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Plasmon-Enhanced Photocatalysis on Anisotropic Gold Nanorod Arrays

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The field of photocatalysis is an active area owing to the possible contributions to solve some challenging problems such as sustainable energy production, environmental pollution control, and even global warming. Unfortunately, traditional photocatalysts, especially semiconductors, suffer from inherent deficiencies, which include high activation barriers, the low mobility of charge carriers, and poor long-term stabilities. Herein, we demonstrate a plasmonic photocatalyst based on unidirectional gold nanorod arrays fabricated by using the oblique-angle deposition (OAD) technique. The fabricated gold nano-

rod arrays exhibit a remarkable plasmonic anisotropy, which depends on the direction of the incoming light. By employing these arrays as a plasmonic catalyst, a clear improvement and control in the catalytic reduction of *o*-nitroaniline to 1,2-benzenediamine, depending on the directionalities and anisotropic plasmonic properties of the gold nanorods, was obtained. These results suggest that such unique characteristics of directional gold nanorod arrays could greatly impact several technological areas, not only in plasmon-enhanced photocatalysis but in biosensing and optofluidic applications.

Introduction

Anisotropic nanofilms are characterized by their unique direction-dependent properties.^[1–3] For example, in nature, water striders can walk on water, butterflies can hold tiny droplets of water in a single direction with their wings, and geckos can also walk on any plain surface, all because of the directional nanostructures possessed by their bodies.^[4–6] Inspired by nature, a number of different approaches have been reported for the fabrication of such nanostructures during recent years.^[7–10] Among them, the oblique-angle deposition (OAD) technique is one of the most useful, and it is possible to process a wide range of synthetic and biological materials with directionality on solid surfaces with unprecedented ease.^[1,8] As anisotropic nanofilms have direction-dependent properties, they have been utilized for a variety of applications, which include tissue engineering, biosensing, catalysis, and digital microfluidics.^[11–13] Especially, in catalysis applications, anisotropic

nanofilms are mostly used as support materials for nanoparticles with catalytic activity or in some cases directly as the catalyst because of their high surface areas.^[14,15]

The effective conversion of light to chemical energy by using photocatalysts has recently attracted increasing interest for various technologies.^[16–18] Although photocatalytic reactions have been mostly driven exclusively by semiconductors, recent pioneering work has revealed that plasmon-resonant nanostructures may also provide significant advances.^[19–23] For example, Linic et al. have demonstrated that Ag nanocubes supported on Al₂O₃ particles may yield chemically useful energetic electrons if illuminated with light and drive some important catalytic oxidation reactions.^[20] Ke et al. also reported that Au nanoparticles may be an efficient photocatalyst for challenging selective reductions of organic compounds on irradiation with light.^[21]

In this work, we propose a new phenomenon, namely, directional plasmon-enhanced catalysis, by employing a unidirectional Au nanorod array fabricated onto BK7 glass surfaces through the OAD technique. We chose Au because of its well-known plasmonic and catalytic properties as well as its chemical resistance against oxidation.

Results and Discussion

A schematic representation of a typical fabrication of the directional Au nanorod arrays is shown in Figure 1a. Notably, by manipulating the substrate normal to the incident direction (α) of the vaporized Au, the tilt angles (β) of the created Au nanorods may be easily varied. The top-view and cross-sectional SEM images of the deposited nanostructures are shown in Figure 1b and c. It is clear that the Au films have aligned and

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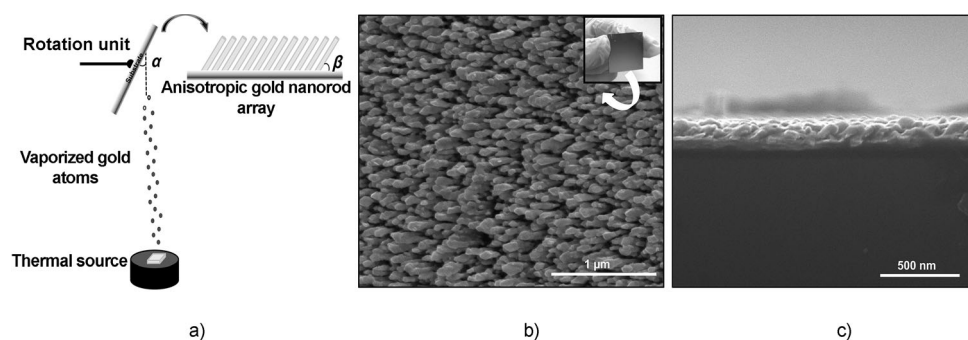


