, O. Hess, and J. J. Baumberg. Single-molecule strong coupling at room temperature in plasmonic nanocavities. *NATURE*, 535(7610):127–130, JUL 7 2016.
- [6] N.-K. Cho, S. M. Lee, K. Song, and S. J. Kang. Enhanced quantum-dot light-emitting diodes using gold nanorods. *JOURNAL OF THE KOREAN PHYSICAL SOCIETY*, 67(9):1667–1671, NOV 2015.
- [7] S. K. Cushing, J. Li, F. Meng, T. R. Senty, S. Suri, M. Zhi, M. Li, A. D. Bristow, and N. Wu. Photocatalytic Activity Enhanced by Plasmonic Resonant Energy Transfer from Metal to Semiconductor. *JOURNAL OF THE AMERICAN CHEMICAL SOCIETY*, 134(36):15033–15041, SEP 12 2012.
- [8] A. Delga, J. Feist, J. Bravo-Abad, and F. J. Garcia-Vidal. Quantum Emitters Near a Metal Nanoparticle: Strong Coupling and Quenching. *PHYSICAL REVIEW LETTERS*, 112(25), JUN 26 2014.
- [9] L. Dyadyusha, H. Yin, S. Jaiswal, T. Brown, J. Baumberg, F. Booy, and T. Melvin. Quenching of CdSe quantum dot emission, a new approach for biosensing. *CHEMICAL COMMUNICATIONS*, (25):3201–3203, 2005.
- [10] V. E. Ferry, J. N. Munday, and H. A. Atwater. Design Considerations for Plasmonic Photovoltaics. *ADVANCED MATERIALS*, 22(43):4794–4808, NOV 16 2010.
- [11] C. F. Guo, T. Sun, F. Cao, Q. Liu, and Z. Ren. Metallic nanostructures for light trapping in energy-harvesting devices. *LIGHT-SCIENCE & APPLICATIONS*, 3, APR 2014.
- [12] A. Hagfeldt, G. Boschloo, L. Sun, L. Kloo, and H. Pettersson. Dye-Sensitized Solar Cells. *CHEMICAL REVIEWS*, 110(11):6595–6663, NOV 2010.
- [13] N. Hildebrandt, C. M. Spillmann, W. R. Algar, T. Pons, M. H. Stewart, E. Oh, K. Susumu, S. A. Diaz, J. B. Deleahany, and I. L. Medintz. Energy Transfer with Semiconductor Quantum Dot Bioconjugates: A Versatile Platform for Biosensing, Energy Harvesting, and Other Developing Applications. *CHEMICAL REVIEWS*, 117(2, SI):536–711, JAN 25 2017.
- [14] X. Huang, S. Neretina, and M. A. El-Sayed. Gold Nanorods: From Synthesis and Properties to Biological and Biomedical Applications. *ADVANCED MATERIALS*, 21(48):4880–4910, DEC 28 2009.
- [15] R. Jiang, B. Li, C. Fang, and J. Wang. Metal/Semiconductor Hybrid Nanostructures for Plasmon-Enhanced Applications. *ADVANCED MATERIALS*, 26(31):5274–5309, AUG 20 2014.
- [16] P. V. Kamat. Quantum Dot Solar Cells. Semiconductor Nanocrystals as Light Harvesters. *JOURNAL OF PHYSICAL CHEMISTRY C*, 112(48):18737–18753, DEC 4 2008.
- [17] T. Kang, H. C. Kim, S.-W. Joo, S. Y. Lee, I.-S. Ahn, K.-A. Yoon, and K. Lee. Optimization of energy transfer between quantum dots and gold nanoparticles in head-to-head configuration for detection of fusion gene. *SENSORS AND ACTUATORS B-CHEMICAL*, 188:729–734, NOV 2013.
- [18] D. Kim, H. Yokota, T. Taniguchi, and M. Nakayama. Precise control of photoluminescence enhancement and quenching of semiconductor quantum dots using localized surface plasmons in metal nanoparticles. *JOURNAL OF APPLIED PHYSICS*, 114(15), OCT 21 2013.
- [19] N.-Y. Kim, S.-H. Hong, J.-W. Kang, N. Myoung, S.-Y. Yim, S. Jung, K. Lee, C. W. Tu, and S.-J. Park. Localized surface plasmon-enhanced green quantum dot light-emitting diodes using gold nanoparticles. *RSC ADVANCES*, 5(25):19624–19629, 2015.
- [20] O. Kulakovich, N. Strelak, A. Yaroshevich, S. Maskevich, S. Gaponenko, I. Nabiev, U. Woggon, and M. Artemyev. Enhanced luminescence of CdSe quantum dots on gold colloids. *NANO LETTERS*, 2(12):1449–1452, DEC 2002.
