Electronic Supplementary Material (ESI) for Soft Matter.

Supporting information

Light-powered Active Colloids from Monodisperse and Highly Tunable Microspheres with A Thin TiO_2 shell

Pengzhao Xu[1], Shifang Duan[1], Zuyao Xiao[1], Zhou Yang[1], Wei Wang[1*]

1. School of Materials Science and Engineering, Harbin Institute of Technology (Shenzhen), Shenzhen, China, 518055

Table of Contents

1. Synthesis details of core-shell TiO_2 microspheres (CS-TiO_2)

The following synthesis is adapted from literature reports[1, 2]. Our synthesis was carried out with two main considerations: 1) TiO_2 coating needs to be of enough thickness to be able to move under ultraviolet radiation; 2) the synthesized TiO_2 needs to be highly monodisperse and of minimal impurities such as dimers, trimers or small TiO_2 particles. Details of the chemicals can be found in the experimental section in the main text. Critical notes are listed under each synthetic step to improve reproducibility.

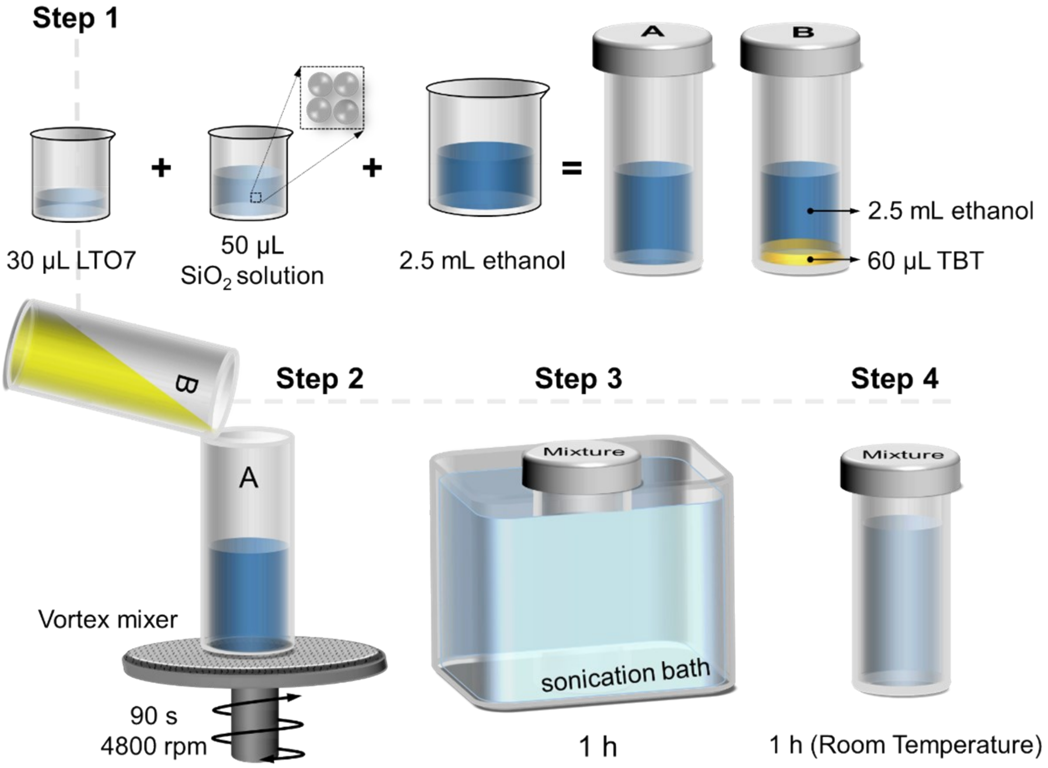

Figure S1. Detailed preparation process diagram of core-shell TiO_2 microspheres

First, 269 µL of Lutensol To-7 was dissolved in 5 ml of de-ionized water to prepare a 0.1 M stock solution of Lutensol To-7.

Second, solutions A and B were prepared in 15 ml centrifuge tubes. To prepare solution A, 50 µL SiO_2 microspheres (5 wt%) and 30 µL Lutensol To-7 solution (0.1 M, prepared above) were added to 2.5 ml ethanol during sonication. SiO_2 cores of different particle sizes were all applied in accordance to this proportion in this paper. Solution B consisted of 60 µL tetrabutyl titanate (TBT) and 2.5 ml ethanol.

(Note that it is normal to see a light-yellow oily substance at the bottom of the centrifuge tube of solution B. However, if white flocculent appeared in solution B, it indicates that TBT has hydrolyzed, and solution B needed to be remade.)

After 60 s of vigorous shaking at 4800 rpm using a vortex mixer (Digital vortex genie 2, Scientific Industries), solution B was poured to solution A while it is being mixed.

Subsequently, the mixture of solution A and solution B was mixed for 90 seconds at 4800 rpm using a vortex mixer.

(Critically, before being mixed, both solution A and solution B should be dispersed as evenly as possible, and they need to be mixed as soon as possible after they are each prepared to avoid impurities forming via TBT hydrolysis.)

