Fuel-free nanocap-like motors actuated under visible light

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Abstract

The motion of nanomotors triggered by light sources will provide new alternative routes to power nanoarchitectures without the need of chemical fuels. However, most light-driven nanomotors are triggered by UV-light, near infrared reflection (NIR) or laser sources. We demonstrate that nanocap shaped Au/TiO$_2$ nanomotors (175 nm in diameter) display increased Brownian motion in the presence of broad spectrum visible light. The motion results from the surface plasmon resonance (SPR) effect leading to self-electrophoresis between the Au and TiO$_2$ layers, a mechanism called plasmonic photocatalytic effect in the field of photocatalysis. This mechanism has been experimentally characterized by electron energy loss spectroscopy (EELS), energy-filtered transmission electron microscopy (EFTEM) and optical video tracking. We also studied this mechanism in a more theoretical manner using numerical finite-difference time-domain (FDTD) simulations. The ability to power nanomaterials with visible light may result in entirely new applications for externally powered micro/nanomotors.

Introduction

Emerging autonomous nano/micromotors are promising man-made devices that could eventually be used in both biomedical and environmental applications.$^{[1]}$ Early research focused on the investigation of catalytic motors, which need chemical components as propellants.$^{[2]}$ The intrinsic biotoxicity of the most widely used fuel, H$_2$O$_2$, hinders a much broader application in biomedicine. Although recent reports demonstrated that bio-friendly fuels such as glucose and urea could power nanomotors,$^{[4]}$ the sustained fuel-consumption severely limits the lifetime of such motors. Therefore, external stimuli, including ultrasound,$^{[5]}$ magnetic$^{[6]}$ and electric fields,$^{[7]}$ have been used as fuel-free and biofriendly power sources.
Visible light is becoming an attractive external stimulus to propel nano/micro objects because it represents a ubiquitous and theoretically unlimited fuel source that is non-intrusive, clean, and easily controllable. Most studies to date focused on nano/micromotors powered by non-biocompatible UV light\cite{8} or not easily accessible lasers.\cite{9} To overcome these challenges, a range of nano/micro objects which can use visible light\cite{10,11} have been explored. Currently, the reported fuel-free light-driven micromotors rely on two mechanisms: thermophoresis\cite{11} and thermocapillary effects.\cite{12} Surface plasmon resonance (SPR) effects have been developed for photocatalysis applications under visible or UV light\cite{13} such as photodegradation\cite{14} and photosplitting.\cite{15} In these systems, photocatalytic materials with large band gaps, like TiO$_2$ (~3.20 eV), are combined with a plasmonic material (gold) to enhance electron transfer in the visible range. Researchers have demonstrated that the catalytic process can be enhanced by charge transfer due to Plasmon induced photocatalytic effects.\cite{16}

We present Au/TiO$_2$ nanocap motors that display enhanced Brownian motion under visible light through the plasmonic photocatalytic effect. The experimental and simulated localized surface plasmon resonance (LSPR) effect in the Au/TiO$_2$ nanostructure,\cite{2b,15b,16a} coupled with the electric field distribution and thermal diffusion of electrons, induce enhanced Brownian motion of nanocap motors. Materials characterization, theoretical simulations, video tracking analysis of nanomotors and control experiments are presented to confirm the motion of nanocaps in a fuel-free manner. These interpretations are consistent with simulations by Crozier et al.,\cite{17} Yuan et al.\cite{18} and Baffou et al.\cite{19} of metallic nanoparticles containing Au and TiO$_2$ materials.
Results and Discussion

The Janus nanocaps were fabricated by combining plasma etching and physical vapor deposition methods (Figure 1a). Monolayers of 200 nm polystyrene particles (PS NPs) were prepared by drop casting method and followed by Ar plasma etching to separate the packed PS NPs with nanogaps.

Figure panels 1b and c show the obtained monodispersed monolayers of PS NPs. The Au and TiO₂ layers were successively evaporated on the loosely packed PS NPs patterns to form Janus PS/Au/TiO₂ particles by electron beam deposition. The obtained Janus nanoparticles were annealed at 600 °C for 1 hour to produce anatase TiO₂ layers. Finally, the removal of PS template by high temperature evaporation results in the nanocap structure (Figure 1d and e).