Figure 1. a) Schematic representation of the fabrication of anisotropic Au nanorod arrays. b) Top-view (inset shows the picture of a surface after deposition) and c) cross-sectional SEM images of a fabricated nanofilm. Scale bars = 1 μm (b) and 500 nm (c).

tilted nanorod arrays. The density and tilt angles of the deposited Au nanorods were calculated from SEM images by using freeware IMAGEJ software as $5.43 \times 10^8 \text{ nanorod cm}^{-2}$ and $37 \pm 2^\circ$, respectively. The average nanorod length was measured as $100 \pm 20 \text{ nm}$. Moreover, the XRD pattern of the deposited film reveals solid evidence for the unidirectionality of the Au nanorods consistent with our previous report.^[24] There were mainly four sharp diffraction peaks with $2\theta = 38, 45, 65,$ and 77° , which correspond to the (111), (200), (220), and (311) planes of the face-centered cubic crystal system of metallic Au.

After we had characterized our films, we investigated their plasmonic properties by using spectroscopic ellipsometry, which depends on the directionality of the Au nanorods. The variations of the ellipsometric variables (Ψ and Δ) and dielectric constants (i.e., real and imaginary parts) of the Au nanorod arrays, which depend on the direction of incoming light, are shown in Figure 2. The fabricated Au nanofilm reveals clear optical anisotropy (Figure 2a–d). We observed a strong plasmon resonance, which indicates dense polariton formation, if the incoming light comes through the Au nanorods along the anisotropic axis. If the incoming light is aligned with the isotropic axis, these resonance bands were shifted to a higher energy value and became broadened. These var-

iations may be discussed in two alternative or parallel mechanisms. In the first, porosity and gaps between the tilted nanorods may cause an increment in the photonic light scattering, which may enhance the local photon intensity, and photonic light trapping, which results in much more excitation of the surface plasmons. In particular, these phenomena occur if the incoming light is aligned with the anisotropic axis. In the second scenario, the observed

variation in the plasmonic behavior may have been caused by the polarization of light (Figure 2e). The p-polarization has the electric field vector oscillating normal to the plane of the nanorods along the anisotropic axis. Thus, it can excite surface plas-

