



Anisotropic Metal Deposition on TiO₂ Particles by Electric-Field-Induced Charge Separation

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Abstract: Deposition of metals on TiO₂ semiconductor particles (M-TiO₂) results in hybrid Janus objects combining the properties of both materials. One of the techniques proposed to generate Janus particles is bipolar electrochemistry (BPE). The concept can be applied in a straightforward way for the site-selective modification of conducting particles, but is much less obvious to use for semiconductors. Herein we report the bulk synthesis of anisotropic M-TiO₂ particles based on the synergy of BPE and photochemistry, allowing the intrinsic limitations, when they are used separately, to be overcome. When applying electric fields during irradiation, electrons and holes can be efficiently separated, thus breaking the symmetry of particles by modifying them selectively and in a wireless way on one side with either gold or platinum. Such hybrid materials are an important first step towards high-performance designer catalyst particles, for example for photosplitting of water.

An efficient use of sun light as the primary and inexhaustible energy source is an essential precondition for the replacement of fossil fuels. Photocatalysis^[1,2] is one of the many ways to employ solar energy, for example, to produce chemicals. Several types of semi-conductors, including TiO₂, ZnO, CdS, Fe₂O₃, MoO₃, are applied as photocatalysts since they have band gaps suitable for harvesting sun light.^[3-7] TiO₂ is the most

popular of these candidates and its properties include non-toxicity, high stability, and efficiency.

Photocatalysts absorb light with energies larger than the band gap and generate electron-hole pairs (e⁻-h⁺); electrons in the valence band are excited to the conduction band, leaving holes behind. The electrons and holes then migrate to the surface to react with chemical species to form products. The major drawback of semiconductor materials is usually charge-carrier recombination. Furthermore, the band gap of some semiconductors, such as TiO₂, has limitations with respect to the utilization of visible light, thus reducing the overall quantum efficiency.^[3,7-9]

Metal-TiO₂ semiconductor (M-TiO₂) hybrids combine the properties of two materials in one, a good strategy to solve the problems encountered with TiO₂. The deposition of plasmonic metals with high work functions, such as Au, Pt, Pd, on a semiconductor enhances the efficiency of charge separation because these metals act as an electron sink and also enhance light absorption in the visible region.^[10-12] For example, the modification of TiO₂ with gold improves charge separation by promoting the transfer of the generated electrons from the semiconductor to the metal.^[13] Many reports studying the deposition of metals on TiO₂ with various methods have shown that the catalytic activity of hybrid materials is much higher compared to that of an unmodified semiconductor.^[14-17] In addition, the morphology of the deposited materials is gaining importance in engineering as it affects the surface plasmon resonance properties, the optical absorption, and the generation of electron-hole pairs for photocatalysis.^[18]

In this context so-called Janus particles^[19,20] are outstanding candidates as multi-functional catalysts, since their surfaces have two or more distinct physico-chemical properties. M-TiO₂ Janus objects in particular are very promising materials because the junction which combines the metal and the dielectric oxide can generate strong local electric near-fields.^[18] For this reason, many examples have been reported showing a high catalytic activity of M-TiO₂ Janus particles for various reactions.^[18,21,22] Seh et al. found that the photocatalytic hydrogen generation on Janus Au-TiO₂ materials is much more efficient owing to the stronger localization of the plasmonic near-field close to the Au-TiO₂ interface at one side of the particles.^[18,23]

M-TiO₂ Janus particles can be synthesized by several methods.^[18,21,24,25] Bipolar electrodeposition, based on the polarization of conducting objects in electric fields is often used to break the symmetry, and in this way generates anisotropic objects.^[26-31] This low-cost and easy to set-up

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approach allows the bulk synthesis of Janus particles^[32–35] However, this strategy cannot be applied directly to the deposition of metals on semiconductor materials owing to the low conductivity of the semiconductor. Therefore, an additional light source is required to activate the formation of charge carriers inside the semiconductor. Based on this concept, Ongaro et al.^[22] reported for the first time a site-selective deposition of gold on TiO₂ nanofibers as anisotropic substrates, using UV light and a strong external electric field. They assumed that the redox reactions occurred by activation through incident light, while the electric field enhances charge separation, leading to electric-field-assisted photochemistry.