X-Ray diffraction (XRD) measurements show that the annealed nanocaps mainly contain anatase TiO₂ (Figure S1a), which provides a good photo-catalytic performance, while the unannealed nanocaps only contain amorphous TiO₂ (Figure S1b). A scanning electron microscopy (SEM) image of the TiO₂ surface layer of the nanocaps is shown in Figure 1f.

Additionally, we characterized the nanocaps by using electron energy loss spectroscopy (EELS) and transmission electron microscopy (TEM). EELS provides information about the elemental composition of nanocaps and is capable of identifying low atomic number materials such as O in the TiO₂ layers. The outer TiO₂ layer and the inner Au layer formed separately without mixing (Figure 2a). In addition, the elemental mapping clearly shows that no elements other than Ti, O, and Au were present in the structure. This clear separation of TiO₂ and Au was confirmed from TEM images of nanocaps (Figure 2b). High resolution transmission electron microscopy (HRTEM) provides evidence of the crystalline structure of the interface between TiO₂ and Au (Figure 2c) with lattice spacings in the anatase TiO₂ layer of 0.17 nm, 0.23 nm, and 0.163 nm of the (1 0 5), (1 1 2), and (2 1 1) planes, respectively.
In order to demonstrate the Plasmon induced photocatalytic effect, we measure the plasmon resonances of a single Au/TiO$_2$ nanocap with EELS and energy-filtered transmission electron microscopy (EFTEM). EELS is among the pioneering methods to map plasmons at nanometer scales.$^{[21]}$ EELS is often assumed to be able to reflect the parameter of photonic local density of states (LDOS)$^{[22]}$ projected along the trajectory of the electron beam. Meanwhile, EFTEM is used to show the spatial distribution of a selected plasmon resonance in a single Au/TiO$_2$ nanocap. A resonant plasmon peak at 1.75 eV (Figure 3a), at both the Au/TiO$_2$ and TiO$_2$/vacuum interfaces (Figure 3a), indicates strong absorption around the 708 nm wavelength. Figure 3b presents the spatial distribution of the surface plasmon resonance at 1.2-2.4 eV. The localization areas with higher intensity indicate stronger absorption for that specific energy range.

The calculated electron-energy-loss probability (Figure 3c) could confirm the experimental finding that plasmon resonances at both interfaces have similar energies. However, a slight energy shift of 1.48 eV in the calculated EEL spectra had been expected because the actual dielectric function of the TiO$_2$ layer and the orientation of the nanocap$^{[23]}$ cannot be exactly determined. The dielectric function of TiO$_2$ strongly depends on its crystal structure. By means of a numerical FDTD simulation, we could show that this nanocap structure sustained a typical dipolar plasmon mode (Figure 3d). Furthermore, the total electric field of the exited surface plasmons ($E_{tot}$) is mostly localized at the outer edge between TiO$_2$/Vacuum and Au/TiO$_2$, as well as at the Si$_3$N$_4$ substrate below the nanocap/substrate interface. It should be noticed that optical excitation can introduce pressure on the structure. The density of the induced electromagnetic momentum and the stress tensor both depend on the electric field and the magnetic field distributions. Symmetries of the different field components however are not the same; This effect introduces an additional
asymmetry to the induced pressure on the particle. Thus the optical pressure manipulates the
motion of the particle dissimilar to the mechanism of heat transfer.

To investigate the influence of this plasmon effect on self-propulsion, a white halogen cold light
source (LCD lamp) with an intensity of 100 mW/cm² was used to illuminate the samples. Surface
plasmon resonance on the Au surface, due to the incident LCD light, excites the free electrons on
the metal surface, causing the nanocaps to appear as bright spots on microscope. The higher light
intensity means more charges are in oscillation (i.e., excited) on the Au surface, which in turn leads
to a more pronounced Plasmon induced photocatalytic effect. Higher light intensities lead to an
increased proton gradient and fluid shear velocity, due to the increased fluid flow around the
particle caused by higher charge separation (Figure 4a). The light absorption spectrum for the
Au/TiO₂ nanocaps showed an absorption peak at 690 nm (Figure 4b).