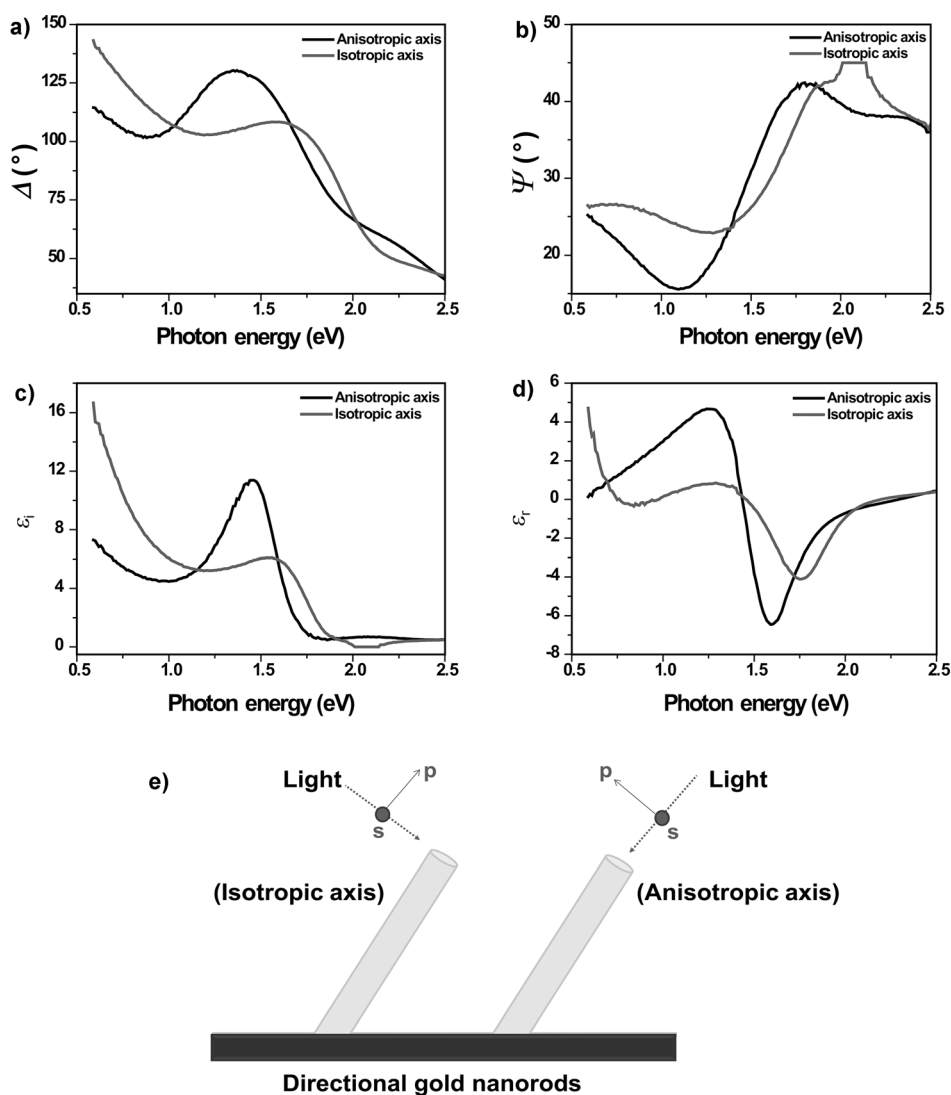


Figure 2. Variations of the ellipsometric parameters a) Δ , b) Ψ , c) imaginary (ϵ_2), and d) real (ϵ_1) parts of the dielectric functions for the unidirectional Au nanorod arrays depending on the direction of incoming light. e) Schematic for the polarization of light with respect to the orientation of the Au nanorods.

mons. In this case, the excitation by s-polarization can be neglected. However, the electric field vector of p-polarization is oriented parallel to the nanorods along the isotropic axis and as a result it cannot excite plasmons sufficiently, and the surface plasmons are mainly excited by s-polarization. In our opinion, these two scenarios may somehow contribute to the understanding of the observed results. To date, several studies reported surface-plasmon excitation on anisotropic materials through experimental or theoretical treatments; however, the fundamental issues behind this interesting phenomenon remain a mystery and require further investigation.

In the light of our results, we envisaged that the structural directionality and plasmonic anisotropy exhibited by our films may open a new avenue to improve and control heterogeneous photocatalysis applications. Therefore, to investigate the catalytic properties of our materials, we designed a special fluidic system based on the Kretschmann configuration, which is needed to excite the surface plasmons. In our experiments, BK7 glass slides with directional Au nanofilms were placed with their backs onto a BK7 prism with respect to their nanorod orientations to evaluate the effect of directionality on catalytic conversion (Figure 3 a). We chose the catalytic reduction of *o*-nitroaniline (*o*-NA) with sodium borohydride as the model reaction for the quantification of the catalytic activities of our surfaces with and without plasmonic enhancement as well as varying the directionalities of the Au nanorods (Figure 3 b). Notably, this chemical reaction in the absence of a catalyst is extremely slow (only $\approx 3\%$ conversion over 24 h). For clarity, we have divided our discussion into two parts. In the first part, the catalytic reaction was evaluated to understand the effect of the directionality of the Au nanorods in the absence of laser illumination. There was a very slow and low conversion if the tilted nanorods were kept parallel with respect to the direction of flow (isotropic axis; Figure 4a). After 180 min, only approximately 20% of *o*-NA was converted to 1,2-benzenediamine (BDA). However, approximately 55% of the *o*-NA molecules were converted to BDA in the same period if the tilted nanorods were perpendicular with respect to the direction of flow (anisotropic axis). It is clear that the orientation of the Au nanorods has an important effect on the catalytic reaction. These differences in catalytic conversion may be attributed to changes in surface porosities and fluid retention, which stem from the direction of the nanorods. We calculated the surface porosities by using the following Equation (1):^[25]

$$\text{Porosity} = 1 - [(n^2 - 1)/(n_d^2 - 1)] \quad (1)$$

in which n and n_d are the refractive indices of nanostructured and smooth Au films at a certain wavelength, respectively. The calculated porosities for the isotropic and anisotropic directions were 69 and 75%, respectively. It is not surprising that the porosity of the Au nanofilm is highly correlated with the direction of the Au nanorods. Starting from this point, it can be argued that the reaction mixture interacts with the Au nanorods along the anisotropic axis much more easily and strongly than that along the isotropic axis. As a result, the catalytic conversion was enhanced. Parallel to porosity, we ob-