Herein, we report on two major advances with respect to the controlled bipolar modification of semiconductor particles:

- 1) the successful modification of isotropic TiO₂ semiconductor objects by light-induced bipolar electrochemistry. Compared to anisotropic objects, such as tubes, rods, or fibers, which orient parallel to the electric field upon polarization,^[36] the use of isotropic objects is much more challenging because they can rotate during the deposition process, thus preventing the generation of well-defined Janus particles.
- 2) the modification of nanosized objects, which is usually not possible with bipolar electrochemistry. This is due to the fact that in classic bipolar electrochemistry the electric field, which needs to be applied, is indirectly proportional to the characteristic size of the object, meaning that nanoparticles usually require fields in the range of MV m⁻¹. Investigating the mechanism of metal deposition on TiO₂, we were able to demonstrate that it is possible to achieve metal deposition with electric fields three orders of magnitude lower than the ones required by the concept of classic bipolar electrochemistry. Consequently, even particles in the 10 nm range can, for the first time, be selectively modified through the synergetic combination of electric field and light. The so-obtained Janus objects might be used for a wide variety of applications, such as hydrogen and oxygen evolution,^[37–39] as well as the catalytic degradation of organic compounds.^[13,24]

To carry out these experiments under the simultaneous influence of light and electric field, a set-up illustrated in Figure 1 has been used. Two electrode compartments are connected by a channel which is filled with the reaction mixture containing a jellified aqueous suspension of TiO₂ particles and the metal salt (see Supporting Information).

To better understand and illustrate the mechanism of asymmetric reduction on semiconductor particles, we carried out a first experiment in which metal ions are reduced on macroscopic TiO₂ objects (macro-TiO₂) made out of anatase with dimensions in the millimeter range (about 3–6 mm). For the first study, gold has been chosen as a deposit (Au/macro-TiO₂). The initially completely white TiO₂ selectively turns deep gray on the right, or positively polarized, side (δ^+) (Figure 2b) after applying an external electric field (E) of about 6 kV m⁻¹ and in the simultaneous presence of 100 %

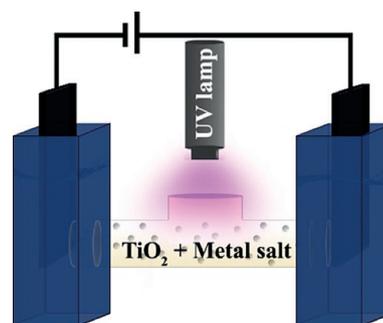


Figure 1. Schematic representation of the bipolar electrochemical cell allowing simultaneous UV irradiation.

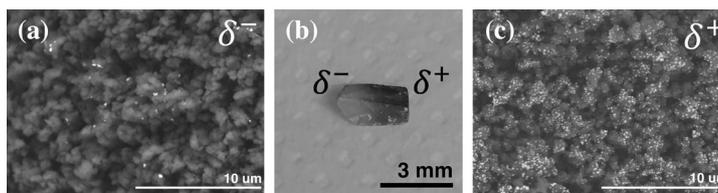


Figure 2. a) SEM image revealing that only very few gold particles are deposited on the negatively polarized side, b) Optical microscopy of the whole macro-TiO₂ object, and c) SEM of the positively polarized side showing a high density of gold particles (white spots).

UV light intensity for 60 s reaction time in HAuCl₄·3H₂O media.

To confirm the asymmetric metal deposition, SEM images were recorded at both sides of the object (Figure 2a,c). The amount of gold particles at the δ^+ side is much higher than on the δ^- part, which is opposite of what would be obtained for conventional bipolar electrochemical deposition on conducting objects.^[19,40] When depositing platinum instead of gold in a second series of experiments identical results are obtained (Figure S1). This counter-intuitive observation can be understood by the generation of an internal electric field inside the semiconductor particle (Figure S2 in the Supporting Information).

These first encouraging results nicely illustrate that the simultaneous application of an electric field and UV irradiation allows very efficient separation of electrons and holes even for very big particles and thus validates the concept. This opens the way for addressing two main challenging issues: the downscaling of the particle size and the use of isotropic particles. Therefore, TiO₂ microspheres (micro-TiO₂) were then modified based on the same strategy. The asymmetric gold deposition on micro-TiO₂ was achieved by exposure to an external electric field of 33 kV m⁻¹ and 20 % UV light intensity for 30 s (Figure S3a,b). Even when the electric field is reduced to 17 and 3 kV m⁻¹, the deposition still results in asymmetric particles (Figure S3c–f). To confirm the chemical nature of the deposits elemental analysis of gold (Au) and titanium (Ti) was performed by energy dispersive X-ray spectroscopy (EDX) (Figure 3).