The plasmonic photocatalytic mechanism results in an increased Brownian motion of the
nanocaps upon visible light. The tracking trajectories of representative light-activated nanocaps
tracked for 10s are displayed in Figure 4c. In order to observe the nanocaps, we had to use the
intensity microscope focus light to illuminate the sample. This means that our “dark” control or
baseline (Fig. 4d, e, f) was in fact illuminated with the microscope’s 1 mW/cm² focus light. The
diffusion coefficient (D) is given by $D = \text{MSD}/i \cdot \Delta t$ and for the case of a two-dimensional Brownian
motion analysis, $i$ is equal to 4. The MSD values (in 1 second interval time) for these low
(microscope only) and high (microscope plus LCD) light intensities respectively are plotted in
Figure 4d. We also tracked 12 Au/TiO₂ nanocaps to investigate how turning LCD light ON and
OFF would affect their mobility. The diffusivity of an individual nanocap decreased from 1.87 ±
0.5 μm²/s (LCD on) to 1.04± 0.2μm²/s when the LCD light was turned off (Figure 4e). These results
provide direct proof of the correlation between increased Brownian motion of nanocap motors and visible light intensity.

Within the plasmonic photocatalytic mechanism, there are two possible contributions that may affect Brownian motion of the nanocaps: (1) electron diffusion between the Au and TiO$_2$ layers due to electrons in the Au layer becoming excited by the incident visible light, and (2) dissipation of part of the incident light energy as heat and its diffusion into the surrounding fluid.\cite{16a,16b,24} In the first mechanism, some separated electrons are lost through recombination and other surface losses, including thermal diffusion of the excited electrons on the Au side, while the remaining electrons are injected into the conduction band of TiO$_2$. This charge separation creates an electric field around the nanocap. The generated protons from the oxidation of water at the Au layer flow to the surface of TiO$_2$ and are then reduced by diffused electrons at TiO$_2$ layer.\cite{8b,25} The diffusion of proton products due to electron flow between the two layers, can induce a solute flow on the surrounding fluid from the Au inner surface to the TiO$_2$ outer surface via self-electrophoresis (Figure 4a). This provides a propelling force to move the nanocaps forward. Self-electrophoresis is a process in which the charged microparticles move in a self-generated electric field due to the asymmetric distribution of ions. In previous reports on visible light activated Au/TiO$_2$ microparticles,\cite{25-26} the electrons produced from the Au layer were transported to and consumed by the exposed TiO$_2$ surface\cite{26} resulting in a fluid flow towards TiO$_2$ and thus propulsion of the microparticles. Hong et al.\cite{8b} showed that anatase TiO$_2$ particles are very active and can move under UV light. The XRD spectrum (Figure S 1a) shows the formation of a uniform anatase phase.

Visible light cause excitation of large amounts of free electrons on the Au layer due to the Plasmon induced photocatalytic effect. This brings about a negative shift in the Fermi energy level of TiO$_2$. In order to investigate the motion mechanism, we performed three control experiments
(Figure 4f). First, the Au layer was replaced by 20 nm Pt layer to form Pt/TiO$_2$ nanocaps. Pt nanolayer is not as active as Au when light is incident on it as showed by the weak visible light absorption in Figure S2. Without LCD light, the diffusion coefficient of Pt/TiO$_2$ nanocaps is 1.31 ± 0.36 µm$^2$/s. When light is turned on, their diffusion coefficient slightly increases to 1.45 ± 0.25 µm$^2$/s (Figure 4f). Pt does not show any significant peak in absorption of visible light, thus causing a shallow Plasmon resonance which explains the low diffusion coefficient for Pt/TiO$_2$ nanocaps and the fact that there is no increase in this diffusion after LCD light illumination. This experiment indicates that Au as active material, with high absorption visible light band is crucial for the enhanced Brownian motion of the nanocaps via Plasmon photocatalytic effect.

In another control experiment, we synthesized nanocaps composed of 20 nm Au, 10 nm SiO$_2$, and 25 nm TiO$_2$ layers. Here, the SiO$_2$ sandwiched layer separates the direct contact between Au and TiO$_2$ blocking the flow of electrons, which leads to a blue shift compared to the UV-vis absorption peak of 20 nm Au/25 nm TiO$_2$ nanocaps (Figure S2). When LCD light is on, the diffusion coefficient value is increased slightly from 0.84 ± 0.26 µm$^2$/s to 0.9 ± 0.24 µm$^2$/s (Figure 4f) with no significant differences, which is much lower than the values obtained with the TiO$_2$/Au nanomotors. These two controls prove the effect of Plasmon induced electron flow in the TiO$_2$/Au nanomotors.