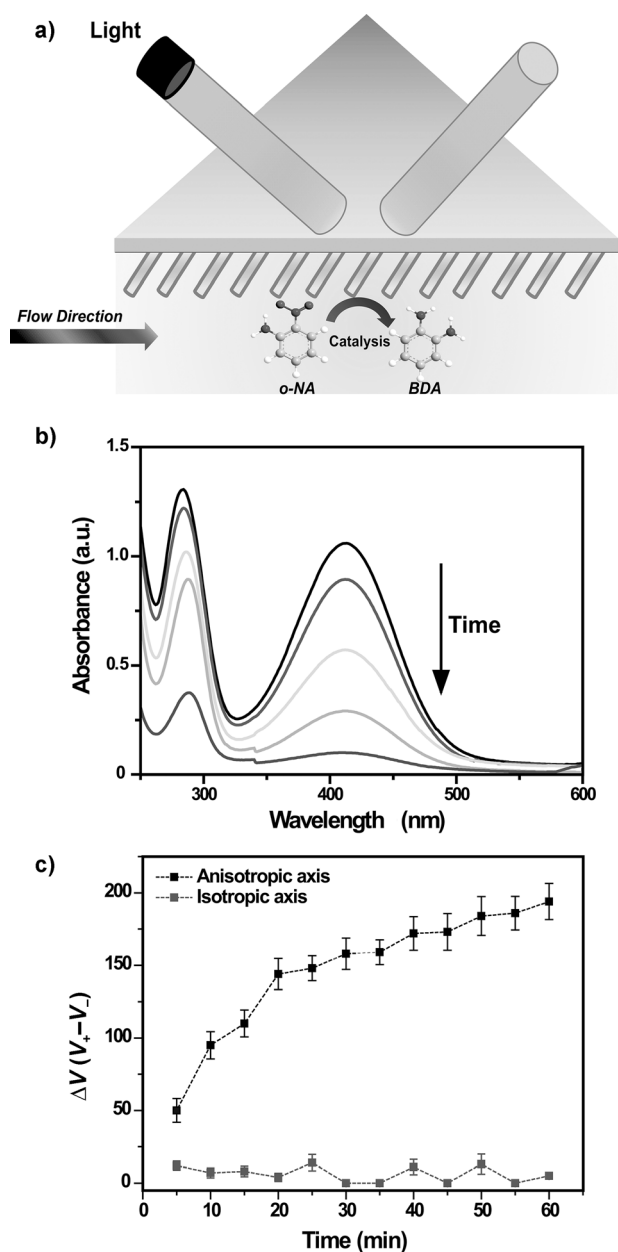


Figure 3. a) Typical catalysis reaction in the fluidic system, b) UV/Vis spectra of *o*-NA reduction with time catalyzed by unidirectional Au nanorod films, and c) volume of retention along the anisotropic and isotropic axes. (V_+ and V_- indicate the volumes of fluid passed through the channel in the isotropic and anisotropic directions, respectively. ΔV also represents the difference between V_+ and V_- .)

served that the retention of fluid was affected significantly by the orientation of the Au nanorods. It is known that directional nanostructures, just like our material, have excellent direction-dependent wetting properties, which means that fluid can flow easily in one direction (isotropic) but not the other (anisotropic).^[1,12] We found that there was almost no difference in the volume of fluid passed through the channel in the isotropic direction, whereas we observed a significant volume of retention in the anisotropic direction (Figure 3c). For this reason, retained fluid along the anisotropic axis may be converted by