Next, the mixed solution was sonicated for about 1 hour in a sonication bath (Branson M2800-C) and left for 1h to react at room temperature.

(Note that water will heat up in the ultrasonic bath and potentially affect the synthesis. To improve the monodispersity of TiO_2 particles, as suggested by ref.1, the warm water in the sonication bath was manually replaced by fresh, cold water. This heating problem does not exist for a temperature-controlled sonicator. Also, it is recommended to occasionally mix the water in the ultrasonic bath to avoid uneven reaction. This can be done by shaking the sonication tank a few times every 10 minutes.)

After that, the suspension was centrifuged at 4000 rpm for 4 minutes to remove the supernatant. The precipitated TiO_2 microspheres were cleaned by re-dispersing by sonication in ethanol, followed by centrifugation at 4000 rpm for 4 minutes. This was repeated again with ethanol, and the same cleaning steps were then repeated twice with de-ionized water. The final, clean microspheres were suspended in water and kept for later use.

If microspheres with multiple layers of TiO_2 shells were desired, the coated SiO_2-TiO_2 particles could be cleaned and collected by centrifugation, and then recoated according to the above steps. During the recoating process, the supernatant was removed after cleaning with ethanol, and then 2.5 mL ethanol was added as new solution A.

There might be some small impurities of TiO_2 particles after the synthesis or sintering, which can be removed by the following procedure: the particle suspension in need of purifying was centrifuged at 4000 rpm for 4 min, and then the supernatant was carefully removed. Then, 5 mL ethanol was added to the centrifuge tube, and it was centrifuged at a much slower spin rate of 1200 rpm for 1 min. At the completion of this step, the supernatant in the centrifuge tube will become turbid because of the presence of small impurity particles that were not able to settle. This turbid supernatant is then discarded. This cleaning process was repeated until the supernatant was no longer turbid. Then, centrifugation at 1000 rpm for 1 min was used to repeatedly remove the turbid supernatant about 3 times until the TiO_2 solution contained few impurities. Note that ethanol is a better solvent than de-ionized water for the centrifugal removal of impurities. Finally, monodisperse particles are collected by centrifugation and dispersed in de-ionized water.

2. Scanning electron microscopy (SEM) image of TiO_2-Pt motors

TiO_2 microspheres, with anatase phase, were sputtered with a platinum metal layer for 200 s and 5 mA, which is a fairly straightforward process, and the additional bright layer in SEM images should provide enough information on the successful deposition of Pt.

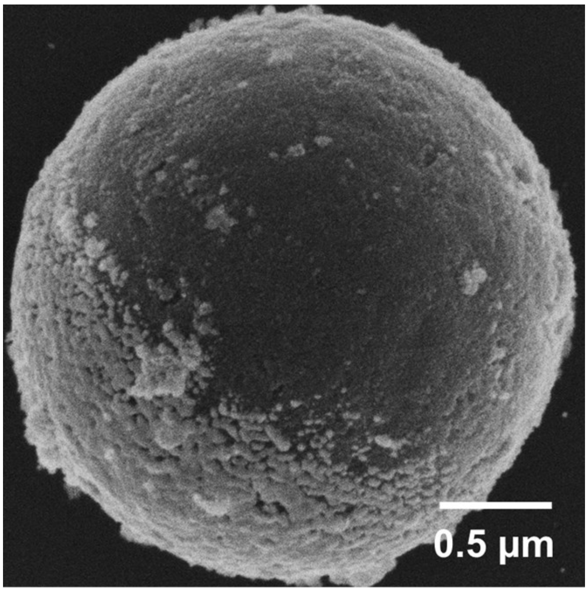

Figure S2. SEM image of TiO_2-Pt motors (coating 3 μm SiO_2 core once)

3. Optical micrograph of TiO_2-Pt motors prepared by the sol-gel method

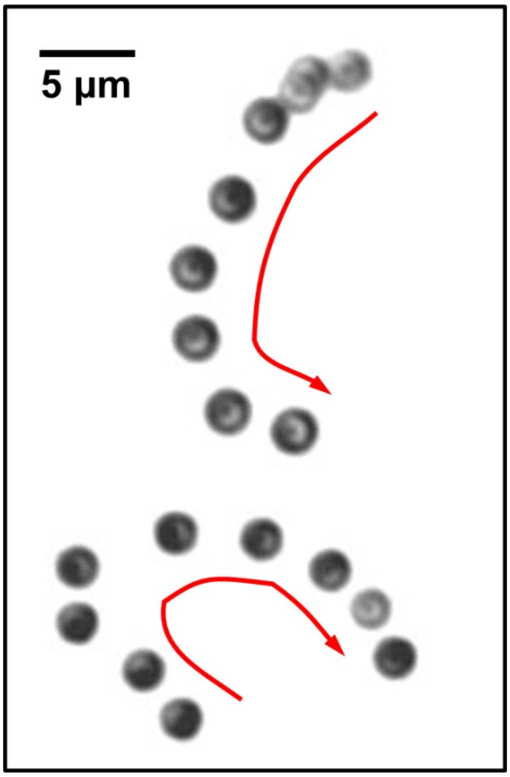

Figure S3. Trajectories of SG-TiO_2-Pt colloids within 10s (50 mM QH_2，23.51 mW/cm^2).