The second contributor to the motion relies on the rapid heat transfer away from the water-Au interface aiding the nanocap movement through thermophoresis. An average temperature increase of 0.2 ± 0.05°C was detected in the bulk solution (Figure S4) when LCD light was turned on the nanocaps. We fabricated Au/ SiO$_2$ nanocaps as the control samples to evaluate the thermophoretic effect of light-driven nanomotors ruling out the Plasmonic photocatalytic effect as the SiO$_2$ layer can prevent hot electrons transport from Au layer. The light absorption spectra of these
modified nanocaps clearly show that Au/SiO$_2$ and Au/amorphous TiO$_2$ nanocaps do not have the ability to absorb visible light (red and blue curves in Figure S2). We measured the diffusion coefficient value of the Au/SiO$_2$ nanomotors (Figure 4f) by tracking them under LCD light is 0.98 ± 0.08 µm$^2$/s, which is almost the same as the value without LCD light (0.97 ± 0.07 µm$^2$/s) with no significant differences. These results indicate that, at this light power and wavelength, the thin Au layer on the nanocaps is not sufficient to provoke an enhanced Brownian motion and hence the thermophoresis is in this case not a significant effect.

Conclusions

We demonstrated that Au/TiO$_2$ nanocaps exhibit active Brownian motion when illuminated by an LCD light, thus becoming nanomotors that were activated by visible light. The mechanism for the motors’ propulsion was interpreted as the fast electron transfer between the two layers of the nanocaps leading to a self-electrophoresis effect under visible light. Both, the experimental and the simulation results of Au/TiO$_2$ plasmon resonance absorption supported this proposed motion mechanism. It was found that these photoactive nanocaps react to changes in light intensity produced by an LCD lamp when light was turned on and off. This work provides a novel structure and fabrication technique which could be used for the activation and manipulation of biocompatible nano/micro machines, merely requiring visible light as a propulsion mechanism.

Experimental Section

Fabrication of Nanocaps. 175 nm Au/TiO$_2$ nanocaps were fabricated by electron beam physical vapor (E-beam) deposition and annealing. A polystyrene monodispersed particle (Sigma-Aldrich)
monolayer was prepared by drop casting method with 200 nm PS in ethanol solution. Followed by an argon plasma etching process (60 W radio frequency power with 0.5 mm Hg). PS particles were separated from one another and their sizes were reduced to 130 nm. Then, 20 nm Au and 30 nm TiO$_2$ layers from pure Au and TiO$_2$ pellets (Kurt J. Lesker Company) were deposited on the upper surface of the PS monolayer. After annealing for 1h at 600 °C, amorphous TiO$_2$ was turned to Anatase TiO$_2$ and PS templates were removed. Finally, Au/TiO$_2$ nanocaps on silicon wafer were collected with DI water by 30 min ultrasound sonication. 175 nm Pt/TiO$_2$ nanocaps were prepared with the same method by using Pt pellets instead of Au. For 185 nm Au/SiO$_2$/TiO$_2$ nanocaps, 20 nm Au, 10 nm SiO$_2$ and 35 nm TiO$_2$ layers were deposited on 100 nm PS monolayer sequentially before 1 h annealing process in 600°C oven. 175 nm Au/SiO$_2$ and Au/amorphous TiO$_2$ nanocaps were prepared by E-beam deposition with 20 nm Au/25 nm SiO$_2$ and 20 nm Au/25 nm TiO$_2$ layers which were then washed with DMF solution to remove PS templates.

**Instruments**

Images of PS particles, Janus structures, and nanocaps were captured by a Zeiss ULTRA 55 SEM. HRTEM and STEM-EELS spectra were recorded in a Jeol ARM 200F-DCOR equipped with a field-emission electron source, a probe Cs corrector, and a Gatan GIF Quantum ERS spectrometer. EFTEM imaging, and EELS measurements were conducted with the Zeiss SESAM microscope. The microscope was equipped with an electron monochromator (CEOS Heidelberg) and the MANDOLINE energy filter. Optical videos were recorded by Leica optical microscopy. The KL 1500 LCD (SCHOTT) close to 100 CRI halogen spectrum and original focus light from Leica optical microscopy were used as illuminators. Testo 85-infrared Thermometer was used to detect the temperature changes of Au/TiO$_2$ nanocaps. DLS measurements were operated by Malvern Zetasizer Nano ZS.
**SPR Peak Absorption and FDTD Simulation**

EELS data were acquired with an energy resolution of 90 meV as determined from the full width at half maximum of the zero-loss peak (ZLP). The acquisition time for each spectrum was 0.8 s. The energy-loss spectrum was dispersed perpendicular to the energy-dispersive direction on the CCD camera in order to make the full dynamic range of almost 1000 between ZLP and plasmon peaks accessible without saturating the camera.