- [21] S. Kundu and A. Patra. Nanoscale Strategies for Light Harvesting. *CHEMICAL REVIEWS*, 117(2, SI):712–757, JAN 25 2017.
- [22] X. Li, J. Qian, L. Jiang, and S. He. Fluorescence quenching of quantum dots by gold nanorods and its application to DNA detection. *APPLIED PHYSICS LETTERS*, 94(6), FEB 9 2009.

- [23] C. Liu, H. Dong, N. Wu, Y. Cao, and X. Zhang. Plasmonic Resonance Energy Transfer Enhanced Photodynamic Therapy with Au@SiO₂@Cu₂O/Perfluorohexane Nanocomposites. *ACS APPLIED MATERIALS & INTERFACES*, 10(8):6991–7002, FEB 28 2018.
- [24] X.-C. Ma, Y. Dai, L. Yu, and B.-B. Huang. Energy transfer in plasmonic photocatalytic composites. *LIGHT-SCIENCE & APPLICATIONS*, 5, FEB 2016.
- [25] P. Mandal and S. Sharma. Progress in plasmonic solar cell efficiency improvement: A status review. *RENEWABLE & SUSTAINABLE ENERGY REVIEWS*, 65:537–552, NOV 2016.
- [26] K. V. Nerkararyan and S. I. Bozhevolnyi. Relaxation dynamics of a quantum emitter resonantly coupled to a metal nanoparticle. *OPTICS LETTERS*, 39(6):1617–1620, MAR 15 2014.
- [27] J. Pan, J. Chen, D. Zhao, Q. Huang, Q. Khan, X. Liu, Z. Tao, Z. Zhang, and W. Lei. Surface plasmon-enhanced quantum dot lightemitting diodes by incorporating gold nanoparticles. *OPTICS EXPRESS*, 24(2):A33–A43, JAN 25 2016.
- [28] C. A. Parker and W. T. Rees. Fluorescence spectrometry. a review. *Analyst*, 87:83–111, 1962.
- [29] S. Pillai, K. R. Catchpole, T. Trupke, and M. A. Green. Surface plasmon enhanced silicon solar cells. *JOURNAL OF APPLIED PHYSICS*, 101(9), MAY 1 2007.
- [30] T. Pons, I. L. Medintz, K. E. Sapsford, S. Higashiyama, A. F. Grimes, D. S. English, and H. Matoussi. On the quenching of semiconductor quantum dot photoluminescence by proximal gold nanoparticles. *NANO LETTERS*, 7(10):3157–3164, OCT 2007.
- [31] R. Roy, S. Hohng, and T. Ha. A practical guide to single-molecule FRET. *NATURE METHODS*, 5(6):507–516, JUN 2008.
- [32] R. Schaller, M. Sykora, J. Pietryga, and V. Klimov. Seven excitons at a cost of one: Redefining the limits for conversion efficiency of photons into charge carriers. *NANO LETTERS*, 6(3):424–429, MAR 2006.
- [33] L. STRYER and R. HAUGLAND. ENERGY TRANSFER - A SPECTROSCOPIC RULER. *PROCEEDINGS OF THE NATIONAL ACADEMY OF SCIENCES OF THE UNITED STATES OF AMERICA*, 58(2):719–&, 1967.
- [34] T. K. Todorov, S. Singh, D. M. Bishop, O. Guawanaw, Y. S. Lee, T. S. Gershon, K. W. Brew, P. D. Antunez, and R. Haight. Ultrathin high band gap solar cells with improved efficiencies from the world's oldest photovoltaic material. *NATURE COMMUNICATIONS*, 8, SEP 25 2017.
- [35] S. Weiss. Fluorescence spectroscopy of single biomolecules. *SCIENCE*, 283(5408):1676–1683, MAR 12 1999.
- [36] C. Yun, A. Javier, T. Jennings, M. Fisher, S. Hira, S. Peterson, B. Hopkins, N. Reich, and G. Strouse. Nanometal surface energy transfer in optical rulers, breaking the FRET barrier. *JOURNAL OF THE AMERICAN CHEMICAL SOCIETY*, 127(9):3115–3119, MAR 9 2005.
- [37] X. Zhang, C. A. Marocico, M. Lunz, V. A. Gerard, Y. K. Gun'ko, V. Lesnyak, N. Gaponik, A. S. Susha, A. L. Rogach, and A. L. Bradley. Wavelength, Concentration, and Distance Dependence of Nonradiative Energy Transfer to a Plane of Gold Nanoparticles. *ACS NANO*, 6(10):9283–9290, OCT 2012.