4. Details of experiments with TiO_2-Pt motors

In this section we list a number of observations we made during our experiments of core-shell TiO_2-Pt motors that are worth noting to readers interested in reproducing our results or performing their own experiments. Many of the following observations have also been reported for TiO_2 colloids prepared by other methods.

First, CS-TiO_2-Pt motors, upon illumination (applied from the bottom), move out of focus followed by suddenly moving towards the substrate and becoming stuck on it. This peculiar "lift-off" and "landing" remain to be understood, and may have something to do with its bottom-heaviness[3-5]. When 50 mM of hydroquinone is added to the solution, this peculiar phenomenon was largely mitigated: although the "lift-off" still occurred, the motors quickly returned to the focal plane and moved well. As a result, an aqueous solution containing 50 mM hydroquinone was used as the fuel throughout the current study, unless otherwise noted. The possible reasons for this lift-off and landing observations, and the role of hydroquinone in its mitigation, remain to be understood.

Second, even in the presence of hydroquinone, TiO_2-Pt motors tended to dash forward at a high speed at the moment of applying light. This translates to a spike of motor speed as that shown in Fig. 3d in the main text. In addition, at the moment of removing illumination, all motors tended to move quickly backwards (i.e. with their Pt cap moving forward). But this backward dash disappeared within 1-2 s. The underlying physical and chemical mechanism behind either the illuminated or dark dash is being investigated by us and will be reported in a separate study. We note that dark dashes are largely eliminated when hydroquinone is used.

Third, as seen in Fig. 6 in the main text, TiO_2 or TiO_2-Pt colloids spontaneously aggregate into a tight cluster in the dark. Upon turning on the light, these clusters expanded. Therefore, in order to minimize the interaction between the motors for the study of their individual dynamics, we suggest that UV light be turned on first so motors are spread before tracking and recording their dynamics. Moreover, clusters of motors naturally formed within minutes under ultraviolet irradiation as a result of motor-motor pair interactions (not shown here). Note that the formation clusters described here also apply to TiO_2 microspheres or TiO_2-Pt motor prepared by the sol-gel method.

Finally, we acknowledge the inevitable presence of a small amount of impurities in our TiO_2 samples, in the form of dimers or trimers as a result of unwanted coating of TiO_2 on multiple SiO_2 cores, or in the form of small, solid TiO_2 particles that formed by hydrolysis away from a SiO_2 core. This is obvious in a cluster in Video S2. The amount of impurities can be minimized to some extent, but we have never been able to produce impurity-free batches.

5. Optical and SEM Micrographs of TiO_2 microspheres with a dynabead core.

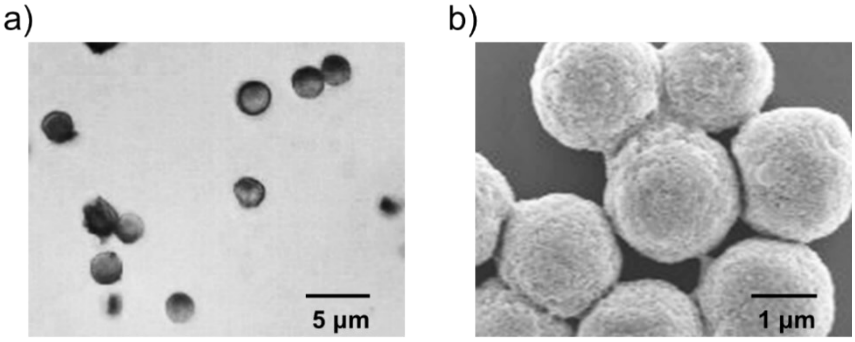

Figure S4. Characterization of microspheres with a magnetic core. a) OM image of dynabead-TiO_2-Pt Janus motors. b) SEM image of core-shell TiO_2 microspheres with a magnetic core. These core-shell microspheres are of visibly poorer coating qualities than those with SiO_2 cores for unknown reasons.

6. Supporting videos

Video S1: CS-TiO_2-Pt motors moving in 50 mM QH_2 solution at a light intensity of 72.2 mW/cm^2.

Video S2: The aggregation and dispersion of core-shell TiO_2 microspheres in 5% H_2O_2.

References

1. A. F. Demirörs, A. van Blaaderen and A. Imhof, *Langmuir*, 2010, **26**, 9297-9303.
2. S. Eiden-Assmann, J. Widoniak and G. Maret, *Chemistry of Materials*, 2004, **16**, 6-11.
3. A. I. Campbell and S. J. Ebbens, *Langmuir*, 2013, **29**, 14066-14073.
4. A. Rashidi, S. Razavi and C. L. Wirth, *arXiv preprint arXiv:1903.09127*, 2019.
5. D. P. Singh, W. E. Uspal, M. N. Popescu, L. G. Wilson and P. Fischer, *Advanced Functional Materials*, 2018, **28**.