In order to perform the simulations, a numerical finite-difference time-domain (FDTD) method was used.\[27\] The whole simulation domain was discretized with unit cells of 1.5 nm edge, and a higher-order absorbing boundary condition has been exploited to meet the far-field radiation boundary conditions. In order to model the permittivity of both gold and TiO\(_2\), a Drude model in addition to two critical-point functions has been introduced into the simulation domain.\[28\]

**Author Contributions**

X.W., V.S. and S.S. initiated the project. X.W. and V.S. prepared the nanocaps and carried out the experiments. S. G., N.T. and P.v.A. provided the plasmon-related experiment and simulation results. K.H. conducted the TEM imaging and EELS mapping. A. M.L. developed a code for tracking nanocaps and analyzed their motion. All the authors contributed to the paper writing. Author 1 and Author 2 contributed equally to this work.

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Figure 1. Fabrication of nanocaps. (a) Schematic of the multi-step fabrication procedure of 175 nm Au/TiO₂ nanocaps. (b-f) Scanning electron microscope images of (b) 200 nm polystyrene particles (PS), (c) loosely packed PS film after Ar plasma etching, (d) Janus PS/Au/TiO₂ particles after E-beam deposition, (e) Au/TiO₂ nanocaps without PS after annealing process, and (f) a single Au/TiO₂ nanocap.
Figure 2. Characterization of nanocaps motors. (a) color-coded elemental map of Au (red, cf. panel d) and Ti (green, cf. panel e). (b) HRTEM image of the 175 nm nanocap with the 20 nm Au core layer shown as dark grey Au surrounded by the 25 nm TiO\(_2\) shell layer (light grey). (c) HRTEM image of the interface between Au and the TiO\(_2\) layer at high magnification. (d–f) EELS images of (d) Au-M\(_{4,5}\) at 2206 eV, (e) Ti-L\(_{2,3}\) at 455 eV, and (f) O-K at 532 eV.

Figure 3. (a) Experimental EEL spectra (zero-loss peak corrected) at the interfaces of Au/TiO\(_2\) and TiO\(_2\)/Vacuum. The inset shows the STEM-HAADF image of a single Au/TiO\(_2\) nanocap and the two highlighted spots indicate the considered impact parameters. (b) 1.2-2.4 eV energy-filtered TEM image of a single Au/TiO\(_2\) nanocap. (c) Calculated electron-energy-loss probability at the interfaces of Au/TiO\(_2\) and TiO\(_2\)/Vacuum. (d) Spatial distribution of the calculated total
electric field (color code) $E_{\text{tot}} = \sqrt{|E_x|^2 + |E_y|^2 + |E_z|^2}$ and $E_z$ in the $xz$ and $xy$ planes (above the substrate) of a single Au/TiO$_2$ nanocap when the structure is excited with linearly polarized light along the $x$-direction at 1.5 eV. The structure is above a 30 nm-thick Si$_3$N$_4$ substrate in FDTD simulations, as in our EELS and EFTEM measurements.
Figure 4. Enhanced Brownian motion of nanocaps. (a) Schematic cartoon for the surface plasmon resonance effect of Au/TiO$_2$ under visible light. (b) Light absorption spectrum of 175 nm Au/TiO$_2$ nanocaps. (c) Trajectory of 12 nanocaps with X and Y coordinates under LCD light tracked for 10 s. (d) Average MSD versus time interval (Δt=1 s) for 12 tracked 175 nm nanocaps with and without LCD light (100 mW/cm$^2$). (e) Diffusion coefficient for 12 Au/TiO$_2$ nanomotors with cycled LCD light (on/off). Each track corresponds to 8 s. (f) Average diffusion coefficient values of Au/SiO$_2$/TiO$_2$, Au/SiO$_2$, Pt/TiO$_2$ nanocaps with focus light (1 mW/cm$^2$) and LCD light (100 mW/cm$^2$).
References