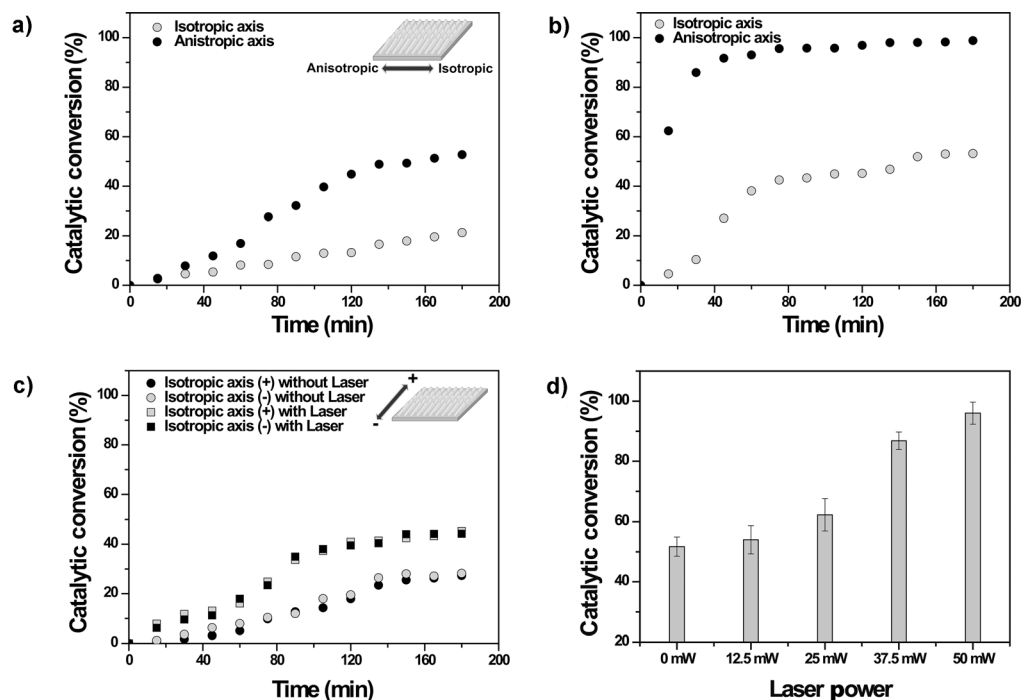


Figure 4. Catalytic conversion as a function of time along the anisotropic and isotropic directions a) in the absence of light and b) in the presence of light. c) Variation of catalytic conversion in the presence and absence of light along the isotropic axis (+ and – signs in the inset define the flow direction). d) Effect of laser power on the catalytic conversion.

the Au nanorods more than that along the isotropic axis. Both effects mentioned above may be responsible for the observed differences in catalytic conversion in the absence of light.

In the second part, the catalytic reaction was also evaluated in the presence of laser illumination (Figure 4b and c). With the help of light, we expected to excite surface plasmons and thus improve the catalytic conversion correspondingly. We found that *o*-NA conversion was rapidly completed in approximately 60 min along the anisotropic axis in the presence of light. In the isotropic orientation, light illumination also improved the catalytic conversion ($\approx 40\%$ in 60 min) but this was approximately 2.5-fold lower than that along the anisotropic axis. This clear difference in the catalytic conversion is possibly because of the variation in plasmonic excitation along the different orientations of the Au nanorods. As we mentioned previously, a strong plasmon-resonance formation was observed along the anisotropic axis, whereas these resonance shifted to a higher energy value and broadened along the isotropic axis. As a result, along the anisotropic axis, the strong plasmon resonance donates energetic electrons to the reaction medium. Therefore, the catalytic conversion is higher along the anisotropic axis than along the isotropic axis because of the increasing number of transferred electrons from the Au nanorods to *o*-NA promoted by light. It is clear that plasmonic enhancement by exploiting the Au nanorods may improve the catalytic conversion significantly. The possible mechanism may be as follows: the *o*-NA molecules first adsorb onto the Au nanorods by direct interaction between their nitro groups and the Au surface (especially onto the edges). It is also possible for *o*-NA molecules to interact with the Au surface in a planar