It is of note that asymmetric gold deposition in a conventional bipolar electrochemical process with conductive objects of comparable diameter (10 μ m) requires theoret-

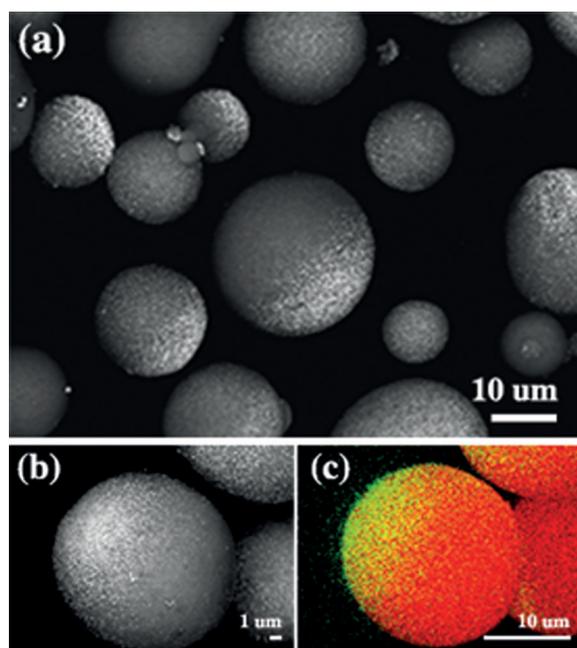


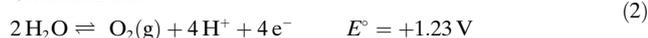
Figure 3. a), b) SEM images of gold deposited on micro-TiO₂ by a simultaneous exposure for 30 s to 20% UV light intensity and an electric field of 3 kV m⁻¹. c) EDX analysis of (b), red Ti, green Au.

ically electric fields over 24 kV m⁻¹ for triggering the chemical reactions [Eq. (1) and Eq. (2)].^[33] In the present series of experiments we could achieve electrodeposition even with an electric field as low as 3 kV m⁻¹, almost one order of magnitude lower than the theoretical value needed for classic bipolar electrodeposition.

Reduction side :



Oxidation side :



This successful use of a low electrical field is because in contrast to normal bipolar electrochemistry, it is not the electric field which generates the chemical driving force, but the light-induced charges provide the chemical energy. The electric field has a different function, namely establishing an internal electric field inside the particle for separating electrons and holes and dragging them towards the opposite extremities of the microparticles. Therefore, even an electric field strength which is far below the one theoretically required for inducing a bipolar electrochemical reaction will have a significant impact on the symmetry of the synthesized particles (see Figure S2).

In contrast to classic bipolar electrochemistry, where it is possible to calculate in a quite straightforward way the minimum potential that has to be applied to the feeder electrodes, this is rather difficult in the present case and actually there should be no real threshold but rather a continuum of efficiency increase, because the higher the applied electric field, the better will be the separation of electrons and holes. Nevertheless we have tried to estimate experimentally

such a threshold for a given set of experimental conditions (micro-TiO₂, illumination time 60 s, concentration of metal salt 1 mM, UV light intensity 5%) and it seems to be between 1.5 kV m⁻¹ (no metal deposit) and 3 kV m⁻¹ (well defined deposit).

Replacing the gold salt by a platinum salt confirms the pronounced asymmetric deposition of the metal, even for 3 kV m⁻¹ (Figure S4), which should in principle not lead to bipolar electrodeposition on normal electric conductors. This is very encouraging and allows speculating whether similar experiments can be carried out even with nanoobjects instead of microobjects.

Normal bipolar electrochemistry encounters severe limitations when experiments need to be carried out with very small objects because the driving voltage that has to be applied between the feeder electrodes scales inversely with the object size.^[40] According to what has been observed with the above microparticles (Figures 3, Figures S3 and S4) this is not the case for semiconductors because the electric field is not the driving force, but is just spatially directing the redox chemistry. Therefore, experiments with TiO₂ nanoparticles were carried out in the following, as the synergy between electric field and light should allow modifying such very small particles (nano-TiO₂). It is worth noting that using normal bipolar electrochemical deposition, an electric field with an amplitude of more than 5 MV m⁻¹ is theoretically needed for metal deposition on nanoparticles with a characteristic size of 100 nm (see Supporting Information for calculation).