fashion through their aromatic rings.^[26,27] During the adsorption of *o*-NA onto the Au surface, BH_4^- ions also interact with the Au surface.^[28] The catalytic conversion of *o*-NA to BDA then occurs on the surface of the Au nanorod. In the reduction process, BH_4^- acts as the hydrogen source and the Au nanorods probably serve as both electron relay (from negatively charged BH_4^- to *o*-NA) and electron provider, which is stimulated by light. In this case, one may argue that the enhancement in thermal energy by laser illumination can be responsible for the resulting catalytic conversion. However, there is a continuous liquid flow in our experimental setup. We calculated the flow characteristic of our reactor by considering the Reynolds number and found that we have a laminar flow in our reactor (< 2300). For this reason, the temperature remains almost constant during the catalytic conversion as the heat transfer is through laminar conduction through the boundary layer and into the bulk. To substantiate our conclusion, we performed some experiments with and without continuous liquid flow. In the case of fluid at rest, during 20 min laser illumination, the temperature of the substrate increased by approximately 8°C as a result of laser heating, whereas there is no clear temperature change under continuous liquid flow conditions ($\approx 1\text{--}2^\circ\text{C}$).

Conclusions

We have successfully fabricated a directional Au nanorod array that has optical anisotropy through the oblique-angle deposition (OAD) technique. By employing the nanorod arrays as a plasmonic catalyst, we were able to observe a clear improve-

ment and control in the catalytic reduction of *o*-nitroaniline (*o*-NA) to 1,2-benzenediamine (BDA) that depends on the directionality and anisotropic plasmonic properties of the Au nanorods. We believe that such a control would have a great impact for several technological applications not only in plasmon-enhanced catalytic reactions but also in other areas, such as biosensors, microfluidic systems, and solar cells. We are currently investigating the potential uses of our systems in these areas.

Experimental Section

Fabrication of unidirectional Au nanorod arrays

The anisotropic Au nanofilm arrays were fabricated by using a conventional physical vapor deposition system (Nanovak HV, Ankara, Turkey) by using homemade OAD equipment. In the deposition, a *p*-type silicon wafer and BK7 glass slides were used as substrates. The nanofilms were created at a deposition angle of $\alpha = 5^\circ$. The thickness of the deposited films was monitored in situ by using a quartz crystal microbalance (QCM). During deposition, the base pressure was ≈ 0.13 mPa and the evaporation rate was 0.1 \AA s^{-1} . The as-deposited nanofilms were characterized by using a Quanta 400F field-emission scanning electron microscope (FE-SEM) with an acceleration voltage of 20 kV. The SEM images were analyzed with the freeware IMAGEJ image analysis software.

Characterization of the optical properties of the nanofilms

The orientation-dependent (i.e., anisotropic and isotropic) plasmonic properties of the anisotropic nanofilms were characterized by using a variable-angle spectroscopic-phase-modulated ellipsometer (UVISEL, Jobin Yvon-Horiba) with a spectral range from 0.5–4.7 eV in steps of 0.01 eV in ambient air at angles of incidence of $65\text{--}80^\circ$. In measurements, the analyzer head focuses the light beam that originates from the 75 W Xe light source on the sample with a polarizing lens. In this configuration, the deposited nanofilms were placed one by one on the stage in both anisotropic and isotropic directions and the conventional ellipsometric angles Ψ and Δ were then obtained according to Equations (2) and (3):

$$I_s = \sin(2\Psi)\sin(\Delta) \quad (2)$$

$$I_c = \sin(2\Psi)\cos(\Delta) \quad (3)$$

In which I_s and I_c are the first and second harmonics of the base modulation frequency of the polarized light.

Catalysis experiments

The special fluidic setup based on the Kretschmann configuration was achieved by using a Teflon reactor with dimensions of $500 \mu\text{m}$ (width) \times $200 \mu\text{m}$ (height) \times 1 cm (length). In measurements, the anisotropic Au nanorod arrays deposited on BK7 glass slides were placed with their backs on a BK7 prism with respect to their nanorod orientations. Catalysis was then evaluated by the reduction of *o*-NA with NaBH_4 both in the presence and absence of light. A green laser (532 nm, 50 mW) was used as a light source in this work. In a typical experiment, NaBH_4 (2 mL, 0.1 M) was first mixed with deionized water (2 mL) and stirred for 30 min at RT. Afterwards, *o*-NA (2 mL, 3.4×10^{-3} M) was added to the mixture with stirring. The final mixture was sent to the fluidic system, in which

the catalysis took place, by using an Ismatec (MCP-Process IP 65, Württemberg, Germany) peristaltic pump with a flow rate of $4.9 \mu\text{L min}^{-1}$. The catalytic conversion was monitored by analysis of the reaction mixture at certain times by using UV/Vis spectroscopy.

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