When nanoparticles are just exposed to light in the presence of metal salt the generated electron-hole pairs lead to a completely unspecific deposition of metal. Figure 4a shows that the aggregate of TiO₂ nanoparticles is completely covered with platinum. However, when applying simultaneously UV light and an electric field the situation drastically changes. The metal is no longer distributed homogeneously over the semiconductor nanoparticles, but rather undergoes single-point electrodeposition of metal nanoclusters on individual TiO₂ nanoparticles, which then aggregate during the iterative washing/centrifugation process and the drying on the TEM grid, leading to objects such as the one shown in Figure 4b. The photoexcitation is the same in both cases, but the observed difference is very striking because without electric field the metal deposition occurs literally everywhere, whereas with the synergy of electric field and light statistically every semiconductor nanoparticle is modified with just one metal nanocluster (black spots with a size of 2–5 nm in Figure 4).

This result indicates that it is possible to break the deposition symmetry with electric fields that are more than three orders of magnitude lower than those required by classic bipolar electrochemistry. Figure 4c shows a HRTEM image of a typical junction between the metal and the semiconductor. Both components of the junction exhibit crystalline order, as reticular planes can be observed and the formation of a coherent heterointerface bridging the metal and the semiconductor is evidenced.

In conclusion, the concept of bipolar electrodeposition has been considerably extended by overcoming two major road blocks:

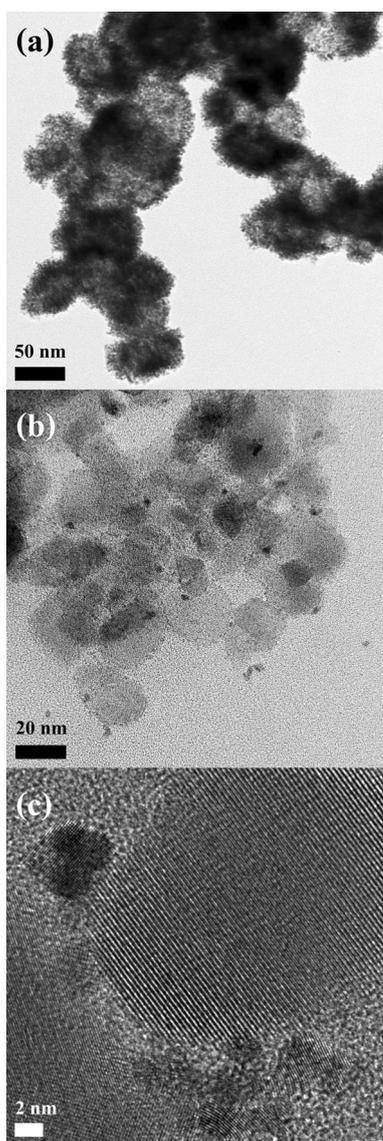


Figure 4. a) TEM image of nano-TiO₂ particles covered with platinum nanoclusters generated in an unspecific way by exposure for 90 s to 50% UV light intensity. b) TEM image of platinum nanoclusters (black spots with a size of 2–5 nm) generated in a selective way on nano-TiO₂ by exposure for 90 s simultaneously to 50% UV light intensity and an electric field of 3 kV m⁻¹. c) HRTEM image for a typical deposit obtained under the conditions in (b), expanding the view of the junction between the metal nanocluster and a nano-TiO₂ particle (see text for details).

- 1) until now it was not possible to modify isotropic semiconductor objects by bipolar electrodeposition of metals because of their rotation in the electric field during the modification step. Modification of conducting isotropic particles has already been demonstrated, but it is not straight-forward to extend the gel-based concept to semiconductors, especially at the nanoscale, because the employed gel needs to be removed without degrading the nano-Janus objects
- 2) classic bipolar electrodeposition intrinsically requires very high electric fields for the modification of nanoobjects and therefore was so far mostly used for micron-sized particles

We could demonstrate that by taking advantage of the synergy between light and an electric field it is possible to induce bipolar behavior also on isotropic semiconductor particles suspended in a gel, and, most importantly, trigger metal deposition on particles with a characteristic size in the 10–30 nm range. This process only requires modest electric fields, which are over three orders of magnitude lower than what is theoretically needed in a classic bipolar electrodeposition experiment without light. Furthermore, it has been possible to provide evidence that the deposition mechanism on semiconducting particles is opposite to what has been observed for normal conductors, meaning that metal-ion reduction occurs at the positively polarized pole of the object owing to the electric field generated inside the semiconductor which allows the efficient separation of electrons and holes over long distances. The process is simple and low-cost and therefore can also be scaled up for industrial production. The so-obtained hybrid micro- and nanomaterials open the door for the synthesis of high-performance bifunctional catalysts for various applications, including water splitting and depollution of organic waste.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: bipolar electrochemistry · Janus particles · metal deposition · photochemistry

- [1] K. Natarajan, T. S. Natarajan, R. I. Kureshy, H. C. Bajaj, W. K. Jo, R. J. Tayade, *Adv. Mater. Res.* **2015**, *1116*, 130–156.
- [2] T. Ochiai, A. Fujishima, *J. Photochem. Photobiol. C* **2012**, *13*, 247–262.
- [3] K. Nakata, A. Fujishima, *J. Photochem. Photobiol. C* **2012**, *13*, 169–189.
- [4] A. Fujishima, X. Zhang, *C. R. Chim.* **2006**, *9*, 750–760.
- [5] A. Fujishima, T. N. Rao, D. A. Tryk, *J. Photochem. Photobiol. C* **2000**, *1*, 1–21.
- [6] J. Schneider, M. Matsuoka, M. Takeuchi, J. Zhang, Y. Horiuchi, M. Anpo, D. W. Bahnemann, *Chem. Rev.* **2014**, *114*, 9919–9986.
- [7] V. Etacheri, C. Di Valentin, J. Schneider, D. Bahnemann, S. C. Pillai, *J. Photochem. Photobiol. C* **2015**, *25*, 1–29.
- [8] T. L. Thompson, J. T. Yates, *Chem. Rev.* **2006**, *106*, 4428–4453.
- [9] L. Sang, Y. Zhao, C. Burda, *Chem. Rev.* **2014**, *114*, 9283–9318.
- [10] B. Gupta, A. A. Melvin, T. Matthews, S. Dash, A. K. Tyagi, *Renewable Sustainable Energy Rev.* **2016**, *58*, 1366–1375.

- [11] A. Bumajdad, M. Madkour, *Phys. Chem. Chem. Phys.* **2014**, *16*, 7146–7158.
- [12] R. Jiang, B. Li, C. Fang, J. Wang, *Adv. Mater.* **2014**, *26*, 5274–5309.
- [13] *Comprehensive Nanoscience and Technology*, Academic Press, New York, **2010**.
- [14] Z. Zheng, B. Huang, X. Qin, X. Zhang, Y. Dai, M.-H. Whangbo, *J. Mater. Chem.* **2011**, *21*, 9079–9087.
- [15] J. Ohyama, A. Yamamoto, K. Teramura, T. Shishido, T. Tanaka, *ACS Catal.* **2011**, *1*, 187–192.
- [16] Z. Zhang, Z. Wang, S.-W. Cao, C. Xue, *J. Phys. Chem. C* **2013**, *117*, 25939–25947.
- [17] Y.-C. Pu, G. Wang, K.-D. Chang, Y. Ling, Y.-K. Lin, B. C. Fitzmorris, C.-M. Liu, X. Lu, Y. Tong, J. Z. Zhang, Y.-J. Hsu, Y. Li, *Nano Lett.* **2013**, *13*, 3817–3823.
- [18] Z. W. Seh, S. Liu, M. Low, S.-Y. Zhang, Z. Liu, A. Mlayah, M.-Y. Han, *Adv. Mater.* **2012**, *24*, 2310–2314.
- [19] G. Loget, A. Kuhn, *J. Mater. Chem.* **2012**, *22*, 15457–15474.
- [20] A. Walther, A. H. E. Müller, *Chem. Rev.* **2013**, *113*, 5194–5261.
- [21] R. Dong, Q. Zhang, W. Gao, A. Pei, B. Ren, *ACS Nano* **2016**, *10*, 839–844.
- [22] M. Ongaro, J. Roche, A. Kuhn, P. Ugo, *ChemElectroChem* **2014**, *1*, 2048–2051.
- [23] S. Pradhan, D. Ghosh, S. Chen, *ACS Appl. Mater. Interfaces* **2009**, *1*, 2060–2065.
- [24] X. Fu, J. Liu, H. Yang, J. Sun, X. Li, X. Zhang, Y. Jia, *Mater. Chem. Phys.* **2011**, *130*, 334–339.
- [25] Z. W. Seh, S. Liu, S.-Y. Zhang, M. S. Bharathi, H. Ramanarayan, M. Low, K. W. Shah, Y.-W. Zhang, M.-Y. Han, *Angew. Chem. Int. Ed.* **2011**, *50*, 10140–10143; *Angew. Chem.* **2011**, *123*, 10322–10325.
- [26] J.-C. Bradley, H.-M. Chen, J. Crawford, J. Eckert, K. Ernazarova, T. Kurzeja, M. Lin, M. McGee, W. Nadler, S. G. Stephens, *Nature* **1997**, *389*, 268–271.
- [27] C. Ulrich, O. Andersson, L. Nyholm, F. Björefors, *Angew. Chem. Int. Ed.* **2008**, *47*, 3034–3036; *Angew. Chem.* **2008**, *120*, 3076–3078.
- [28] S. Inagi, Y. Ishiguro, M. Atobe, T. Fuchigami, *Angew. Chem. Int. Ed.* **2010**, *49*, 10136–10139; *Angew. Chem.* **2010**, *122*, 10334–10337.
- [29] S. Ramakrishnan, C. Shannon, *Langmuir* **2010**, *26*, 4602–4606.
- [30] S. Munktel, M. Tydén, J. Höglström, L. Nyholm, F. Björefors, *Electrochem. Commun.* **2013**, *34*, 274–277.
- [31] G. Loget, S. So, R. Hahn, P. Schmuki, *J. Mater. Chem. A* **2014**, *2*, 17740–17745.
- [32] C. Warakulwit, T. Nguyen, J. Majimel, M.-H. Delville, V. Lapeyre, P. Garrigue, V. Ravaine, J. Limtrakul, A. Kuhn, *Nano Lett.* **2008**, *8*, 500–504.
- [33] G. Loget, V. Lapeyre, P. Garrigue, C. Warakulwit, J. Limtrakul, M.-H. Delville, A. Kuhn, *Chem. Mater.* **2011**, *23*, 2595–2599.
- [34] G. Loget, J. Roche, E. Gianessi, L. Bouffier, A. Kuhn, *J. Am. Chem. Soc.* **2012**, *134*, 20033–20036.
- [35] G. Loget, J. Roche, A. Kuhn, *Adv. Mater.* **2012**, *24*, 5111–5116.
- [36] Z. Fattah, P. Garrigue, V. Lapeyre, A. Kuhn, L. Bouffier, *J. Phys. Chem. C* **2012**, *116*, 22021–22027.
- [37] S. Chen, S. S. Thind, A. Chen, *Electrochem. Commun.* **2016**, *63*, 10–17.
- [38] M. G. Walter, E. L. Warren, J. R. McKone, S. W. Boettcher, Q. Mi, E. A. Santori, N. S. Lewis, *Chem. Rev.* **2010**, *110*, 6446–6473.
- [39] A. Fujishima, K. Honda, *Nature* **1972**, *238*, 37–38.
- [40] G. Loget, D. Zigah, L. Bouffier, N. Sojic, A. Kuhn, *Acc. Chem. Res.* **2013**, *46*, 2513–2523.

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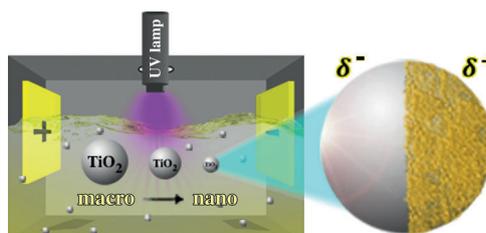
Communications



Janus Particles

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Anisotropic Metal Deposition on TiO_2
Particles by Electric-Field-Induced Charge
Separation



Taking sides: The bulk synthesis of anisotropic metal– TiO_2 particles is possible through the synergy of bipolar electrochemistry and photochemistry. Bipolar

behavior is induced in isotropic semiconductor particles suspended in a gel allowing metal deposition to generate Janus nanoparticles.